Zep
Zero emissions platform

Future CCS Technologies

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1 Introduction & Motivation

The Intergovernmental Panel on Climate Change (IPCC) recently announced that without additional efforts, the global mean temperatures are likely to increase between 3.7 and 4.8°C compared to pre-industrial levels. At the COP/MOP meeting in Paris, governments worldwide were asked to submit their Intended Nationally Determined Contributions (INDCs)[1] and plans how to achieve these targets. With INDC's suggesting a development towards a 3°C range. Scenarios which limit the global mean temperature rise to 2°C will involve deep cuts in Greenhouse Gas (GHG) emissions over the coming decades, requiring radical changes to industry, energy and transport systems and a step-change in the uptake of low carbon technologies. As the COP21 meeting in Paris in December 2015 agreed on the long term target to limit global warming to 1.5°C, the worldwide efforts in cutting GHG emissions have to be even more ambitious.

Carbon Capture and Storage (CCS) represents techniques which have the ability to prevent hundreds of millions of tonnes of CO_2 generated by large point sources to enter the atmosphere. The IEA and IPCC consider CCS a vital component of a portfolio of abatement options available to achieve the 2°C target with CCS anticipated to mitigate about 8 Gt/a in the 2050's. The technology represents a key mitigation option in most of the emission reduction pathways described by IPCC. Studies show that both the total investment cost and the cost of emission reduction are higher for scenarios that exclude CCS. According to IEA calculations, CCS can reduce the cost of climate change mitigation by up to 40% [1].

Current forecasts assume fossil-based power generation and industrial output from major emitting sectors such as cement, iron and steel to rise globally, driven by economic growth in emerging economies [2] CCS is the only technology which can achieve deep cuts in carbon dioxide (CO_2) emissions across fossil-fired power generation and carbon intensive industries – e.g. steel, cement, refineries, natural gas processing, chemical plants, etc.

While there are zero and low emission power generation technologies commercially available today, although many of these are intermittent, there are no such carbon free alternatives yet foreseeable for most energy intensive industries.

However, as CO_2 emissions in some industries derive from intense power consumption as well as carbon intense input to the process, several CO_2 emission reduction options or combinations are possible, e.g. process modifications for efficiency improvement and fuel switching, e.g. to biomass. In this context, CCS can also be deployed in combination with the use of biomass to deliver negative emissions. Given that the ambitious target of limiting global warming to 1,5 °C shall be achieved and that the worldwide peaking of GHG emissions will be delayed, biomass CCS and hence, negative emissions will be an inevitable tool.

[1] http://unfccc.int/focus/indc_portal/items/8766.php

Therefore, the application potential of CCS has to be considered broader than just for the power sector. It is not a 'one size fits all' technology but it can be applied to a wide range of carbon intensive sectors and sources which also reflect national or regional circumstances. For some countries, the focus might be on coal-fired power generation due to their power generation mix. For others, the focus might be on energy intensive industries they host in their countries or high-purity sectors, such as natural gas processing and hydrogen production.

Worldwide, first-generation capture technologies have already been tested at large pilot-scale facilities and demo plants. At the time of writing this report, there were 15 large-scale CCS projects in operation worldwide, capturing nearly 28 million tons of CO_2 per year across a range of sectors and more large scale applications will come into operation within the next 2-3 years [3].

Although capture technologies are commercially available and operating, there is still improvement potential with respect to cost, performance and operational flexibility.

CO_2 capture is in continuous development. Historical experience with comparable processes suggests that significant improvements are achievable through further well-targeted Research and Development (R&D). This is the reason why ZEP started in 2010 with its reports on "Recommendations for research to support the deployment of CCS in Europe beyond 2020", which identified the main R&D areas for driving down costs through well-targeted R&D programmes.

The purpose of this report, "Future CCS technologies", is to provide an updated overview about the evolving 2nd and 3rd generation CCS technologies, their current technical maturity (based on TRL – Technology Readiness Level) and in particular for capture technologies their improvement potential with respect to cost, performance and operational flexibility as well as scale. Operational flexibility and scale addresses differences in the boundary conditions and operation of plants in different branches, likely having an impact on the choice of capture technology. While today's 1st generation technologies are designed for large flue gas streams and preferably continuous operation, future applications will face broader and diverse operational requirements, especially in the power sector.

CCS is an infrastructure type project, not just a single product. Therefore, challenges and barriers faced by one part of the CCS chain will delay or prevent the whole CCS technology from being applied. Hence, the report looks into emerging technologies along the whole value chain of CCS (capture, transportation and storage).

The improvement potential of the 1st generation capture technologies deployed worldwide in large-scale applications (post-, pre- and oxy-CCS) may be modest while their cost reduction potential due to standardisation/replication of scale and supply chain is substantial. The current costs of 1st generation technologies will serve as a performance and cost benchmark for the assessment of the 2nd and 3rd capture generation technologies, provided in chapter 2.1 in this report. Chapter 2 will further provide an overview about emerging capture technologies and their current TRL status, including more precise definitions for 2nd and 3rd capture generation technology. Chapter 3 will assess the emerging CO_2 technologies thereby using major scientific review papers like a special issue of the International Journal of Greenhouse Gas Control, IEA GHG etc. reports etc. which are all listed in the references.

Chapter 4 evaluates the technical progress on transport technologies, both on pipeline and shipping technologies, including aspects of 'clusters' of multiple CO_2 sources, CO_2 purity and gas cleaning while chapter 5 provides an overview on the status of CO2 injection and storage.

Chapter 6 will then close the report with 'conclusions & recommendations' as well as an outlook identifying working areas or gaps this report could not consider in the limitation of time and resources but which might justify future NWT group work.

This report also includes CCS application in energy intensive industries and foresees the potential for mixed CCS clusters of power and industry sources. Emerging CO_2 capture technologies are not only assessed by their potential to reduce cost and improve performance but also by their potential to best match with the various boundary conditions of respective industries, even if at a quite high level.

Chapter 6 will therefore indicate which emerging CCS technologies might likely suit certain applications in industry or power better than others, and thereby allow the respective industries as well as public R&D programmes to promote or accelerate the development of these solutions.

2 CO_2 capture technology

CO_2 capture is a process that involves the separation and removal of CO_2 from a gas streams. These gas streams could include but are not limited to combustion flue gases, process off-gases (i.e. by-product gases from blast furnaces, basic oxygen furnace; tail gases from steam methane reforming (SMR) and various refinery processes, etc.), syngas (i.e. syngas produced from coal gasification, hydrocarbon reforming, coke oven, etc.) or natural gas (i.e. from NG processing). For many decades, these processes have been used in several industrial applications at scale close to those required in any CCS applications.

In general CO_2 capture processes can be classified according to their gas separation principle, namely chemical absorption, physical absorption, adsorption, calcium and reversible chemical loops, membranes, and cryogenic separation. Brief descriptions of the major CO_2 capture processes are as follows:

Chemical absorption: Chemical absorption processes utilize the reversible chemical reaction of CO_2 with an aqueous solvent, usually an amine. CO_2 is separated by passing the flue gas through a continuous scrubbing system. The absorbed CO_2 is stripped from the solution in a desorber, and a pure stream of CO_2 is sent for compression while the regenerated solvent is sent back to the absorber.

Physical absorption: In cases where there is a highly concentrated stream of CO_2 at high pressures, it is advantageous to use a physical solvent. The absorption capacity of these solvents increases with external gas pressure and decreases with temperature. Hence, CO_2 can be separated from such solvents mainly by reducing the pressure in the desorber, significantly reducing the energy requirements in the desorption process.

Adsorption: The gas is fed to a bed where CO_2 is selectively adsorbed. The CO_2 loaded bed is then regenerated by pressure swing adsorption (PSA) or temperature swing adsorption (TSA). In PSA, CO_2 is preferentially adsorbed on the surface of a solid adsorbent at high pressure, which will swing to low pressure (usually atmospheric) to desorb the adsorbent and release CO_2 for subsequent transport. In TSA, the adsorbed CO_2 is released by increasing the system temperature using hot air or steam injection.

Chemical looping: In Chemical Looping Combustion systems (CLC), the combustion of a fuel is achieved by transferring the oxygen to the combustor chamber using an oxygen carrier (usually a metal oxide that is reduced in such process). This enables an almost pure CO_2 gas to be produced, which can then be relatively easily stored without any further major processing. The reduced metal is then oxidised by air in a separate reactor, closing up the chemical loop.

Calcium looping: In calcium looping (CaL), a metal (M) is reversibly reacted between its carbonate form (MCO3) and its oxide form (MO). The two species are calcium carbonate (CaCO3) and calcium oxide (CaO). CO_2 is released from $CaCO_3$ in a subsequent thermal regeneration. Over multiple cycles, CO_2 is separated from other gases coming from either power generation or an industrial plant.

Membranes: Gas separation membranes allow one component in a gas stream to pass through faster than the others. There are many different types of gas separation membranes, including porous inorganic membranes, palladium membranes, polymeric membranes etc. To be effective for CO_2

capture, membrane materials should exhibit a number of features including high CO_2 or H_2 permeability, high CO_2/N_2 selectivity, thermal and chemical stabilities, resistant to plasticization and aging, and so on.

Cryogenic separation: CO_2 can be separated from other gases by cooling and condensation. For CO_2 separation, flue gas containing CO_2 is cooled to desublimation temperature (−100 to –135 °C) and then solidified CO2 is separated from other light gases and compressed to a high pressure.

In power generation sector, CO_2 capture processes are traditionally classified as post-combustion CO_2 capture, pre-combustion CO_2 capture, and oxy combustion CO_2 capture.

Further, CO_2 capture technologies can be labelled in accordance to their technology maturity, classifying them as 1st, 2nd and 3rd generation technologies.

2.1 Benchmarking the Performance and Cost of Today's CO_2 Capture Technologies

2.1.1 Maturity of the CO_2 Capture Technologies (Technology Readiness Level)

The maturity of the CO_2 capture technologies can be ranked in accordance to Technology Readiness Level or TRL.

Definition – Technology Generation

Generally, 1st generation CCS technologies can be considered as mature technology with TRL between 7 & 9; fully ready for wide spread deployment in the immediate future. On the other hand, emerging technologies could offer potential cost reduction and increased efficiency. Typically, 2nd generation CCS technologies can be considered as late stage emerging technologies with TRL between 3 & 6; whilst 3rd generation CCS technologies are usually early stage emerging technologies with TRL between 1 & 3.

Table 2.1 presents the range of TRLs adopted in this report. This is based on definitions as established from bodies such as the US Department of Energy National Energy Technology Laboratory[2] and the European Horizon 2020 program,[3] but adapted to expand on CO_2 capture as well as CO_2 storage

[2] https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/Program-Plan-Carbon-Capture-2013.pdf
[3] http://ec.europa.eu/research/participants/data/ref/h2020/other/wp/2016_2017/annexes/h2020-wp1617-annex-g-trl_en.pdf

technologies. It shall be noted that these TRL indicators are to be used in the analysis of emerging future technologies reported in this document.

2.1.1 Definition – Technology Generation

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Table 2.1 Technology Readiness Level (TRL).

Full Commercial Application	9	Actual system proven in operational environment (competitive manufacturing of full system, at scales of several 100s of MW_{th} or around $1MtCO_2/a$ stored)
Demonstration	8	System complete and demonstrated at industrial scales of 10s of MW_{th} or 0.1 to 1 $MtCO_2/a$ stored
Pilot	7	System prototype demonstrated in operational environment (industrial pilots operating at 10s of MW_{th} and/or separating 10s of kt CO_2/a)
	6	Technology demonstrated in relevant environment (steady states at industrially relevant environments: pilots in the MW_{th} range and/or separating 1 to 10 kt CO_2/a)
Small Pilot	5	Technology validated in relevant environment (pilots operated at industrially relevant conditions at 0.05–1 MW_{th}) and/or less than 1 kt/a captured/stored
Lab/Bench	4	Technology validated in the lab (continuous operated pilots at lab scale <50 kW_{th})
	3	Experimental proof of concept (pilot testing of key components at small bench scale)
Concept	2	Technology concept formulated (basic process design)

	1	Basic principles observed

1st generation CCS technologies:

- CO_2 capture technologies that can be categorised as commercially available or near-commercial technology today. These technologies have been tested or operated as demo- or widely deployed in various commercial applications. In the near or medium term, it is expected that these technologies would likely involve further development to achieve incremental improvement.

2nd generation CCS technologies:

- Emerging CCS technologies which can be demonstrated at pre-commercial scale and may become commercially available in the coming decade (i.e. between 2020 and 2030). 2nd generation CCS technologies are likely to be based on the scale-up of technologies which are assessed today with a TRL in the range of 3-6, likely achieving the TRL of 6 or 7 in the next five year (i.e. by 2020), including refinements of the 1st generation CCS technologies.

3rd generation CCS technologies:

- Emerging CCS technologies which may become commercially available during the next two decades (i.e. beyond 2030). 3rd generation CCS technologies are likely to be based on the progress of technologies which are today assessed with a low TRL in the range of 1-3, including likely refinements of the 2nd generation technologies.

2.1.2 Existing Demonstration and Commercial Plants

There are several CO_2 capture facilities operating worldwide – several of these involves the production of CO_2 for various commercial users (i.e. EOR, industrial, medical and food grade CO_2 for various uses). But this section of the report will only highlight and focus on the Large Scale Demo or Commercial Plants which include the integration of the CO_2 capture facilities with CO_2 transport and storage (including EOR operation).Recent GCCSI report [3] have identified numerous large scale integrated CCS projects undertaken worldwide in various stages of development.

Generally, any existing demonstration or commercial scale CCS plants that are in operation or under construction today could be broadly categorised in following sector described in the following sections.

2.1.2.1 CCS in the Power Generation Industry

In the power generation sector, the capture of CO_2 based on post-combustion capture and pre-combustion CO_2 capture technologies have realised full commercial scale demonstration. Whilst oxy combustion technology have achieved a mini-demonstration status.

For post-combustion CO_2 capture technology – the key demonstration projects include:

- Boundary Dam Unit #3 (Saskatchewan, Canada) is the world's first large scale demonstration project capturing 1 Mtpa CO_2 from 115MWe coal fired power plant using Cansolv Solvent. The plant commenced its operation in 2014. For further details – see Box 1. The captured CO_2 is mainly used for EOR operation, with a small part of the CO_2 also being injected in saline aquifer (via Aquistore Project).
- By 2018, the Petra Nova Unit #8 (Texas, USA) will be the largest post-combustion CO_2 capture demonstration project worldwide (using MHI's KS1 solvent). The plant will capture 1.4 Mtpa CO_2 from a slip stream (equivalent to 240MWe) of a coal fired power plant. This will be used for EOR operation.
- In Europe, ROAD (Rotterdam, Netherlands) is the remaining large scale CCS demonstration project in the power generation industry that could be realised by the end of this decade. This project involves the capture of 1.1 Mtpa CO_2 from a slip stream (equivalent to 250MWe) of a coal fired power plant using Fluor's Econamine solvent. The CO_2 will be stored off shore in a depleted gas field but an oilfield closer to shore is also now considered.

For Pre-Combustion CO_2 Capture, the world first commercial scale demonstration project is the Kemper County Energy Facility (Mississippi, USA).

- The plant is currently in commissioning phase and expected to be in service toward the end of 2016 or early part of 2017. The plant captures about 60% of the CO_2 from a lignite fired IGCC plant (using TRIG gasifier with Selexol based AGR). The captured CO_2 (3.o Mtpa) is to be used for EOR operation.

For oxy combustion CO_2 capture, due to several projects being cancelled – it is not expected to realise any full demonstration for this technology in the short to medium term. Nonetheless, it is worthwhile to emphasise that this technology has achieved mini-demonstration status based on the accomplishment of the following projects:

- Callide Oxy fuel Project (75 tonnes CO_2 per day)
- Flexiburn (oxyfuel CFB – 11 tonnes CO_2 per day) tested at Ciuden[4],
- Schwarze Pumpe (Vattenfall Oxy-fuel project – 75 Mtpa)[5] and
- Huazhong University of Science and Technology (HUST) Oxyfuel Plant (100 Mtpa).[6]

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[4] http://cordis.europa.eu/project/rcn/94480_en.html
[5] https://sequestration.mit.edu/tools/projects/vattenfall_oxyfuel.html
[6] http://www.globalccsinstitute.com/insights/authors//2016/05/05/milestone-oxyfuel-plant-going-operation-hubei-china?author=MTY4OTg%3D

2.1.2.2 CCS in the Industrial Sector

According to IEA [4], CCS is expected to have an important role in mitigating CO_2 emissions from the energy intensive industries.

Energy Intensive Industries could include the steel, cement, fuel transformation (including oil refining, GTL, CTL, SNG, etc.), chemicals and petrochemical, pulp and paper industries.

In some of these industries (i.e. ammonia/urea production, some DRI[7] plants, several of the SMR plants, etc.) could include the CO_2 removal as an integral part to their process or operation. For the purpose of this report, it is worthwhile to note about the key experiences gained from operating these plants.

However, with full chain CCS applied to the energy intensive industries, there are only a limited numbers of industrial CCS (with capacity of greater than 0.8 – 1 MPTY) that are in operation or under construction. The Global CCS Institute database provides a complete overview[8] but some of the notable examples include:

- Great Plain's Synfuel Plant (Dakota, USA) could be considered the world's first fully integrated CCS in energy intensive industry. The plant produces synthetic natural gas (SNG) from lignite using Lurgi gasifiers. About 3 MTPY of CO_2 (~50% of the total emissions) is captured from the syngas using Rectisol unit. This is then transported to Weyburn / Midale field for EOR operation. This has been in operation since 2005.
- Port Arthur Project (Texas, USA) captures CO_2 from two trains of SMR based hydrogen plant attached to an oil refinery. The CO_2 is captured from the syngas of the SMR using VSA. This plant has been in operation since 2013 and has the capacity to capture around 1 MPTY for EOR operation.
- Shell Quest Project (Alberta, Canada) captures CO_2 from three trains of SMR based hydrogen plant attached to Scotford Oil Sand Upgrader. The CO_2 is captured from the syngas of the SMR using Adipic-X solvent. This plant has been in operation since 2015 and has the capacity to capture around 1 MPTY for deep saline aquifer storage.
- Before the end of this decade, there are three other notable industrial CCS demonstration projects to come on-stream, these include:
    - ADM's Illinois Industrial CCS Project (Decatur, Ill., USA) – which is expected to capture around 1 MPTY of CO_2 from an existing ethanol plant and storing it in a saline aquifer. This project is the continuation of the Illinois-Decatur project which has already successfully stored a total of 1 Mt of CO_2 over the course of approximately 3 years. The capture of CO_2 only involves compression and dehydration (i.e. with minimal processing or purification). This should start its operation by 2016.

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[7] Direct Reduced Iron (DRI) plant mainly based on Energiron technology requires the removal of the CO_2 from its off-gas before being recycled as feedstock.

[8] http://www.globalccsinstitute.com/projects/large-scale-ccs-projects

- ADNOC CCUS Project (Mussaffah, UAE), also known as ESI CCS (Abu Dhabi), will be the **first steel mill** to integrate CO_2 capture and EOR operation. Around 0.8 MPTY of CO_2 will be captured from the DRI plant (based on Energiron III configuration). This should start its operation by 2017.
- Alberta Carbon Trunk Line (ACTL) project (Alberta, Canada) – will demonstrate the first industrial CCS cluster and once it becomes operational by 2018, it will initially capture around 1.7 MPTY CO_2 for EOR operation. It should be noted that the pipeline is designed to accommodate the transport of up to 14 MPTY of CO_2. This initial phase of the ACTL project covers the capture of CO_2 from Sturgeon Refinery (coming from H_2 production based on Lurgi Gasifer and Rectisol AGR) and NWR fertiliser plant (coming from SMR and its existing amine based CO_2 capture for Ammonia production).

2.1.2.3 CCS in the Natural Gas Processing Industry

Most of the early deployment of large scale demonstration of CCS involves the capture of CO_2 using chemical absorption in the natural gas processing industry. The captured CO_2 is then used as the working fluid for EOR operation or permanently stored in saline aquifer.

Some of the key examples include:

- In Europe, projects involving the capture of CO_2 (using amine solvent) from NG Processing Industry such as Statoil's Sleipner Project (Norway) has been operational since 1996 and Snøhvit Project (Norway) being operational since 2006.

  Sleipner was the world's first demonstration of CCS technology for a deep saline reservoir. The injection rate of almost one Mtpa also makes the project one of the largest demonstrations of CCS in the world to date.

  Approximately 0.85 million tonnes of CO_2 has been injected per annum. The purity of the CO_2 is at 98 per cent. The remaining 2% is mostly methane.

  Around 16.2 million tonnes of CO_2 have been injected since inception to June 2016.

  At Snøhvit, the amine-based CO_2 removal process is designed to capture 0.7 million tonnes of carbon dioxide annually when the facility is at full capacity.

  Injection started in April 2008 and to date nearly 3 million tonnes of CO_2 has been stored. With a life span of around 30 years for the LNG plant, the total volume of CO_2 to be stored is estimated at between 15 to 20 million tonnes. The purity of the injected CO_2 is at around 99 per cent.[9]

[9] https://member.globalccsinstitute.com/GSOCCS/Projects/Pages/Large-Scale-CCS-Projects---Project-Descriptions.aspx

- By 2018, Largest CCS project in Natural Gas Processing Industry will be demonstrated once Gorgon project (Australia) becomes online (i.e. this will involve the capture and storage of nearly 3 to 4 MTPY of CO_2 off-shore).

BOX 1

Boundary Dam Unit 3 (BD3) is the first-ever, commercial–scale, coal-fired power plant incorporating post-combustion CO_2 capture technologies using Cansolv solvent. This plant is situated near Estevan, Saskatchewan, Canada. The demonstration plant commenced its operation in October 2014. This is an important milestone proving that integrating CCS to a power plant works.

BD3 was approaching retirement. In 2010, Saskpower has made a landmark decision to proceed with the refurbishment of the unit and fully integrating the CO_2 capture system. Such decision allows the extension of the life of the coal fired power plant by at least 30 years – meeting the stringent regulations on GHG emission set by the Province of Alberta.

CO_2 capture system is based on Cansolv Technologies – which consists of two stage removal of SOx and CO_2. In the first absorption column, SOx is removed; and in the second column CO_2 is removed.

The captured CO_2 then geologically stored at two locations: in an oil reservoir approximately 1.4 kilometres deep at Cenovus' CO_2–EOR operation near Weyburn, Saskatchewan; and in a deep saline aquifer approximately 3.2 kilometres deep at the SaskPower Carbon Storage and Research Centre, located near the Boundary Dam Power Station. The latter geological storage site is the subject of the measurement, monitoring and verification (MMV) activities of the Aquistore Project that is managed by the Petroleum Technology Research Centre in Regina, Saskatchewan.

Details of the lessons learned in building the world's first full scale CCS plant is presented in the recent IEAGHG report [5]

To date, BD3 has achieved the following:

- Produces 115-120 MWe of power, which is enough to cover the electricity demand of 100,000 local homes
- Surpassed the 1 $MtCO_2$ milestone in July 2016 reducing nearly 90% of the plant GHG emissions. [10]
- Reduces SOx emissions from the coal-fired power plant.
- Demonstrate the economic, technical and environmental feasibility for coal-fired power generation with CCS
- Support the development of industry-wide CCS regulations and policies

[10] http://www.saskpower.com/about-us/blog/bd3-status-update-july-2016/

2.1.3 Performance of the First Generation CO_2 Capture Technologies and its Future Development and Improvement

CO_2 capture technologies have undergone notable development in the last decade. With the current large-scale CCS demonstrations underway, it is expected that further development and improvement will be realised as part of learning by doing.

With the current generation of CO_2 capture technologies, the main focus of development in the short to medium term will be on cost reduction (i.e. in terms of CAPEX and OPEX) and on solvent/emission management.

In the power generation industry, further development in response to the requirement for plant flexibility (i.e. due to growing penetration of renewable energy) will be expected. Development of "energy storage" should also have an impact in the future development of CCUS technologies in the power generation industry.

In the energy intensive industries, the development of the CO_2 capture technologies would come hand in hand with the improvement to their energy efficiency (not only in the CO_2 capture plant but also to their respective manufacturing processes). This is a necessity to maintain their competitiveness. CCU could play a role in the short to medium term deployment of large-scale CCS to make early projects profitable (additional revenues). However, it has to be stressed that CCU is no long-term GHG mitigation option to cope with Climate Change as the products formed of CO_2 usually have short lifetimes (weeks to years) and will soon be emitted back to the atmosphere. Therefore, each CCU application requires (on a case by case basis) a detailed Life Cycle Assessment (LCA) to demonstrate the eventual climate change mitigation potential of the respective use of CO_2. Apart from the lifetime of CCU products there is a huge discrepancy between the annually worldwide emitted amount of energy related CO_2, hence the annual mitigation potential of CO_2, and the anticipated worldwide market size of CCU products, i.e. more than 32 Gt of energy related CO_2 emission versus 100 – 250 Mt (CO_2 consumed) of CCU products per year.

2.1.3.1 Post Combustion CO_2 Capture – Chemical Absorption

The use of chemical solvent to capture CO_2 from combustion flue gases is well established. The review of literature [6, 7, 8, 9, 10] could indicate that solvents used in CO_2 capture plants now include wide variety of amines, amino acid salts, aqueous ammonia, and many others. Table A.0.1 in the Annex presents a list of amine solvents that are commercially offered in the market to capture CO_2 from flue gases. This could indicate the current state of the art technology for 1st generation post-combustion CO_2 capture technologies.

Throughout the past decades, lessons learned from operating various pilot plants have been projected into the design of large scale demonstration and commercial plants worldwide. Studies have generally indicated that through the improvements of solvents, processes and equipment, the efficiency has increased significantly, as the steam demand for solvent regeneration has been reduced from 3.8 – 4.0 GJ/t CO_2 (reported in 2005) down to 2.7– 2.9 GJ/t CO_2 [10] or even to 2.3 – 2.4 GJ/t CO_2 [11].

Figure 2.1 illustrates the theoretical minimum separation energy required to separate the CO_2 from the flue gas. The figure further re-emphasises that the current first generation chemical absorption

technologies (30% MEA) has improved its thermodynamic efficiency (W_{ideal}/W_{real}) from 25% to 37% in the past decade.

For the first generation chemical absorption technology, it is expected that development work will continue to improve the efficiency and cost reduction that could cover:

- Better formulation of the solvent to enhance kinetics and mass transfer.
- Improvement to the process – i.e. split flow configuration, inter-cooling, vapour recompression, etc.
- Better integration with the host power plant or industrial complex
- Improvement to the equipment – i.e. absorber packing, heat exchangers, stripping column, etc.
- Scaling up of the equipment
- CO2 release at higher pressures, leading to a reduction in energy consumption of the compressors
- Solvent regeneration at lower temperatures (<80C)

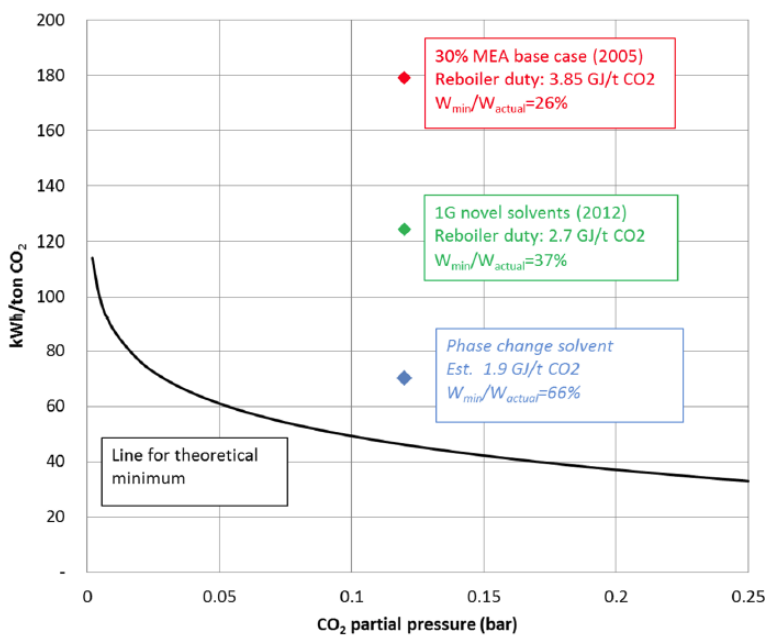

Figure 2.1 Theoretical minimum separation work of CO_2 capture [10][11]. See Raynal et al. (2011) for phase change solvents.

[11] Figure presents the theoretical minimum separation work. The values are calculated based on the actual work done by the working fluid (i.e. steam) at around 20-25% thermodynamic efficiency. For comparison, 100 kWh ~ 0.36 GJ.

Further development will also cover in general areas such as materials (i.e. corrosion issues), environmental impact (i.e. air emissions, water usage, etc.), solvent degradation (i.e. handling of degradation product, impact of inhibitors, etc.), and operation flexibility.

2.1.3.2 Pre-Combustion CO_2 Capture – IGCC based Power Plant

In power generation, pre-combustion CO_2 capture is generally synonymous to coal fuelled IGCC plants. In recent years, several pilot plants[12] have been implemented to validate the performance of capturing CO_2 from syngas.

Crucial to the development of Pre-Combustion CO_2 capture are the following elements:

- Improvement to the gasification process (i.e. syngas production and cleaning)
- Development of novel oxygen production
- Integration of the water-gas shift reactor
- Improvement to the acid gas removal unit (AGR)
- Development of gas turbine suitable for firing H_2 rich syngas (i.e. using lean premix burners).

It should be noted that this report would only focus on the development related to the acid gas removal. Other areas are not discussed as they are beyond the scope of this report. An overview to the key development necessary in these areas is given in various papers and reports (e.g., [9], [12]). Enabling technologies for novel power cycles (i.e. involving solid oxide fuel cells or new turbomachinery) have also been put outside the scope of this particular report.

The integration of CO_2 capture in an IGCC plant could be achieved in two steps - this involves (a.) the conversion of CO to CO_2 in the water gas shift reactor; and (b.) the separation of the CO_2 from the syngas in the AGR unit.

For pre-combustion CO_2 capture, the "conventional" CO_2 removal processes could be considered as the first generation technology.

There are broadly classified under two general types of solvent that could be used to remove both H_2S and CO_2 – namely: (1.) chemical solvent or (2.) physical solvent. However, there are other solvents which could be considered as physico-chemical (hybrid) solvent.

For chemical solvent, the most commonly referenced solvent is the MDEA. For physical solvent, the most commonly referenced solvent is the Rectisol (cold methanol) and Selexol (dimethyl ether of poly-ethylene glycol).

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[12] Various pilot plants (using slip stream of syngas taken after the gasifier) at Buggenum (NL), Puertollano (Spain), and Polk (Fl, USA) – evaluated the performance of various physical and chemical solvents including the performance of the shift reactor - See Ref [9].

The performance of the Pre-Combustion CO_2 capture is dependent on the cumulative performance of all the integrated units of the whole IGCC plant (i.e., from gasification to gas turbine operation – it should be noted that this is not limited to the performance of AGR alone). Nonetheless, specific to the AGR unit – several incremental improvements should be expected.

MDEA has been commercially employed, hence any improvements should be expected on a trajectory similar to that discussed for post-combustion CO_2 capture (section 2.1.3.1).

With regards to the physical solvent, the list below highlights some of the key areas where potential improvement to either Rectisol or Selexol are desirable.

- For Rectisol Unit – operating temperature as low as -40°C is typical. The cost and energy penalty during refrigeration should be an area where further development is expected. Also, through modularisation and standardisation of the process will be one of the aims to reduce cost of Rectisol units.

- For Selexol Unit in standard configuration, the purity of the CO_2 at >99% is a limitation. To achieve higher than 99% purity – a configuration with addition of chillers to reduce temperature down to around 5°C is necessary which would add cost and inefficiency.

- For both Rectisol and Selexol a small amount of CO and H_2 slip are to be expected. Reducing such slip is an area of development that is necessary to address purity issues and energy penalty.

- Additionally, some ppm level of H_2S would also be co-captured with the CO_2. This becomes an important issue if the CO_2 captured from physical solvents will be delivered to a pipeline network.

In conclusion, it should be noted that there is a wealth of experience already gained in existing commercial plants using chemical or physical solvents. These include the Great Plains Synfuel Plant (Rectisol), Coffeeville Gasification – Ammonia Complex (Selexol), and many other coal to liquid (CTL) or coal to chemical (CTC) plants deployed worldwide. Additionally, the use of chemical solvent in various ammonia/urea production is considered as the current state of the art application for CO_2 capture in an industrial setting.

2.1.3.3 Oxy Combustion

Oxy Combustion technology is one of the important routes developed in the past decade to capture CO_2 from coal or gas fired power plants.

There are 4 different key areas of development within oxy fuel combustion technology and these include:

- Boiler/gas turbine and burner development
- Air separation unit (ASU)

- Flue gas processing unit
- CO_2 processing unit (CPU)

It should be noted that this report would not be able to cover several of these areas of development (except for the oxygen production) as these are not part of the scope of this report. Nonetheless, details of its development have been reviewed in several literature [9], [13, 14, 15, 16].

In principle, this technology when applied to power plants could provide near zero gaseous emissions (with only a small vent stream from the CPU and atmospheric CO_2 from the ASU). Similarly to post-combustion, water is a co-product also in oxy combustion. Unfortunately (unlike post- or pre-combustion CO_2 capture technologies), it is not possible to demonstrate this technology on a sub-scale or slip stream type of projects given that it requires the full conversion of the boiler or gas turbine.

In the past decade, significant advances have been made in all areas of development. Today, several boiler manufacturers could deliver oxy fuel fired boilers in demonstration or near-commercial terms. Likewise, all major industrial gas companies are also in position to offer a suite of technologies in ASU and CPU to suit the requirements of oxy fuel combustion technology.

It should be emphasised that the distinction between current and future generation oxy fuel combustion technology is not a clear cut. It is important to note that the development of oxy combustion is evolutionary in nature. It should be expected that development pathway would be very similar to how conventional boilers (PC or CFB) are developed.

To enable the future development of new emerging oxy fuel technology it is required to deploy the first generation oxy fuel combustion technology as several components in the first generation technologies will also be used in any emerging novel oxy fuel technologies. Thus demonstration of first generation technology is an important target to any successful deployment of future emerging technologies.

In the area of boiler and burner development, fundamental work will continue with an aim to accumulate knowledge database in flame management, pollution formation and impact of process configuration. These type of development shows huge similarity to how conventional boilers are developed and improved.

In oxygen production, customised cryogenic ASU that suits the requirement of oxy combustion are well established. It is expected that these ASUs will have energy efficiency at 25 – 30% better as compared to conventional ASU. However, the cost reduction and optimisation will be the main focus of future work. Furthermore, large scale ASU (with capacity of greater 5000 TPD) are now under construction in India and South Africa. Despite that these are mainly used in gasification process, key learnings from building these mega-ASU units will be mutually beneficial to any future demonstration of 1st generation oxy combustion.

There are several development in CPUs. Several of these components are extensively tested in various pilot plants and mini-demo plant. Despite shelving of several oxy combustion projects, large scale demonstration of the CPU have been achieve through applications in other industries. For example,

principles of CPU process has been deployed by Air Products in recovering helium from natural CO_2 field; similarly, Air Liquide used the same class of technology in demonstrating their CRYOCAP concept to capture CO_2 from SMR based H_2 plant.

In summary, demonstrating oxy combustion is an important target in order to achieve wide deployment of this technology. It is essential to establish long term performance of the plant – which also include management of air ingress (as this contribute to the main uncertainties in maintaining the long term performance target of the power plant).

Further, improvement to oxy combustion technologies is also aimed to optimise the process integration between boiler, flue gas processing units, ASU and CPU. Whereas, opportunities for co-production of water with oxy combustion plant is a potential and opportunity that is currently being explored [17].

Flexibility of the power plant has been addressed in various FEED studies. Options for energy storage has been noted as viable addition through the integration and management of the ASU and CPU.

In the medium to long term future development of novel technologies in oxygen production will be an important goal to reduce cost and improve performance. Novel oxy-GT technologies is now moving toward large scale pilot demonstration. Development in pressurised oxy combustion is an area where R&D interests is growing.

2.2 First Generation CO_2 Capture Technologies costs overview

In 2013, the CCS Cost Reduction Task Force estimated that generation and capture costs could drop approximately 17% for plants reaching FID in 2020. In the late 2020s generation and capture costs could drop further 25% [18]. Key to the successful wide spread deployment of CCS is to achieve the cost reduction target by 2030.

In 2011, ZEP reported costs of 1st generation CO_2 capture technologies, also comparing results against numerous studies in the literature [19]. More recently, Rubin et al. [20] presented current cost estimates for CO_2 capture, based on studies published until 2014.

Table 2.2 presents representative values as reported in various references used as cost benchmark for different CO_2 capture processes as applied to power plants (cost are adjusted to 2013€[13]).

[13] 2013 EUR/USD exchange rate=1.301 (Rubin, et al., 2015)

Table 2.2 Representative values of cost measures for power plants without and with CO_2 capture (adjusted from Rubin et al [20]).

Performance and Cost Measure	Post – Combustion		Pre- Combustion	Oxy Combustion
Fuel	Bituminous coal	Natural gas[14]	Bituminous coal	Bituminous/Sub-bituminous coal
Reference plant	SCPC	NGCC	IGCC	SCPC
Total capital requirement w/o capture (2013€/kW)	2,012	806	2,445	1,990
Total capital requirement w/ capture (2013€/kW)	3,520	1,584	3,356	3,796
LCOE w/o capture (2013€/MWh)	54	49	69	49
LCOE w/ capture (2013€/MWh)	87	71	92	85
Cost of CO_2 captured (2013€/t CO_2)	35	57	26	40
Cost of CO_2 avoided[15] (2013€/t CO_2)	48	67	[33 – 48][10)]	48

[14] The gas CCS costs are very dependent on the fuel price and fuel price sensitivities should be included in evaluations

[15] Excluding Transport and Storage.

[10] Reference plant is IGCC w.o. CCS although there are only 4-5 IGCC (1st of kind) IGCC plants worldwide operating. The ZEP Capture cost study [19] took a PC plant w.o. CCS as reference also for IGCC with CCS, in brackets are given the cost for a 1st of its kind plant (higher) and the cost for a nth of its kind (lower).)

3 Emerging CO_2 Capture Technologies for Power Generation and Energy Intensive Industries

3.1 Introduction

There is a range of 1st generation CO_2 capture technologies that can be deployed immediately as long as there is an economic incentive to produce the separated stream of CO_2. In Chapter 2, these 1st generation technologies have been described and can be taken here as benchmark to assess the performance and cost of any emerging CO_2 capture technology.

First generation technologies will naturally evolve and improve as experience is gained with an increasing number of plants (NOAK) built and operated successfully. Therefore, the main strategic objective of any emerging CO_2 capture technologies must be to grow up in scale and compete against existing benchmarks, demonstrating during such scaling up process their perceived benefits when compared to current 1st generation technologies.

In this chapter, several of the future CO_2 capture technologies have been identified and classified according to 2nd or 3rd generation technologies based on their TRLs. An assessment has been made to indicate their potential application in a variety of industrial settings (power generation, natural gas processing, and several energy intensive industries). The criteria for assessment should include performance parameters that are common in current debates: (a.) potential for cost reduction and efficiency improvement (b.) operation flexibility, (c.) retrofitability, (d.) health safety and environment (HSE) issues, (e.) reliability and material availability.

Emerging technologies which can be retrofitted or adopted to existing 1st generation large scale CCS plants will provide additional value as these technologies are able to enter the market faster, hence time to market will be shorter.

Combinations of 1st, 2nd and 3rd generation technologies, so called “hybrid systems” have been receiving a growing research interest. These are expected to eventually offer individually shaped solutions to many different applications in the future, e.g. absorption followed by cryogenic capture or the combination of chemical looping with H_2-membrane reactors for H_2 production with integrated CO_2 capture, but are beyond the scope of this study. There are expectations that different (combinations of) technologies will compete depending on the CO_2 concentration in the flue gas and production capacity (also in view of decentralized capture).

In order to achieve the assessment objective set by this task force, this chapter is organised as follows:

- Selection of a representative **set of boundary conditions** for the future capture technologies in different industrial settings (Power, Natural Gas processing, Iron& Steel, Cement, Refineries, Paper/biofuel sectors). See Section 3.2.
- Discussion on characteristics of the emerging technologies that could qualify best for different industrial environments (3.3 Power sector; 3.4. Natural gas processing, 3.4 Iron & Steel, 3.6. Cement, 3.6Refineries, 3.7 Other), focusing on those that have experienced a recent progress

towards high Technical Readiness Levels and defining key challenges and future priority areas for R&D.

- Assessment of emerging technologies along a defined set of performance parameters based on a qualitative expert judgement. The assessment highlights the relative **strengths** and **weaknesses** of emerging CO_2 capture technologies compared to benchmark 1st generation technologies of today and point out the main gaps of knowledge. The result of this assessment is reflected in Table 3.2 by a simple traffic light system.

3.2 Definition of a set boundary conditions for emerging capture technologies in different industrial settings

The development of many of the new CO_2 capture technologies (2nd and 3rd generation) referred in the previous sections has been traditionally focused on the power sector [21], as this is the main source of anthropogenic CO_2 emissions. However, deploying CCS to energy intensive industries has rapidly gained strategic importance in Europe. This changes the boundary conditions for the capture operation. Even for "add-on" post-combustion systems, the composition (CO_2 concentration, impurities) of flue gas or off-gas streams as well as flow rate (scale) are different in different industries and might favour different capture technologies depending on the application.

Table 3.1 provides an overview of boundary conditions relevant for CO_2 capture systems operating in typical power plant and industrial settings. These parameters will influence possible capture applications and, therefore, will be used to discuss the status and suitability of different emerging technologies under the different industrial boundaries in the following sections. Table 3.1 is only indicative as some of the assumptions in such table can already be challenged: coal power plants have been designed in the past for base load, thus operating at least 6'000 hours per year, while gas power plants in many countries in the world have been mostly used to provide part-load, thus operating between 4'000 – 5'500 hours per year (this is mainly due to the more expensive fuel natural gas, which shifts gas power plants to the higher end of the merit order). More recently, in many parts of Europe, an increasing share of intermittent renewable power have been installed leading to a drastic reduction in the annual operational hours for gas power plants as well as coal power plants. Lower overall operational hours ask for more flexible CO_2 capture concepts, may be at the expense of lower total capture rates or efficiency penalties. Different emission sources and non-steady operation (from power or industry) will also have a notable impact on the transport and storage infrastructure.

A brief review of the status of development of different emerging CO_2 capture technologies is given for the most relevant sectors in the following sections.

Table 3.1 Differing boundary conditions for CCS in the Power and energy intensive industry sector:

	Hard Coal (Advance USC PC equipped with SCR & FGD)	Lignite (Advance USC PC equipped with SCR & FGD)	NGCC (F-Class GT with 2-2-1 arrangement)	Integrated Steel Mill (BF-BOF Route)	Cement (Dry Kiln w/ 5 Stage Preheater & Pre-calciner)	Hydro-skimming Refinery	Medium to High Complexity Refinery	High Complexity Refinery	Hydrogen (SMR with Pre-Reformer, HT Shift and PSA)
Nominal Capacity	1000MWe (Net)	800MWe (Net)	900MWe (Net)	4 million tonne HRC/y	1.0 million tonne clinker/y (1.4 million tonne cement/y)	100,000 bbl/d (~5 million tonne crude/y)	220,000 bbl/d (~11 million tonne crude/y)	350,000 bbl/d (~17 million tonne crude/y)	100,000 Nm3/h
Emission Factor	0.75-0.80 t CO2/MWh	0.85-0.90 t CO2/MWh	0.35-0.40 t CO2/MWh	2.0-2.1 t CO2/t HRC	0.66-0.68 t CO2/t cement	0.14-0.16 t CO2/t crude	0.20-0.22 t CO2/t crude	0.22-0.24 t CO2/t crude	0.80-0.81 kg/Nm3 H2
Emission Sources	Single Point Source	Single Point Source	Single Point Source	Multi-Points Sources	Single Point Source	Multi-Points Sources	Multi-Points Sources	Multi-Points Sources	Single Point Source (Modern SMR)
Annual Operating Hours	7,500	7,500	7,500	8,784 (See Note 7)	8,400	8,400 (See Note 8)	8,400 (See Note 8)	8,400 (See Note 8)	84,00
Annual CO_2 Emissions (MTPY)	5.80 - 6.20	5.00 - 5.40	2.30 - 2.70	8.00 - 8.40	0.90 - 0.95	0.70 - 0.80	2.20 - 2.40	3.50 - 4.00	0.65 - 0.70
Typical Fuel	Hard Coal	Lignite (with 50% moisture)	Natural Gas	Off Gases supplemented by NG	Coal, Petcoke, Waste, Biomass	Off Gases	Off Gases	- Off Gases	PSA Tail Gas supplemented by NG

	Hard Coal (Advance USC PC equipped with SCR & FGD)	Lignite (Advance USC PC equipped with SCR & FGD)	NGCC (F-Class GT with 2-2-1 arrangement)	Integrated Steel Mill (BF-BOF Route)	Cement (Dry Kiln w/ 5 Stage Preheater & Pre-calciner)	Hydro-skimming Refinery	Medium to High Complexity Refinery	High Complexity Refinery	Hydrogen (SMR with Pre-Reformer, HT Shift and PSA)
Volume (Wet)	3100 - 3200 KNm3/h	3250 - 3350 KNm3/h	4000 - 4200 KNm3/h (Based on the cumulative volume of the 2 flue gas stacks)	For furnaces, utility boiler, hot stoves - 1.3-1.35 KNm3/h per t/h BFG; 2.1-2.2 KNm3/h per t/h BOFG; 11.8-12.5 KNm3/h per t/h of COG - all burned @15% x'ss air	210-220 KNm3/h	14-17 kNm3/h per t ROG or fuel oil	14-17 kNm3/h per t ROG or fuel oil	14-17 kNm3/h per t ROG or fuel oil	200-220 kNm3/h
Pressure	1.0-1.1 Bara	1.0-1.1 Bara	1.0-1.1 Bara	1.0-1.1 Bara	1.0-1.1 Bara	1.0-1.1 Bara;	1.0-1.1 Bara; For **FCC** - 2-3 Bara	1.0-1.1 Bara; For **FCC** - 2-3 Bara	1.0-1.1 Bara
Temperature	80-90°C	80-90°C	80-90°C	Depending on process (between 120-250oC)	110-120°C	For **Fired Heater**s – process dependent ~ambient to 400°C; **Utility**	For **Fired Heater**s - process dependent ~ambient to 400°C; **Utility Boilers: –**	For **Fired Heater**s - process dependent ~ambient to 400°C; **Utility Boilers:** - up to	130-140°C

	Hard Coal (Advance USC PC equipped with SCR & FGD)	Lignite (Advance USC PC equipped with SCR & FGD)	NGCC (F-Class GT with 2-2-1 arrangement)	Integrated Steel Mill (BF-BOF Route)	Cement (Dry Kiln w/ 5 Stage Preheater & Pre-calciner)	Hydro-skimming Refinery	Medium to High Complexity Refinery	High Complexity Refinery	Hydrogen (SMR with Pre-Reformer, HT Shift and PSA)
						Boilers: up to 140-160°C	up to 140-160°C; For **FCC** – up to 300°C;	140-160°C; For **FCC** – up to 300°C;	
CO_2 Concentration (%v dry basis) in the stream to be separated	12-15%v	12-15%v	3-4%v	Any combustion appliance burning: **COG** - 4-5%v; **BFG** - 25-30%v; **BOFG** - 18-20%v	22-26%v (See Note 9)	For Fired Heaters and Utility Boilers - 4-5%; ROG: 12-14%	For **Fired Heaters** and **Utility Boilers** - 4-5%; ROG: 12-14% ; For **FCC** - 12 - 16%;	For **Fired Heaters** and **Utility Boilers** - 4-5%; ROG: 12-14% ; For **FCC** - 12 - 16%;	20-22%v
Non-CO_2 species in Flue Gas	SOx, NOx, N_2, O_2, Ar, H_2O, CO, dust, heavy metal	SOx, NOx, N_2, O_2, Ar, H_2O, CO, dust, heavy metal	NOx, O_2, N2, Ar, SOx (if H_2S is present in NG)	Depending on process & fuel	SOx, NOx, N_2, O_2, Ar, H_2O, CO, dust, heavy metal	Depending on process & fuel	Depending on process & fuel	Depending on process & fuel	NOx, O_2, N_2, Ar, CO

Abbreviations: ARU - acid gas removal unit; BFG – blast furnace gas; BOFG - basic oxygen furnace gas; COG - coke oven gas; DCK - delayed coker; FCC - fluid catalytic cracker; HC – hydrocarbons; HCK – hydrocracker; HRC-Hot Rolled Coil; LPG - liquefied petroleum gas; NG - natural gas; ROG - refinery off-gas; SDA - solvent de-asphalting unit; SMR - steam methane reformer; PSA - pressure swing adsorption; HTS - high temperature shift; TRT - top gas recovery turbine; PRT - power recovery turbine; FGD - flue gas desulphurisation; SCR - selective catalytic reactor (De-NOx)

3.3 Emerging CO_2 Capture Technologies for Fossil Based Power Plants

There are recent reviews and reports on emerging CO_2 capture technologies that could be applied to power plants [22, 23, 24]. This report will not attempt to re-write or update these reviews. The target here is to introduce the different families of emerging CO_2 capture technology applicable to the power sector, provide an overview on their current development status, point out the R&D challenges ahead to enable these technologies to live up to their expectations and anticipated key benefits, and identify their potential application in industrial sectors.

The emerging technologies are usually classified by their gas separation principles which is at the core of every CO_2 capture system [21]. For simplicity, we are not reviewing other important enabling future technologies for CCS in the power sector (i.e. new turbomachinery, fuel cells, new combustor or gasifiers designs etc.) as these are considered outside the scope of this report. However, it should be emphasised that these can strongly affect the final viability of 2nd and 3rd generation technologies. Therefore, some reference to the status and TRL of these enabling technologies will be made when needed.

Table 3.2 provides an overview of different classes of 2nd and 3rd generation (emerging or novel) capture technologies that are proposed for capturing CO_2 from power plants. These are characterised by their potential to achieve substantial improvement either with respect to the functional material, the reactor/contactor design or in the gas separation concept. This table presents the progress of their development towards their scale up and commercialisation goals. Their TRL assessment in 2005 is presented to indicate their progress over the last decade of development.

These emerging technologies are compared against 1st generation capture technologies which, as described in Chapter 2, are used as a benchmark - i.e. the commercial separation processes based on amine based chemical absorption technologies (that have reached TRL8 - 9 in the power sector); physical absorption technologies to separate CO_2 from syngas or fuel gases at high pressure (that have reached TRL8 - 9 in several industries) and cryogenic air separation technologies used to deliver O_2 to an oxygen blown gasifier or oxy combustion systems (TRL8-9 for the power sector and TRL9 for industries).

It should be noted that there are many more scientific and patent references presenting many more proposals for advanced separation technologies. Typically, these are assessed at TRL1-2 (i.e. encapsulated solvents, ionic liquids, electric regeneration, reactive gas electro-sorption, Metal Organic Frameworks). These technologies are considered to be too premature to be included in this assessment of emerging concepts as they need to demonstrate proof of concept under representative conditions (typical boundary conditions) relevant to power plants and industrial applications.

Some of the emerging technologies presented in Table 3.2 have not evolved in their TRL in the last 10 years, perhaps indicating some fundamental challenge to further development (i.e. functional material reactivity and/or stability, need of extreme operating conditions, limitations in gas-liquid/solid contact area etc.). These technologies may have been fallen into the “valley of death” where further development may not be viable.

Numerous R&D projects worldwide have been completed in recent years to achieve the progress in TRLs as presented in Table 3.2. In the EU, 9 currently active R&D CO_2 capture projects have been identified within the 7th framework program (FP7) and more projects have just started under the EU's Horizon 2020. The Joint Programme on CCS of the EERA (40 participant R&D institutions from 14 countries,[16] attempts to provide coherence and strategic vision to the energy research capabilities and ongoing projects on CO_2 capture at MS and EU levels. In Europe, ECCSEL is a project dedicated to organize and share resources in a common pool amongst participating organisations, by making use of readily available laboratories, modifying existing ones, and planning and building entirely new advanced laboratories.[17]

Table 3.2 Perceived status of a range of emerging 2nd and 3rd generation CO_2 capture technologies, by referring to their maximum TRL (cited by a reference) achieved in 2015 with respect to 2005 (advanced process variants tested at lower TRL exist for each of these category of technologies)

Separation Process	TRL 2005	TRL 2015	Reference
Precipitating solvents	3	5	[25, 26]
Biphasic solvents	3	4-5	[27, 28]
Catalysed enhanced solvents	4	5	[29, 30]
Vacuum Pressure Swing Adsorption (post combustion)	2	5	[31, 32, 33]
Temperature Swing Adsorption (post combustion)	2	3-4	[34]
CO_2 liquefaction/partial condensation	2-3	6	
Chemical looping combustion of solid fuels	3	6	[35]
Calcium looping, post combustion	2	6	[36]
Metallic membranes for H_2	3	4-5	[37, 38]
Polymeric membranes for CO_2	3	5-6	[39]
Ceramic membranes for O_2	4	4	[40, 41]

[16] http://www.eera-set.eu/eera-joint-programmes-jps/carbon-capture-and-storage
[17] http://www.eccsel.org/

We briefly summarise the status of the technologies referred in Table 3.2 as applied to the power generation industry.

3.3.1 Solvent - based Processes

The 2nd or 3rd Generation solvent based processes comprise precipitating solvents, bi-phasic solvents and catalyzed enhanced solvents. This class of technologies can be considered as refined version of the 1st generation amine-based post-combustion CO_2 capture technologies as reviewed in Chapter 2. Therefore, the fundamental advantage of these 2nd generation solvent systems with respect to other emerging technologies is their potential adaptability/retrofitability. This means that such systems can mostly rely on components and equipment demostrated in large scale power plants with CO_2 capture and in other industries (which have achieved a TRL of 9).

Solvent systems causing precipitation of bicarbonates, amino acids or other salts (solid phase formation) can speed-up absorption kinetics and lead to almost complete turn-over (shift of chemical equilibrium) in the absorber. Depending on the insolubility of the precipitated salt, its separation or the significant reduction of the CO_2 rich solution is possible, consequently reducing the regeneration energy in the stripper. The reduced amount of co-evaporated water in the stripper offers potential to reduce OPEX as well as the efficiency penalty. Moreover, the fast absorption kinetics due to the salt formation might make precipitating solvent processes better as compared to conventional amine processes when dealing with flue gases having low CO_2 concentration (i.e. for post-combustion capture in NGCC).

However, due to the nature of the precipitation, it may encounter some operational issue – i.e. blocking of the packed bed or other equipment and subsequently fouling problems. On the other hand, the use of precipitating solvent might not show superior against amine based chemical absorption technologies with respect to operational flexibility. This is due to the fact that all solvent based technologies will show some physical inertness towards fast shut down and turn on, especially when high volumes are circulated and a certain temperature level has to be kept.

3.3.1.1 Enzyme catalysed enhanced solvents

A known performance limitation of enzyme catalysed enhance solvents is that they do not withstand temperatures of over 100°C, lower than the 120°C of a conventional regeneration (desorption) process. Options proceeded to manage this include the immobilization of enzymes on packing in the absorber column, the filtration of enzymes out of the solution before it reaches the regenerator and the operation of the stripper at lower temperature and pressure. All of these options come with significant challenges and have yet to be demonstrated as viable options for large scale CO_2 capture. If the enzymes are immobilized on the packing in the absorber, it is not clear if they will perform as efficiently as when they are freely floating in aqueous solution. The catalytic effect is most needed on the gas-liquid interphase, and a catalyst sitting on the packing may therefore be less effective. Filtering the enzyme out before it reaches the regenerator obviously requires new process equipment in the plant. Any filter is also likely to reject some solvent together with the enzyme, this may impact the overall efficiency of the capture cycle.

Another concern on enzyme catalysis is which solvent systems benefit to which extent. Many conventional amine solvents already show fast kinetics, hence the potential benefits of an enzyme catalysed process are likely quite limited. Carbonate solvents have been proposed as candidate solvents for enzyme catalysis. However, with respect to carbonate solvents kinetics does not appear to be the only issue as they show under various conditions also low cyclical capacity and are hard to regenerate. It is therefore not clear if a carbonate system with enzyme catalysis will be competitive with conventional amine solvents. It is uncertain if there is any solvent system that will benefit enough from enzyme catalysis to justify the additional complexity of the system.

3.3.1.2 Encapsulated solvents

Encapsulated solvents are thin polymer beads that contain a liquid solvent. CO_2 will diffuse unimpeded through the particle and absorb in the liquid. Encapsulated solvents intend to combine the benefits of liquid solvents with the benefits of solid sorbent process configuration, e.g. non volatility of solvent, no co-evaporation etc. Another stated advantage of this concept is that it can utilize solvents with higher viscosity although higher viscosity also slows down diffusion of the CO_2 through the gas-liquid interphase. This problem is not addressed by encapsulation. If the encapsulated solvents are to be utilized in a thermal swing process there is a need to heat and cool the liquid, the encapsulation would appear to have a potential detrimental effect on the heat transfer in the medium.

While the encapsulated solvents represent a novel concept, it is not clear if it offers a path to more efficient CO_2 capture processes. Further work on encapsulated solvents should identify process configurations suitable to demonstrate that the technology can gain energy benefits on the overall system level.

3.3.1.3 Ionic liquids

Ionic liquids have been explored as novel solvents for CO_2 capture. Ionic liquids however tend to have high viscosity, which can impact the capture process in a number of ways. High viscosity affects the diffusion of free CO_2 through the liquid and thereby has an impact on the wetting of packings required for efficient gas-liquid contacting. Higher viscosity also influences the heat transfer properties of the liquid, potentially requiring larger equipment for heat transfer. The likely biggest merit of ionic liquids, their non-volatility, shows potential advantage in the stripper and in terms of emission control but might be (over)compensated by higher energy consumption of pumps and higher vulnerability for corrosion of equipment. Moreover, the cost for the solvent will be significantly higher than for a conventional system. While higher viscosity requires more energy to pump the ionic liquid through the capture process the potential overall system benefits remain vague.

3.3.1.4 Challenges and R&D targets

Key challenges and R&D targets for solvent-based capture in the power sector include:

- Flexible operation of integrated capture and power plants. Develop processes that enable the integrated plant to respond quickly and efficiently to changes in power and carbon markets.
- Focus more on system level perspective: Process strategies shall be developed on how and to which extent to integrate capture facilities into different power plants indicating and guiding the

trade-off between high degrees of integration and minimised efficiency penalties and lower degrees of integration at higher operation flexibility

- The high energy requirement of the separation process; a penalty of~8-12% points in efficiency loss on total plant level with present technology (MEA). A long-term R&D target (beyond 2030) should be to reduce this to **below 5% points.** Most of the recovery energy of CO_2 (efficiency penalty) is due to desorption of CO_2 from aqueous solution.
- The low CO_2 partial pressure (especially for NG power plants) and the large flue gas volumes imply very large equipment volumes and contacting surfaces. Reduce equipment volumes by developing more effective contacting surfaces and faster cycles
- Flue gas impurities (depending on fuel/industrial process). Develop capture processes independent from, or at least very robust with respect to composition of impurities in the flue gas.
- Degradation and environmental aspects. Ensure that capture processes have no significant effect on human health or the environment, e.g. emissions and/or degradation products. Deploy online technologies to constantly monitor plant emissions and allow for immediate actions in case thresholds are exceeded.
- Material of construction: Develop abundant, lower cost materials for construction of capture plants.

3.3.2 Solid Sorbent Processes

This section assesses emerging solid-sorbent based systems (using PSA, VPSA and TSA) for large-scale separation of CO_2 from flue gases of power plants or other industries. It further includes Sorption Enhanced processes conceived for pre-combustion applications that may be particularly relevant for industrial applications discussed in section 3.3.

High temperature solid looping systems are discussed separately in section 3.2.3. The use of pressure swing adsorption (i.e. PSA or VPSA) process are considered commercial in many gas separation applications. These could be predominantly seen in the production of H_2 from syngas of IGCC, ATR, POX or SMR plants; in small scale production of nitrogen or low purity oxygen (i.e. up to 300 TPD of O_2 at 90-95% purity with the balance being typically Argon) from air; or purification of air (i.e. removal of H_2O, CO_2 and others) in a cryogenic Air Separation Unit. However, many of these separations processes are not directly applicable to CCS for the power sector because they tackle relatively small flows of gases adsorbed by the solid (i.e. impurity removal) and/or sorbent regeneration steps that do not/cannot release a concentrated stream of CO_2 for subsequent purification and disposal.

The use of VPSA is demonstrated in the Air Product's SMR plant at Port Arthur (Texas, USA) capturing around 1Mtpa of CO_2 from the shifted syngas, transported and used for EOR operation. These mature capture systems have been discussed in Chapter 2.

The novelty of emerging solid sorbent system (2nd or 3rd generation) is usually linked to the properties of a novel adsorbent materials selectively capturing the CO_2 from the flue gas as well as the design of more efficient cycle configurations. It is also crucial to evaluate the **viability** of these novel concepts when handling **large volume** of flue gas at near atmospheric pressure. The cost of compressing the flue gas

will outweigh any advantages if the stream to be treated is dilute in CO_2. Furthermore, the scale of the gas flows requires that the adsorption processes are run at fast cyclic conditions in order to maximise the productivity [24]. However, temperature swing adsorption would be technically feasible.

There are several solid adsorbent materials being investigated for capturing CO_2 from flue gases. This could include activated carbons, zeolites, meso-porous silica, metal organic frameworks (MOF's), silicates, hydrotalcites etc. Depending on the type of interaction between CO_2 and the adsorbent material, different process configurations can be applied to separate the CO_2. Sorbents which show weak interaction with CO_2 (physisorption) usually show a high CO_2 loading or working capacity (2-4 mol/kg = 9–17 wt.%) with small heat of adsorption (0.34 – 1 GJ/tCO_2), depending on the pressure/temperature dependency of the adsorption equilibrium and on the operating pressures/temperatures. This type of adsorbent could be suitable for separating CO_2 from flue gas (with high concentration at >15%) using a VPSA configuration [24].

There are also different adsorbents being developed which are enhanced by the addition of chemically active surface to provide stronger interaction with CO_2. These types of adsorbent usually shows lower working capacities (1-2.5 mol/kg = 4–11 wt. %**)** but are highly selective towards CO_2; therefore could be suitable for flue gases with lower CO_2 concentrations. The heat requirements for regeneration are similar to the ones of solvents and range from 1.1 to 2.3 GJ/t CO_2, with the advantage that the heat capacities are lower since there is no need to dilute the amines in water. In applications to CO_2 concentrations below 10%, these materials can be used in temperature swing (TSA) processes.

The performance of a novel material in an adsorption process is difficult to predict from simple physical parameters, because for a given material the process itself can be optimized and adapted to achieve improved performance [42].

A PSA (pre-combustion capture) or a VPSA (post-combustion) carbon capture process will be designed in a configuration that is not like conventional processes (hydrogen production or air separation) because CO_2 will always be the more strongly adsorbed component. The actual configuration will depend on the specified purity and recovery. These are typically fixed at 95+% purity and 90+% recovery, but if these are allowed to vary, a broader range of process configurations and materials would be of interest. The greater flexibility would require a combined polishing step in hybrid system to achieve pipeline quality conditions.

In a VPSA cycle the recovery will depend on the vacuum pressure that can be achieved and for large scale systems (vacuum pressure ~ 0.2 bar) this constraint is likely to lead to two-stage multicolumn configurations.

In PSA cycles single stage multicolumn systems can achieve the required separation, possibly including a vacuum swing step to desorb fully the CO_2.

For low concentration streams, rapid TSA processes can be achieved using fluidized beds [43] or rotary wheel adsorbers (RWA) [44]. For higher concentration streams, PSA or VPSA processes will always be

preferred since the cycle time will be at least an order of magnitude lower than that of TSA cycles (i.e. much higher productivity).

To achieve very fast cycles in PSA, VPSA and RWA systems, structured packings that minimise pressure drop and maximise productivity need to be developed.

In power plant applications, it is likely that multiple trains will be needed. While in the short term this may seem to result in a higher cost, it does introduce flexibility in operation given that this will allow the carbon capture unit to operate at near optimal conditions even when the power plant varies its output, especially for PSA and VPSA systems which can be turned on and off with relatively short lead times. In industrial applications, where scales are smaller, it is likely that a single train will suffice.

Adsorbents are also used in the high temperature Sorption Enhanced Water Gas Shift SEWGS [45] process where an active component in the solid sorbent (hydrotalcite material) reacts with CO_2, shifting the WGS equilibrium towards H_2. CO_2 is released in concentrated form by a pressure swing and purge of the bed with low pressure steam. Proposals have been made to implement such process in pre combustion power plant systems, but the main developments are currently taking place in Europe focused on industrial applications (i.e. H2020 Stepwise project)[18] as will be discussed below.

Key challenges and R&D targets include:

- Development of structured packings or monoliths for novel families of adsorbent materials
- Develop standardized testing procedures of new materials, including the effect of steam and flue gas impurities
- Optimize materials and processes to decrease CAPEX (size of equipment) and OPEX, primarily by minimizing the cycle time and optimising the productivity of the unit. The use of more advanced structured materials, will further decrease relative contribution to the cost of the process.
- Develop reference process specifications to allow comparisons between different combinations of materials/processes, including the effect of water present in the flue gas.
- Stabillity of adsorbents and reduce adverse effects minor impurities present in gas.

3.3.3 Chemical Looping and Calcium Looping High Temperature Systems

These are a family of processes that can exploit the reversibility and high reaction rates of certain gas-solid reactions taking place at very high temperature (i.e. from 600ºC to over 1,000ºC depending on processes and reactors). This allows for the efficient energy recovery from the heat flows involved in the chemical loop, using conventional steam cycle equipment. In the most developed versions of these systems (TRL6 has been reached for chemical looping combustion of solid fuels at atmospheric pressure and for post-combustion calcium looping) the main reactors used are circulating fluidised beds, that

[18] http://www.stepwise.eu/

closely resemble the thermal and mechanical characteristics of Circulating Fluidised Bed reactor systems that are mature in the power and refining sectors.

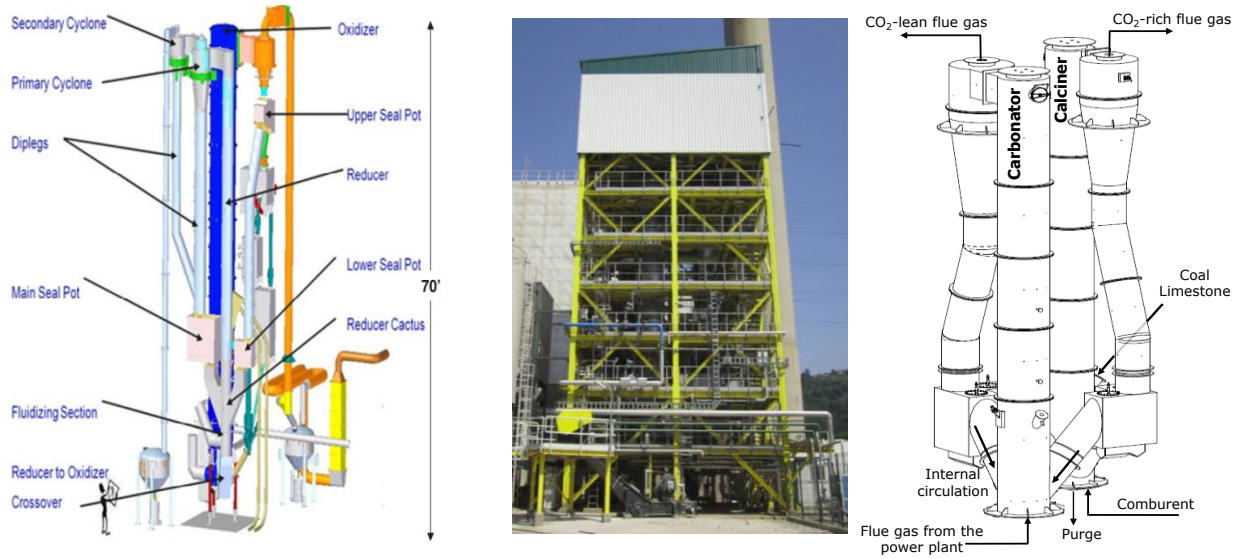

Figure 3.1Left: ALSTOM 3 MWth chemical- chemical-looping combustor pilot [46], Center-right: "la Pereda" 1.7 MWth Calcium looping pilot [36].

In the Chemical Looping Combustion systems (CLC), the combustion of a fuel is achieved by transferring the oxygen to the combustor chamber using an oxygen carrier (usually a metal oxide that is reduced in such process). The reduced metal is then oxidised by air in a separate reactor, closing up the chemical loop.

In the post-combustion Calcium Looping systems (CaL), it is the CO_2 contained in a flue gas who reacts with a solid (CaO) forming $CaCO_3$. This is then regenerated back to CaO and pure CO_2 by oxy combustion of additional fuel in an additional oxy-fired CFBC power plant. The large surplus of high temperature heat from the Calcium loop makes this technology unsuitable for any application where power and/or high temperature heat is not a desired product. Both CLC and CaL have rapidly developed to TRL6 in recent years in process versions designed using interconnected fluidised bed reactors at atmospheric pressure (Table 3.1).

Key issues for CLC for solid fuels are linked to the reactivity, chemical and mechanical stability of the oxygen carrier (in relation to its specific cost and environmental impact), and the incomplete conversion (i.e. not full oxidation) of the fuel in the fluidised bed fuel reactor. This later problem can be managed by using an additional combustion step of fuel gas traces involving pure O_2 (i.e. "oxygen polishing") or by recovery of the unconverted fuel gas in the CPU. The unconverted fuel in solid form can be minimized by a "carbon stripper", where the fuel rich material has to be segregated from denser ash and oxygen carrier and recycle back to the fuel reactor. It is necessary to expand the experience in steady state operation when operating with solid fuels, in order to confirm the similarity with existing CFB boiler systems despite the differences in solid circulation rates and operation with interconnected reactors.

On the other hand, high pressure CLC systems for NGCC are in theory highly energy efficient, but far less developed (TRL 2) as they require the operation of an interconnected fluidized bed system involving oxidizing and reducing atmospheres at high pressure and both upstream of a gas turbine that usually demands strict limits in loading of solid fines.

For post combustion CaL systems the key issues are related to minimize O_2 consumption in the calciner, or with the integration of solid purges in other applications (i.e. Desulphurisation, cement etc). Material integrity (i.e. attrition) is an issue for some limestones and operating conditions.

Advanced concepts for fluidised chemical looping combustion and reforming systems (3rd generation) are also under development. In addition, some new developments exploiting theoretical advantages using packed bed reactors operated at high pressure are progressing towards TRL3-4[19] are progressing towards TRL3-4 [47]. Also for NG, high pressure Ca-looping pre-combustion concepts (sorption enhanced reforming) are being developed but remain at TRL<3.[20]

Key challenges and R&D targets include:

- Scale up fluidised bed looping systems to confirm process and cost advantages by using mature CFB power plant technology. CLC and CaL technologies (currently at TRL5-6) should move to TRL7, which is the "dead valley" for emerging technologies, as it requires very large investments to build pilots of 10s of MW_{th}. Also, demonstration of these technologies for biomass and other opportunity fuels need to be advanced to higher TRL.
- Improve stability of CLC materials.
- A priority for CLC reactor systems is to optimize the solid fuel reactor by maximising fuel conversion. Also, to test CLC systems using lower cost and high durability oxygen carriers while reducing the need of oxygen polishing. For natural gas systems, is still necessary to achieve experimental proof of concept of the highest efficiency chemical looping systems, which require combustion or reforming at high pressures.
- Calcium looping post-combustion systems can further reduce energy penalties by demonstrating novel methods to minimise heat requirements in the calciner and reduce make up flows of limestone using sorbent reactivation strategies.
- Proof of concept of advanced CaL and CLC flexible concepts (at TRL1-2 today) to exploit the thermochemical energy storage potential of the reversible chemical reactions at high temperatures.

[19] https://www.sintef.no/projectweb/democlock/
[20] see FP7 project http://www.ascentproject.eu/

3.3.4 CO_2 Liquefaction/Partial Condensation for Pre- and Post-Combustion CO_2 Capture Applications

The basis for CO_2 liquefaction as an option for separating CO_2 from other gaseous species is by partial condensation of CO_2 in a gas stream that is compressed and cooled down (typically between -20 to -55°C depending on the cold box configuration). Capture rate and CO_2 purity will depend on the CO_2 concentration of the feed stream, as well as the process design (pressure and temperature at which the CO_2 condenses). The limitation to this capture principle is that it requires a feed stream that contains at least greater than 50% of CO_2 for post-combustion flue gases and at least around 40% for syngases.

The technology behind CO_2 Liquefaction on its own is considered a mature technology. Most of the components of these technologies are developed in the CPU development for oxy combustion application. Several of these components are demonstrated in industrial scale pilot plants.

Some of the key innovations using CO_2 liquefaction involves the use of "auto-refrigeration" cycle using impure CO_2 as refrigerant, and the additional recovery of CO_2 from the vent using commercially available equipment such as membrane or PSA/VPSA.

CO_2 liquefaction as stand-alone CO_2 capture technology was investigated theoretically for an IGCC power plant in the FP7 DECARBit project.[21] The stand-alone application is possible in this case since requirements on hydrogen purity are relaxed (a gas turbine actually operates better if the hydrogen is diluted), and the CO_2 capture rate is limited to 80%.

A wider range of applications for CO_2 liquefaction in IGCC with limited capture rate is possible if syngas (consisting of CO_2, CO, H_2, H_2S, H_2O and others) is processed with the purpose of producing hydrogen of a certain purity *and* capture CO_2 with a purity that complies with CO_2 transport and storage specifications. CO_2 liquefaction is then typically envisaged as the second CO_2 separation stage of hybrid CO_2 capture processes (i.e. located downstream of PSA, VPSA or membrane).

The technology developed for this application is similar to the large scale demonstration for CO_2 removal from the PSA tail gas of Air Liquide's SMR plant at Port Jerome (i.e. CRYOCAP Technology) – capturing 100,000 TPY of CO_2 for the food grade market.

The key research challenge in hybrid liquefaction process design lies in defining the techno-economic optimum between the two separation technologies. The TRL level for the hybrid capture system will be defined by the upstream capture technologies – which could be PSA, VPSA, membrane or others - that would sufficiently enriched the CO_2 composition of the gas stream making it a suitable feed gas to the CO_2 liquefaction plant.

A critical element to the development for pre-combustion capture from coal based power/hydrogen production lies in the processing and removal of H_2S. Such removal may be required due to the

[21] http://www.sintef.no/projectweb/decarbit/

constraints set by the upstream separation technology under considerations (i.e. PSA, VPSA, membrane or others).

Furthermore, it should be noted that an additional challenge lies in the lack of publicly available high-quality experimental VLE data for CO_2/H_2 mixtures (although in-house data are believed to exist among key industry stakeholders). Such data are required in order to ensure confidence in CO_2 liquefaction process designs required for determining the optimum interface with the upstream separation technology.

To capture CO_2 from conventional flue gas (consisting of N_2, Ar, O_2, CO_2, H_2O, SOx, NOx and others) using CO_2 liquefaction as a stand-alone capture technology is not viable due to very low CO_2 concentration. However, the liquefaction technology becomes an option in hybrid systems, after CO_2 enrichment through e.g. use of membranes producing a gas streams with CO_2 concentration of ~50-70% (currently being investigated in the H2020 project CEMCAP[22]), or use of oxygen enriched combustion, or both. This concept of post-combustion capture technology is not yet validated, but is expected to advance from TRL 2 to TRL 6 by 2017 (when the CO_2 liquefaction test rig becomes operational as part of the ECCSEL lab infrastructure at SINTEF). It should be noted that the overall TRL of this technology is governed by the TRL of the upstream CO_2 enrichment technology to be used rather than the CO_2 liquefaction plant. Additionally, the treatment to the NOx and SOx will be an important element to the development of the whole capture system.

One of the advantages of capturing CO_2 in its liquid state is the flexibility it could offer in terms of choice of transport mode. The CO_2 can either be obtained at conditions ready for ship transport, or slightly heated and pumped to pipeline transport conditions. Redesign of the CO_2 capture process between the two options should be straightforward (Figure 3.2).

A number of projects such as Prometheus (Joule-Thompson), Clodic/Younes (heat exchangers), IFP (fluidized beds), Shell/TU/e (packed-beds) are developing different processes for cryogenic freeze-out of CO_2 as a solid, to avoid compression of the flue gas. This CO_2 freeze-out technology appears particularly interesting as part of hybrid technologies (downstream purification), specifically for biogas as cold duty at LNG regasification stations.

3.3.5 Membranes

Membrane technology can be relevant within capture lines such as post-, -pre-, and oxy-fuel. In principle, membranes allow the selective permeation of a target gas from one side of the membrane to the other. The driving force for the gas separation is a gradient in gas concentration, i.e. high partial pressure in the feed or vacuum in the permeate. Selectivity and permeability of the material, as well as stability and durability under realistic process conditions, are the key properties defining the suitability of a membrane for large scale CO_2 capture systems.

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[22] See https://www.sintef.no/projectweb/cemcap/.

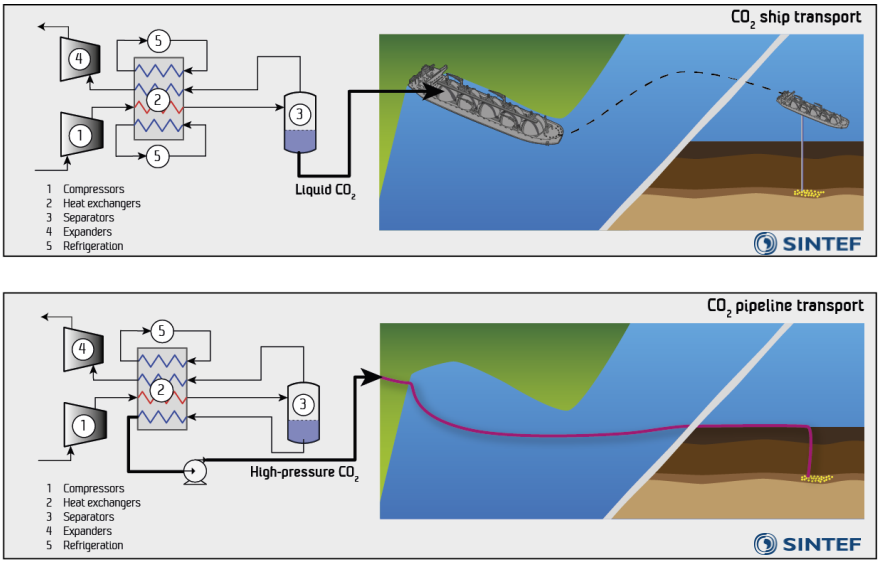

Figure 3.2 The CO_2 liquefaction process principle, and its flexibility with respect to ship/pipeline CO2 transport. The process flow diagrams to the right are simplified, and can in practice include several process units of each kind.

Membrane separation technology is mature in some industries, but its application to the power sector for large scale CCS is still the subject to R&D work. Polymeric membranes, which target the separation of CO_2 from flue gases, have experienced the greatest advance in the last 10 years. These have been commercially used in natural gas separation but some notable advances have also been achieved with inorganic membranes for oxygen transport and the pre-combustion separation of CO_2 from H_2.

3.3.5.1 Post-combustion application

Polymeric membrane systems for removing CO_2 from flue gas have received a lot of attention during the last decade. The technology is currently being tested at a 20 TPD scale demonstration (TRL~6) of the MTR membrane technology at the NCCC, and at two projects in Norway at Norcem's Brevik cement plant and one for various types of flue gases at the Tiller demonstration plant (TRL~5). Membrane modularity and easy scale-up opens chances for retrofitting of existing plants as well as flexibility with respect to the CO_2 capture rate.

Due to the limited membrane selectivity of standard polymeric membranes and the need for a driving force for permeation, it is difficult to use one-stage membrane systems to achieve 90% removal efficiency and 95% purity [43], as usually targeted. Membrane systems using multiple stages could fulfil the targets of removal efficiency and product purity for CO_2. However, a cost minimization analysis shows that membranes are particularly well-suited for partial capture (40-60%) [48].

Standard membrane systems are always subject to a trade-off between permeance and selectivity. Progress in membrane development over the years led to an outperformance of the traditional Robeson plot, the plot of membrane selectivity versus membrane permeability. New developments on facilitated transport membranes in the recent years show that these membranes are able to achieve both high

permeance and selectivity. Passing the Robeson trade-off line with respect to performance, they are able to reach the purity demand of 95% [49, 50].

Key issues are related to water vapour present in flue gases that is known to have a strong influence on permeability and performance of polymeric membranes (except for the facilitated transport membranes) e.g. causing competitive sorption plasticization and ageing. Below the dew point, water condensation on the surface and inside porous structures can cause severe reduction of permeance and selectivity. The presence of impurities such as SOx and NOx in conjunction with water vapour may form acids [25].

3.3.5.2 Pre-combustion application

A promising option for pre-combustion CO_2 capture in both coal and gas fired power stations [51] is the utilization of high temperature H_2-selective membranes. These are “Pd-based membranes'' or ''ceramic membranes (HTM)'') that can selectively transport hydrogen over other gases. Applied in a reactor integrated in a combined power cycle, this membrane technology combines the conversion of fuel into H_2 for large-scale power production with capture of CO_2. The process leaves concentrated CO_2 at high pressure reducing the compression energy for transport and storage. Key challenges are related to the further upscaling of the membrane manufacturing and the membrane stability at operating conditions and against contaminants. For successful commercialization of Pd-based membranes, the membrane must have sufficient permeability, selectivity, robustness, and durability in relevant environments. With current understanding, production of hydrogen from coal and other sulphur-containing sources is challenging for Pd-based membranes particularly due to their limited stability towards sulphur. Initiatives such as the Horizon 2020 project BIONICO, are undertaken on alloying Pd/Ag membranes with metals such as Au and Ru to improve membrane stability under mild H_2S conditions (1-5 ppm).

The membrane technology is also relevant for the production of hydrogen as a decarbonised fuel for many applications, such as boilers, furnaces, engines and fuel cells. Tokyo Gas has demonstrated the world’s largest scale Pd membrane reformer with a rated H_2 production capacity of 40 Nm^3/h (150 kW_{th}) from natural gas, claiming to be achieving the world’s best hydrogen production efficiency (HHV) of 81.4% [52]. The high temperature H_2-selective membrane technology is currently in the TRL 4-5 level, and further upscaling projects have been established [53, 54, 55].

Alternatively, high temperature membranes can be applied to separate CO_2 from the other species present in a pre-combustion decarbonisation scheme. For this dual-phase process, membranes that are highly selective to CO_2 at an operating range of 400-700 °C are under development [56]. This technology is still at a low TRL level of ~1-2.

3.3.5.3 Oxy Combustion Application (i.e. Air Separation)

Oxygen Transfer Membrane (OTM) technology is an oxygen production technology for use in oxy-fuel capture processes. Air Products and Praxair have developed and demonstrated this membrane technology in TRL level 4-5, and tested several modules containing > 200 planar/tubes units for more than 4000h in the scale of 5 tons O_2/day. This technology shows an efficiency comparable to cryogenic air separation unit (CASU), but due to the low difference in efficiency and the lack of scale up demonstration, CASU technology is often preferred.

3.3.5.4 Challenges and R&D targets

Key challenges and long term R&D targets include:

- Enhance permeance to reduce the required membrane area (material cost) especially with respect to large flue gas streams.
- Enhance CO_2 selectivity compared to other flue gas constituents and impurities which will have great impact on CAPEX and CO_2 purity, hence the number of required membrane stages and the required membrane area.
- Address membrane sealing as it appears to be one of the most important challenges (ceramic – metal connection) with respect to CO_2 selectivity for ceramic and metallic membranes.
- Enhance O_2 selectivity and permeance for air separating membranes.
- Enhance stability of Pd-based membranes.
- Improve stability and resilience of membranes against mechanical stress, impurities and fouling, especially long term durability of membrane towards CO_2 atmospheres, SOx, NOx and particles in flue gas.
- Address the requirement for handling condensed water in the process.
- Introduce novel reactor designs to decrease concentration polarization effects.

New membranes which show promising results often remain for years on the same low TRL level because further up-scaling and development is blocked by the non-availability of the tested material in large amounts (no commercial supply chain in place). The up-scaling of non-commercially available materials showing promising results on lab-scale, could support the technology moving up on TRL. European Horizon 2020 projects such as Fluidcell[23] and FERRET[24] are expected to contribute on this.

3.4 Emerging CO_2 capture technologies in the Iron & Steel industry

The main source of CO_2 emissions from integrated steel mills (based on the BF-BOF steelmaking route) is the coal used to reduce iron ores in the blast furnace. Additional fuel is often imported as natural gas. Depending on specific site configuration, a variety of CO_2 emission points will exist on any site. The main CO_2 emission points are the blast furnace hot stoves, steam boilers, sinter plant, hot strip mill, BOS plant and coke plant. Assuming that works arising gases are utilized for electrical power, the largest CO_2 emission will be caused by the power plant, which can be located on- or off-site.

The ULCOS project has investigated the following strategies for CO_2 reduction in the steel industry:

- Decarbonising, replacing coal by natural gas, hydrogen or electricity for iron ore reduction
- Usage of sustainable biomass as carbon source for iron ore reduction

[23] http://www.fluidcell.eu/
[24] http://www.ferret-h2.eu/objectives

- Introduction of CCS technology

After evaluation of nearly 200 different process route options, 4 technologies were selected for further development and scale-up. These technologies are the blast furnace with top-gas recycling (ULCOS-BF), HIsarna (coal based smelting reduction technology), natural gas based reduction and electrolytic iron making. Carbon and gas based technologies require carbon capture and storage to achieve the target of >50% reduction of CO_2 emissions. To improve process efficiency and to reduce capture costs both the retro-fitted ULCOS-BF and HIsarna are based on the use of pure oxygen instead of air, thus increasing CO_2 % in the flue gas.

3.4.1.1 Post combustion capture technology

A conventional amine system, like the MEA amine system, can be considered a first generation capture technology. A weakness of the amine system is its need for large amounts of steam. The amine technology could be applied to flue gases with relatively lower CO_2 concentrations, such as from hot stove flue or steam boilers It strongly depends on steel plant configuration whether it makes sense economically to combine smaller flue gas streams into one large capture plant. BF gas can be made richer in CO_2 by oxygen enrichment of the hot blast air, which will influence the cost of CO_2 capture. PSA or V-PSA technologies are more cost effective when CO_2 concentrations in the flue gas are higher.

PSA is already used at commercial scale in the Finex process (South Korea) and the Corex process (South Africa). As with the ULCOS-BF process, the purpose of the PSA is then primarily to separate the CO gas for re-use in the process. The produced CO_2 would fail to meet transport and storage specifications, requiring an additional separation step such as cryogenic purification.

3.4.1.2 Oxy-combustion capture technology

Drivers for oxy-combustion technology are greater process or cycle efficiency and higher CO_2 concentration in the flue gas, thus leading to lower cost CO_2 capture technology like cryogenic separation. The concept of oxy-combustion can be applied to power plants using works arising gases but also to all other combustion processes in integrated steel mills, such as hot stoves, reheat furnaces, etcetera. In the ULCOS-BF project carbon capture technology was demonstrated at pilot scale using VPSA technology.

3.4.1.3 Pre-combustion capture technology

By sorption enhanced water-gas shift (SEWGS) or conventional WGS it is possible to convert the CO content of blast furnace gas and BOF gas into H_2, thus enabling the capture of a large proportion of steelmaking CO_2. H_2 can also be harvested from coke oven gas directly but this is not directly linked to CO_2 capture. Even though the CO-to-H_2 technology conversion is mature, its practical application is constrained by the impact on the gas and energy balance of an integrated steelmaking site, including the required burner modifications for high H_2 concentrations.

3.5 Emerging CO_2 capture technologies in the Cement industry

Cement production globally contributes to approximately 5% of anthropogenic CO_2 emissions. A major share (~60%) of the emissions occurs from the conversion of $CaCO_3$ to CaO, meaning that fuel switching is not sufficient to achieve significant CO_2 emissions reductions from this sector. Very few new cement

plants are being built or are foreseen to be built in Europe, meaning that CO_2 capture technologies for the European cement sector have to be retrofitable to existing plants.

Cement plants typically operate at steady state, i.e. deliver a steady-state production of clinker that is grinded and mixed with additives to produce cement. Downtime is typically scheduled during the winter, since construction activity is lower then. Although operation mainly is stationary, CO_2 emissions may vary over time from a plant, due to factors such as type of clinker being burnt, type of fuel, type of raw meal (limestone) being employed as well as amount of air leakage and process design (heat recovery or not). What is important from the perspective of the adaption of post-combustion CO2 capture technologies to cement plants, even with constant clinker production and fuel feed, is that the flue gas flow is likely to vary on a daily basis.

A cement plant is run in *interconnected mode* when the raw mill is operating, and in *direct mode* when the mill is out of operation. In interconnected mode, the air leakage into the flue gas stream is significantly higher, i.e. gas volume flow increases and CO_2 concentration decreases. It is normal to switch between the operating modes every day (typically 10% direct mode operation every day, although this varies over a year). In short, requirements on flexibility with regards to flue gas volumes and CO_2 concentrations are higher for post-combustion capture technology for cement plants, compared to power plants. The CO_2 concentration in the exhaust gases can be 14-22% in interconnected mode and 20-35% in direct mode without exhaust gas heat recovery. Cement plants vary in size, but a typical European cement plant emits around 0.8-1.0 Mt CO_2/year.

Post-combustion capture with amines is the obvious first-generation technology for cement plants. Norwegian cement manufacturer Norcem have tested an amine for CO_2 capture from the flue gas in their on-site CCS test centre in Brevik with very satisfactory results. Generally speaking for cement plants, it will depend on the amount of heat required for drying of the raw meal if a cement plant will have available waste heat that can supply part of the heat required for amine regeneration.

Key process advances could include Chilled ammonia process (CAP) capture, advanced amine capture process configurations, oxy combustion capture (with cryogenic ASU), membrane assisted CO_2-liquefaction, end-of-pipe post-combustion Calcium looping and entrained-flow Calcium looping. These are discussed.

2nd generation capture technologies

1. Chilled Ammonia Process (CAP) is a solvent technology perceived as first generation technology for power plants and other CO_2 sources with CO_2 concentrations below 20%. The technology has however never been tested for concentrations as high as what could be relevant for cement plants (up till to 35%). Such testing will be done in synthetic flue-gas flows of 1 tonne/day in the ongoing H2020 project CEMCAP.
2. Although oxy combustion using cryogenic ASU and other commercial technologies can be seen as a first-generation CO_2 capture technology for coal-fired power plants with the definitions employed in this report, this is not quite the case for cement plants. Components need to be tested and designed specifically for cement plants. CEMCAP will test oxy-fuel burners, calciner and clinker cooler for

cement plants, and the results will be fed back to the ongoing ECRA CCS project and be used in the design of a oxy-fuel cement demo plant.

3. Calcium looping capture: post-combustion capture of CO_2 emissions from the cement plant exhaust gases, after material pre-heating, with subsequent cooling and grinding of CaO is a 2nd generation capture technology for cement plants. ITRI's high-efficiency calcium-looping technology pilot (Heclot) is planned to capture 1 ton CO_2 per hour in Korea. Tests with high make-up rates will be done up till 200kWth in CEMCAP project, continuing work undertaken by the University of Stuttgart [57]. Also, exploratory work on more integrated concepts of calcium looping will be investigated at TRL4 , involving the CO_2 capture step directly integrated in the raw meal pre-calciner systems and particle sizes directly suitable for the clinker burning process (30-50μm), meaning that no subsequent grinding of CaO particles is necessary. This is believed to make the Ca-looping capture technology more efficient for cement plants.
4. Membrane-assisted CO_2 liquefaction is considered to be a 2nd generation technology and is a concept suitable for higher CO_2 concentrations than power plants. The principle is to apply bulk separation of CO_2 up to a concentration of ~60% CO_2 through the use of polymeric membranes, followed by compression, cooling and condensation of CO_2. The concept needs to be demonstrated, but should be possible to quickly advance to TRL 6 since it can be realized with a combination of commercially available components (polymeric membranes, compressors, expanders, heat exchangers, phase separators). Initial testing to define optimum interface between membranes and CO_2 liquefaction, and confirm the operability of the CO_2 liquefaction technology will be done in CEMCAP. New membrane materials with high performance (permeance and selectivity), a technology currently at TRL 5, is also being assessed as 2nd generation capture process within the cement industry.

3rd generation capture technologies

5. Amine-impregnated polymeric sorbents have been tested in the Norcem CCS project. CO_2 absorption occurs at 70°C and desorption at 110°C. The test phase in real cement plant flue gases is ongoing at a scale corresponding to 600-1600 SLPM.

6. Fixed-site carrier membranes have been tested on-site at the Norcem cement plant in the Norcem CCS project for 6 months. The core technology has proved to be functional, but the membrane module design needs improvements. Test results have proven to be satisfactory enough for the technology to proceed to a second test phase at Norcem.
7. O_2 production with high-temperature ceramic membranes has to date not been evaluated for integration in cement plants.

3.6 Emerging CO_2 capture technologies in the Refinery Industry

With the exception of the H_2 plant, CO_2 is emitted in flue gases from a larger number of different units throughout the refinery/petrochemical plants with fairly low CO_2 concentrations, typically in the order of 3–12% CO_2. Combined stacks can have a CO_2 content of up to 15% emitting in the order of 1 Mton/year [23, 58]. Because of the resemblance with the power sector flue gasses it is expected that the opportunities for applying CO_2 capture technologies in the refinery sector will follow the

development in the power sector. Post-combustion capture with amines is thus the obvious first-generation technology for retrofits of existing refineries. Other technologies like chemical and physical absorption, adsorption, and membranes are regarded as 2nd or 3rd generation capture technology.[25]

Demonstration projects on hydrogen projects with CCS has commenced at Port Arthur (VPSA), Scotford (ADIP-X amine)[26] and at Port Jerome applying the Air Liquide Cryocap technology (CPU-derived technology).

3.7 Comparative assessment of emerging CO_2 capture technologies

Cost and energy use reduction remain an essential criteria when assessing future CCS technologies. However, this report tries to go well beyond, by introducing in the assessment of emerging technologies some parameters that are considered highly relevant in the current energy and industrial markets where CCS is expected to operate:

- Cost reduction potential (Capex & Opex),
- Energy efficiency or efficiency penalty reduction
- Operational flexibility,
- Health, Safety & Environment (HSE),
- Retrofitability,
- Materials Availability.

We are aware of the uncertainties that are inherent to a comparative assessment of emerging technologies using all these categories. Even parameters of purely quantitative character (like CAPEX, OPEX or full system energy penalties) cannot accurately be estimated for emerging technologies as it well known that advocates of new technologies tend to under-estimate these parameters in early stages of the development of the technologies. Having said this, an assessment of the overall cost structure of the novel capture system is usually possible once the proof of concept (TRL 4-5) has been established. This estimation of CAPEX will depend on the nature of the construction material (functional and structural) of the equipment, the complexity of the capture process, the expected scale and the size of the main elements (which in turn depends on the kinetics of the capture process, e.g. residence times, CO_2 loading capacity of solvent or sorbent, etc.).

Opex is directly affected by the efficiency penalty as well as the cost of replacement of the capture functional material (i.e. the degradation rate or stability of solvent, sorbent, oxygen carrier, CO_2 carrier, or membrane material).

The energy efficiency of the overall capture plant process depends not only on inherent thermodynamics aspects of the chosen CO_2 separation system, but also on the level of heat integration.

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[25] http://ieaghg.org/education/19-ccs-resources/technical-workshops/523-ccs-in-process-industriesstate-of-the-art-and-future-opportunities

[26] http://www.shell.ca/en/aboutshell/our-business-tpkg/upstream/oil-sands/quest.html

Therefore, the efficiency of any new capture system has to be assessed under a holistic system level perspective.The criterion "operational flexibility" attempts to indicate whether a certain capture technology is capable to operate in load-following mode within a short response time, e.g. daily cycling up and down or, to put it simply, the system's ability for rapid switching on and off. This is an issue that has only recently been considered by developers of emerging technologies.

HSE evaluates the different emission and degradation risk of the materials used in various capture systems and eventual toxic waste disposal.

The criteria "retrofitability" indicates whether a technology can be integrated into an existing, already operating plant at a later stage, thereby making no statement about the level to which integration is feasible and assuming that there are no space restrictions. It should also be noted that capture technologies which can be retrofitted to existing and relatively modern equipment will likely enter the market earlier than technologies which require a completely new built plant.

"Material Availability" addresses a potential shortage of either rare or non-commercial materials needed in the novel capture system. 'Non-commercial' refers to a yet non existing manufacturing capacity or supply chain. Some emerging capture technologies require materials which today have no commercial supply chain, e.g. a lot of Metal Organic Framework (MOF) or other sorbent or functional materials (i.e. membranes or O_2 carriers in chemical looping). Many of these materials are synthesized in university labs on a milligram or gram scale and tested on lab bench scale for limited life times. In case of promising results at lab scale, the next logical step is the testing on larger scale and/or longer operating times. This up-scaling step often suffers from the non-availability of these materials in larger amounts, thus on the scale of kilograms or even tons, at least not at reasonable cost.

In order to progress towards the final assessment of technologies, a process of expert judgement among the authors and reviewers of this Report has been followed to build Table 3.3. In this table, each family of emerging technologies discussed in previous sections is represented by a couple keywords at the top of each column and all the assessment criteria referred to such technology are listed in the different table lines. Each cell is then given a colour (green, yellow, red) representing the main strengths (green) and weaknesses (red) of emerging CO_2 capture technologies with respect to the established benchmarks of 1st generation technologies discussed in Chapter 2. A final row mentions the industrial environments where we perceive these technologies can best fit when taking into account their reviewed characteristics.

In assigning colours to the individual cells, the following set of criteria has been adopted (to avoid a final table filled with all green cells):

- For each category of technologies, we refer only to the most developed version (i.e. highest TRL). Usually, "promising" versions of these technologies are also being considered at lower TRL, but these cannot be assessed as present.
- While all 2nd and 3rd generation technologies might bear significant improvement potential it is difficult to achieve a reliable assessment of technologies below a certain TRL status due to their prematurity. Therefore, no assessment of technologies with a TRL<4 has been attempted.

- When there is a large uncertainty in a certain assessment parameter a red colour has been given to such parameter.

The overall target in this assessment is therefore to identify the main strengths and weaknesses of emerging CO_2 capture technologies when deployed at the necessarily large scales required in the power and large industrial sectors.

Table 3.3 Traffic light table for emerging separation processes for CO_2 capture (process with TRL>4 only) with regards to assessment criteria Green means improvement potential compared to benchmark, today's 1st generation demo plants. Yellow means indifferent, same or similar level and red means worse (or very uncertain) than benchmark. Yellow/green means could be better but in worst case similar than benchmark.

Process	Solvent based processes	Solid sorbent processes	High temperature solid looping systems		Membrane systems		
Separation Technology / Assessment criteria			Chemical looping	Calcium looping	Polymeric (post)	Ceramic (Oxy)	Metallic (pre)
Cost CAPEX					2)		
Cost OPEX							
Efficiency penalty (thermodynamics, T- and P-level)							
Degradation solvent, sorbent, membrane							
Operational flexibility (on/off)					2)	2)	2)
HSE (waste, toxicity)	1)	1)					
Retrofitability[3)]					2)		
Materials availability (abundance, manufacturing chain)							
FOAK cost							
Applicability, most suitable to	Power, NG processing, Steel, Refineries, other	Power (pre combustion), Steel, Refineries	Power (solid fuels), Refineries	Power (post combustion, solid fuels), Cement	Power, NG processing, Cement, Steel	Power (oxy and pre combustion)	Power (pre combustion), Refineries

Notes to Table 3.3:

1) All solvents or solids containing amino-groups might show due to operation conditions disamination reactions which can lead to nitrosamine formation or degradation.
2) Depends very much on process integration of the membrane system. For example the retrofitability of polymeric membranes in a post-combustion configuration in general is possible, however, the feasibility in a detailed set-up which might require several membrane stages, compressors or vacuum pumps has to be individually assessed [59, 60].
3) The retrofitability criterion is a yes or no criterion, therefore only green or red.

We summarise below some comments on the decision process that has been followed to provide the colour codes of Table 3.3.

3.7.1 Solvent based processes

Solvent based post-combustion technologies are considered the current benchmark for CO_2 capture technologies due to their commercial availability and the substantial experience with this technology from a large number of pilot plants, including experiences gained from the first commercial plant at Boundary Dam. A number of different aqueous amine/ammonia solvent technologies are being offered commercially, but it is at present difficult to judge the relative performance of technologies from different vendors. Management of solvent degradation and emission control, namely handling of nitrosamines, has been a challenge for amine based CO_2 capture technology, these issues are being managed but there may be room for further improvements in terms of having the most cost efficient emission control technology.

All currently emerging solvent capture technologies can be considered as refined versions of existing 1st generation amine/ammonia based solvents which try to overcome some of the particular weaknesses of 1st generation solvents. While precipitating and enzyme catalysed enhanced solvents speeds-up the absorption kinetics in order to reduce CAPEX for the absorber, other approaches like encapsulated solvents and ionic liquids try to reduce/avoid steam co-evaporation , the main energy consuming step in the capture process, in the stripper where CO2 recovery occurs.

All emerging solvent capture technologies show selective improvements within the process e.g. faster absorption kinetics or no volatility, less co-evaporation etc. However, these selective improvements in parts of the process come all along with trade-offs at other parts of the process, thus compensating or levelling the achieved benefits, or require additional equipment which increases cost.

At the current status it is not foreseeable whether these emerging solvent developments will lead to an overall net improvement of the process compared to the available 1st generation amine/ammonia solvents.

Amine/ammonia technology is likely to see gradual improvements in terms of optimal solvent formulations, individual process optimization and heat integration within the respective power and industry process it is applied to.

For applications outside the power sector and gas processing industry there is less experience with amine technology. Development of solvent technology should also address optimal solutions for other than specific power applications. Key issues are likely to be management of various impurities

in the flue gas, as amines are sensitive to SOx and other oxidizing pollutants leading to amine degradation, and optimal heat integration.

Solvent based capture technologies are best suited for steadily or continuously operated processes due to the high inertia of large amounts of liquid and the temperature profile required in the stripper for CO_2 recovery. Quick shut downs, ramp-ups are not optimal and will enhance operation cost. Very low CO_2 concentrations like in the flue gas of natural gas power plants (3-4 vol.%) require large absorber columns and the treatment of large diluted volume streams which lead to higher specific cost per tonne of CO_2 than for more concentrated CO2 flue gas streams e.g. from a coal power or cement plant.

One way to reduce equipment volume at low CO_2 concentrations is more effective contacting surfaces, eventually by the means of nano-engineered surfaces, and faster cycles. Another approach is to develop abundant, lower cost material for the construction of capture plants which keep cost of even huge plants low.

3.7.2 Solid sorbents processes

Solid sorbent batch processes for large scale continuous flue gas treatment will require more than one batch reactor, eventually multiple batch reactors, depending on the cycling time which entails higher CAPEX cost.

PSA and VPSA process show at least an order of magnitude higher cycling times compared to TSA processes and greater operational flexibility with respect to power/industry plant output variations as the pressure build-up and vacuum generation can be turned on and off with relatively short lead time. TSA lacks operational flexibility for the same reason solvents do due to the heat supply for the stripping off of CO_2.

Solid sorbent capture processes have the potential for ng lower net energy consumption (lower efficiency penalty) compared to solvent based capture processes.

Improvements are anticipated by novel material developments and novel process configurations. Ideal sorbent materials that are looked for ideally show a high affinity to CO_2 (high CO_2 selectivity) but at the same time no affinity to other polar molecules like water. Materials showing also a big affinity towards steam which is a major component in any combustion process, achieve low purity of CO_2 in the separation process and high energy consumption in the CO_2 recovery process as the adsorbed steam has to be recovered as well. It causes a similar inefficiency of the CO2 recovery process as the occurring steam co-evaporation in solvent capture processes.

Highly CO_2 selective materials therefore possess a reduction potential for OPEX due to the subsequently lower regeneration energy.

The big advantage of solid sorbent processes in order to lower heat requirements (CO_2 recovery) is the huge variety of potentially available high active surface adsorption materials, ranging from activated carbon to Metal Organic Frameworks (MOF) which can be precisely designed to the target molecule.

To achieve very fast cycles (minimum cycling time) and minimize pressure drop in PSA, VPSA and RWA (Rotary Wheel Adsorbers) structured packings or monoliths need to be developed. Solid

sorbent capture systems show a clear benefit with respect to HSE and waste minimization, as no aqueous solvents or toxic compounds are released.

3.7.3 High temperature solid looping systems

The potential for the highest efficiencies achievable with Chemical looping combustion systems is recognised in Table 3.3 with the only full green light on the energy penalty cell. However, this is only valid if CLC can adapt and operate at similar temperature and pressure conditions as in the reference system without capture. Chemical looping combustion has developed only recently to TRL5-6 for atmospheric pressure solid fuel combustion systems while high efficiency high pressure systems linked to NGCC are not considered in the table because they remain at TRL<3. Efficiency penalties can be extremely low for CLC systems, as long as fuel conversion are high and blower consumption for high solid circulation and inventories in CFB's is moderate.

The potential for low CAPEX in CLC systems at atmospheric pressure (green box in Table 3.3) exists if it is experimentally confirmed that the CLC system can closely resemble the commercial Circulating Fluidised Bed (CFB) boiler for solid fuels, despite their substantial differences in solid circulation rates, bed inventories and nature of the circulating materials. These differences justify a red colour for a FOAK plant. OPEX can also be very low if the performance as O_2 carriers of natural occurring minerals is demonstrated in stable pilot trials, but material availability for large pilots may be an issue if this is not the case (i.e. when synthetic oxygen carriers are needed in large quantities). CLC systems cannot be retrofitted to existing power plants and require new plants to be built.

In what refers to post-combustion Ca-looping, the post-combustion concept has been demonstrated in several pilots at TRL5 and 6, while pre-combustion concepts remain at TRL<3. Applying Ca-looping as post-combustion capture technology to an ordinary coal power plant requires effective energy recovery in a new power cycle linked to the oxyfired CFB calciner. The need for an additional steam cycle to generate power increases the total CAPEX (in €) with respect to other post-combustion capture systems, while the specific CAPEX (in €/kWe), the specific OPEX and the energy penalties, is relatively low and remains competitive as a result of the capture system generating additional electric power. However, a partial yellow colour is given to efficiency penalty cell, as an ASU is still required to run the oxy fired calciner in the most mature CaL technology (other options under development to avoid¡ air separation units are still at TRL<3). The availability of sorbent precursor (limestone) is very high and the purge of solid material (rich in CaO) can find uses in power (i.e. desulphurisation) and cement plant environments. Cost of a FOAK could be relatively low because the tight similarity of CaL with CFBC boiler technology. However a red/yellow represents the increased uncertainties when designing interconnected system respect to single loop CFBC designs.

3.7.4 Membrane based separations

Post-combustion polymeric membranes systems could exhibit low energy requirements for the CO_2 separation. This justifies the green colour for OPEX although pressure drop can be an issue. The major cost for membrane systems are capital costs associated with compressor or vacuum pumps needed, and the membrane material (€/m^2). Separation of power plant flue gases with low CO_2 concentration and large volume streams, generally require large membrane areas in a single stage process, or several membrane stages. As the membrane cost could contribute to 50-60% of the system equipment cost, CAPEX was assessed in a yellow colour in Table 3.3. It will be important that

new materials are designed to minimize the size and cost of the membranes, as well as the auxiliaries for compressors and vacuum pumps.

The number of membrane stages to achieve a certain CO_2 purity is affected by the CO_2 selectivity of the membrane while the size is determined by its permeance. However, post-combustion polymeric membrane systems bear opportunities with respect to operation flexibility as they can be switched off and on, similar to gas power plants. In addition, the technology does not apply aqueous solvents or toxic compounds and does not need regeneration steps.

Upon meeting their performance expectations, e.g. high CO_2/N_2 selectivity, high permeance etc. membranes might become an attractive capture technology for power plants. Within the challenge for commercial applications, the stability and lifetime of membranes are of great importance. Potential clogging, fouling and cracks, as well as their sensitivity towards flue gas impurities will be determining – frequent membrane substitution would drive up OPEX. A given sensitivity of membranes towards other flue gas components determines the flue gas cleaning requirements and might therefore as well affect CAPEX and OPEX.

Metallic H_2-separation membranes for pre-combustion have reached a certain level of maturity in terms of H_2 permeability and selectivity. Ceramic O_2-selective membranes for integration in oxy-fuel processes are less developed and potentially more CAPEX intensive. OPEX can be low because of the low energy penalty, provided that the performance and stability of these membranes at their typically high operating temperatures are demonstrated. While retrofitting of an ASU unit installed in an existing plant is feasible with the membrane system replacing a cryogenic ASU unit, it is not possible to retrofit an already operating power plant with pre-combustion Pd membrane technology. In addition to challenges related to membrane availability and manufacturing value chain, this justifies a red colour for a FOAK plant.

4 Transport technology

4.1 Transport needs

Volumes of captured CO_2 will grow significantly over the coming decades, reaching the tens of megatonnes range at country level and for heavily industrialised regions between 2030 and 2050 [e.g., Neele et al., 2011]. For comparison, the largest CCS projects currently in operation capture, transport and store volumes typically in the order of 1 mtpa. The transport of CO_2 for EOR purposes in the US is considerably more significant and in the order of tens of megatonnes per annum.

Transport and storage of these large volumes requires transport and storage networks that utilise economies of scale by linking several sources and sinks of CO2. While today's one-on-one type of CCS projects represent the proving ground for CCS technologies, new developments will be required for the networks of the future.

Transport of CO_2 by pipeline onshore over long distances and over a range of pressures and temperatures is a well-established technology. Small scale transport of CO_2 by ship and the onshore loading and offloading of CO_2 at ports is an established and commercial technology, but will require substantial upscaling to be relevant for CCS (both for ships and storage). Offshore unloading of CO_2 directly into subsea wells via buoys or platforms will require substantial technology development (heating and/or intermediate storage offshore) and further demonstration.

1st Generation Technology Readiness Levels

Technology	TRL	Comment
Pipeline transport	9	Based on US EOR, Quest and Boundary Dam Limited experience in European context: more densely populated
Shipping (port to port)	7	Small-scale LPG vessels (semi-refrigerated) demonstrate concept Large scale to be reached yet: ships and loading / unloading facilities
Shipping (port to offshore facility)	4-5	Further development required: impact of batch-wise injection on injection system, low-temperature flexible hoses, offshore buffering requirements, ship design

4.2 CO_2 pipeline transport experience

4.2.1 Operating pipeline projects

Bulk transportation of naturally occurring, and to a lesser extent, anthropogenic CO_2, is an established practice in the US where the main business driver has been to facilitate Enhanced Oil Recovery (EOR) rather than carbon dioxide sequestration. There are over 7,000 kilometres of pipelines in North America transporting significant volumes of CO_2 from natural reservoirs to oil fields (60 mtpa in 2010) (e.g., NETL, 2015), with an increasing volume of CO_2 from industrial plants

such as the facility at Port Arthur, Texas. The largest network supplies Permian Basin operators in Texas and New Mexico, which have been injecting CO_2 for 40 years. The existence of these businesses gives confidence that transportation of CO_2 in dense phase is already at high TRL level. However, there are a number of important topics that need to be understood, before CO_2 large scale transportation is applied in a wider European context.

- If not purified, anthropogenic CO_2 could potentially contain impurities that cause the product to behave differently in contact with materials (pipelines, seals etc.) and cause movement of phase boundaries potentially affecting transportation efficiencies. The impurities emitted from power plant capture in particular will result in different CO_2 compositions from those currently transported by pipelines in the USA. However, the CO_2 produced by almost all currently available capture techniques has a purity of >99% [Eickhoff et al., 2014]; with sufficient dehydration to levels below about 250 ppm of water, impurities at these concentrations can be handled using carbon steel pipelines and injection wells [Brunsvold et al., 2016]. The exception to this is CO_2 from oxyfuel systems and natural gas processing, which contains relatively high levels of air components or gas (several percentiles), which may need to be removed prior to transport and storage. The 'non-condensable' impurities (N_2, O_2, CH_4, Ar and H_2) have a relatively strong effect on the amount of compression (e.g., Wetenhall *et al.*, 2014).
- Water, as an impurity in the CO_2, has the strongest effect on transport and storage. Removing water to sufficiently low concentrations prevents corrosion and hydrate formation. Water content can be reduced by multi-stage compression and water knock-out systems and chemical dryers.
- CO_2 received into a network from multiple sources creates complexity for control and operations that needs to be understood through transient analysis.
- Standards applied for pipelines in remote areas of the USA are not necessarily appropriate for application in the more densely populated environment that can be expected in Europe. This is an important consideration in the context of Quantitative Risk Assessments (QRA's), differing expectations of safety levels and public acceptance in general.
- Design Life of Assets comprising networks and other shared infrastructure may be greater for CCS operations than they are for EOR requiring different materials choices and/or standards of stewardship. That said, the USA Permian basin pipelines, developed originally by Shell, have been in place since the 1980s.

On-shore pipelines transporting CO_2 in vapour phase are currently also in use. In the Netherlands about 400 ktpa CO_2 (of which 300 ktpa from the Shell Pernis Refinery) is supplied to 500 greenhouses in vapour phase, re-using an existing 85 km 26" diameter pipeline between the Rotterdam industrial area and port of Amsterdam. This 'OCAP' pipeline is currently operating at about 20 bar(g) and is also used for buffering/storage of CO_2 [27].

The only off-shore CO_2 pipeline worldwide was installed by Statoil in Norway, during 2005. This pipeline was installed by (un-)reeling, recognizing the challenging environment of the Barents Sea.

[27] Information about the OCAP pipeline can be found at www.ocap.nl/files/Ocap_Factsheet2012_UK.pdf.

CO_2, co-produced with the natural gas stream from the Snøhvit field, is separated at the Hammerfest LNG Plant on Melkøya Island and then transported, injected and stored in an aquifer about 2,600 meter below the seabed. Since April 2008, dry CO_2 is transported through a 153 km 8" Carbon Steel off-shore CO_2 pipeline and injected into the reservoir using a single subsea well at 330 meter water depth. Approximately 700 ktpa of CO_2 can be stored.

4.2.2 Planned projects

CCS holds investment potential for the development of transportation networks serving the many geographic clusters of CO_2 emitters. The concept of multi-user transportation networks is an important development on the journey towards developing a cost competitive CCS solution for carbon abatement. The benefits of economies of scale and the security provided by shared infrastructure are well understood through the development of gas, electricity, water and telecoms networks. A number of CCS networks have been considered across North West Europe which also raises the possibility of the North Sea being developed as a shared storage resource, raising the prospect of further economies of scale.

In the UK, the Yorkshire and Humber region has one of the highest concentrations of carbon dioxide emitters in the UK. Work on a multi user pipeline with a capacity of up to 17 million tonnes per annum in the region was well advanced, aiming to see carbon dioxide captured from this 'cluster' transported by pipeline and safely and permanently stored in geological formations beneath the North Sea[28]. This development, known as the White Rose CCS project (e.g., Global CCS Institute, 2015), was intended to start from a state-of-the-art coal-fired power plant equipped with full carbon capture and storage technology. This starter project was intended to prove CCS technology at commercial scale and demonstrate it as a competitive form of low-carbon power. The recent decision by the UK Government to withdraw funding for CCS Commercialisation has put this vision in jeopardy.

The Teesside region aims to become Europe's first CCS equipped industrial zone. The Teesside Process Industry Cluster is one of the largest in the UK and includes a range of chemical, petrochemical and energy companies. The CO_2 emissions are an inherent part of many of the processes being utilised on Teesside[29].

In Scotland, plans have been developed for a proposed full–chain 570 MW Carbon-Capture-Storage (CCS) coal-gasification power station located in Grangemouth. The proposed power station could be fitted with CCS technology designed to capture 90% of CO_2 emissions which would then be transported via existing on-shore pipelines and existing sub-sea pipelines for permanent geological storage 2 km beneath the North Sea. The aim was to link up with the offshore pipeline from the Peterhead CCS Project. Up to 10 million tonnes of carbon dioxide emissions could be captured from the Peterhead Power Station and transported by pipeline offshore. When connected together, through existing natural gas pipelines, the CO_2 transportation system in Scotland would be capable of taking CO_2 from the central belt of Scotland where most Industry and population is situated

[28] See http://www.ccshumber.co.uk/.
[29] Blueprints for deployment of CCS in the Teesside industrial area can be found at http://www.teessidecollective.co.uk/category/reports-publications.

(Brownsort *et al.*, 2016). The withdrawal of funding for CCS commercialisation by the UK Government has significantly delayed this vision to be realised.

The combined region of Rotterdam/Antwerp, with pipeline connections to Ijmuiden, Amsterdam and potentially the Ruhr Area in Germany would assemble the largest CO_2 cluster in Europe by far. In the Netherlands the Rotterdam Capture and Storage Demonstration Project (ROAD) is an initiative of Uniper (previously E.ON Benelux) and ENGIE Energie Nederland (previously GDF SUEZ Energie Nederland). ROAD plans to capture part of the CO_2 from a new power plant at the Maasvlakte and store the captured CO_2 in a depleted gas reservoir under the North Sea. ROAD aims to demonstrate the technical and economic feasibility of CCS and how it can be deployed on a large scale for power plants and energy-intensive industries. The knowledge and experience acquired within ROAD can be instrumental in the commercial introduction of CCS. The first infrastructure will be designed to facilitate the next phase of transport and storage in the region.

4.2.3 Potential development

An integrated connected network throughout the North Sea and around the Baltic will grow from these regional cluster projects. Other disconnected networks will develop in Eastern and Southern Europe as dictated by concentrations of emissions clusters and storage locations. The development of large, connected networks has been the subject of several studies[30].

The development of a large scale north-west & central European CO_2 transport infrastructure was studied as part of the CO2Europipe Project, financed under the EU FP7 framework (see Neele *et al.,* 2011). An inventory of large emission sources was established, assuming realistic economic scenarios. The captured CO_2 volumes were linked to potential storage locations (either depleted oil and gas fields or aquifers), for 3 different scenarios: on-shore & off-shore storage (Reference Scenario), off-shore storage only and an EOR scenario. By 2030 the transport network is expected to grow to 14,500 km (Reference Scenario) or even 21,000 km (Off-shore storage only & EOR scenario) in order to store 360 mtpa of CO_2. In order to store about 1,200 mtpa by 2050, the transport system length should increase to 25,000 km (reference scenario) or even 33,000 km (both other scenarios). This is comparable with the existing oil/products transmission network in Europe (35,000 km), but smaller when compared with the European gas transmission network having a length of 130,000 km in total. It can be concluded this is technically feasible, but the cost for development of this CO_2 transportation network is significant: about € 55 billion at current cost level for the Reference Scenario by 2050. This increases to even € 75-80 billion for the other scenarios, as the storage locations are more distant (off-shore storage only and CO_2 used for EOR). These findings are reasonably consistent with figures published in studies performed by other parties (e.g., Arup, 2010; Morbee *et al.*, 2011).

Similar studies have also been performed for the US and Canada (e.g., ICF, 2009), showing the extent of the CO_2 network and associated costs.

[30] For example, see Yorkshire Forward (2008), Element Energy (2010), Neele *et al.* (2011).

4.3 Status of Pipeline technology

Transport by pipeline is an existing proven technology. The major considerations for designing CO_2 pipelines are:

- Transport capacity, which is related to number, size and location of (future) carbon capture plants and storage sites/well locations, onshore or subsea pipeline route options, ambient conditions such as soil, air temperature and (prevailing) wind conditions, geographical features and populated areas defining the pipeline route options and total length, burial requirements, variation in elevation, and options for compressor and/or pump stations along the onshore pipeline route or at injection points;
- Selection of standards applicable for pipeline design and operations;
- Selection of pipeline route corridors ensuring safe operations transporting CO_2 (risk reduced to As Low As Reasonably Practicable: ALARP), especially onshore nearby populated areas with elevation changes present (low lying areas);
- The compatibility of the CO_2 mixture in relation with material selection – corrosion (dehydration requirements for carbon steel), risk of fracture propagation (wall thickness, material grade and toughness requirements) and phase behaviour/transition during blowdown (low temperatures);
- Transient phenomena such as depressurization which could lead to substantial cooling, resulting in low temperatures and potential for formation of hydrates (having free water present) or dry ice.

4.3.1 Phase Behaviour

It is important to bear in mind that CO_2 does not behave like water, hydrocarbon liquids, chemical liquids or methane, and varying the levels of impurities in the CO_2 will affect the phase behaviour. Understanding the phase diagram is critical, as under specific operating conditions (e.g. pressure reduction or blowdown) the fluid enters the two-phase regions (liquid and gas). Experience, research and design together highlight the importance of avoiding operating CO_2 pipelines in the two-phase region, although moving into two-phase flow cannot always be avoided. Depressurising a CO_2 filled pipeline or vessel can take much longer than for a natural gas and low temperatures could potentially result in brittle fracture and crack propagation.

Most long distance CO_2 transportation pipelines are operated in dense phase, or as a liquid. Operating in gas phase gives least operational complexity, e.g. the OCAP pipeline mentioned in Section 4.2.1 is operated at 20 bar. But operating in gas phase means, in order to get reasonable throughput, large diameter pipelines are required, increasing construction cost and thus transportation costs (per ton of CO_2 transported) substantially (see, e.g., Knoope *et al.*, 2014).

Operating in dense phase results in increased throughput in the same diameter but if a system is shut down and temperature falls the contents can convert to two phase, depending on temperature and pressures levels. Two-phase flow at start-up can lead to slugging of liquid CO_2 in the pipeline, therefore start-up should always be performed in a controlled manned to avoid potential damage to pipeline.

Avoiding two-phase flow can be achieved by designing systems to operate well above the critical point by controlling the outlet pressure, even under shut down conditions, which means the pipeline

is operated at high pressure over the full length. An overview of operating conditions of current and planned CO_2 pipelines is provided by IEAGHG (2014).

4.3.2 Contamination and Material Selection

CO_2 pipelines require adequate dehydration of the CO_2 to prevent corrosion of carbon steel pipelines and specified fracture toughness levels of steel, or alternatively the installation of crack arrestors to minimise the impact of running ductile fracture in the unlikely event of a pipeline failure. Future technologies requiring research include alternative pipeline materials like CO_2 compatible composites which also have the potential for lower installation costs (reels with couplings without on-site welding).

Although the TRL level for transport by pipeline is high and indicative of a proven and commercially available technology (TRL 9), specific individual components could be at a much lower level. This will create a demand for focussed R&D to improve these sub-system components. Components of particular interest include the following.

- **Measurement of constituent components** in the individual and combined product streams. One process upset from one source can upset a larger part of a network. From an operator's perspective real time measurement is the ideal condition to assist safe and efficient management of the transportation system. This condition does not exist at present for all constituent components. The measurement process is further complicated if there is a need to extract samples in dense phase and then reduce the pressure and state to vapour phase prior to measurement. The need for and desirable frequency of CO_2 composition monitoring will depend on the system's sensitivity to CO_2 composition variations.
- **Metering** of volumes to the required fiscal standards is hampered by a lack of calibration facilities for the various metering technologies. Metering accuracy may be affected by impurities and techniques used for natural gas, such as ultra-sonic flow meters, may not be suitable for CO_2. Metering of flow in a pipeline undergoing two phase flow would be extremely unreliable. It will always be the intention of pipeline designers and operators to operate in single phase, but operating upsets may occur.

4.3.3 Compression

A significant cost in CCS transportation systems will be for compression. Transporting CO_2 in dense phase or liquid is more efficient (requires smaller diameter pipeline) than in gas phase. Compressing to well above the supercritical pressure of 73.8 bar will mean that in spite of frictional losses the CO_2 can arrive at the end of the pipeline in dense phase. Compression will heat up the CO_2, and in order to increase throughput, density may need to be increased by cooling the compressed CO_2 before entering the pipeline. In order to transport dense phase CO_2 through very long pipelines, pump stations (rather than compression stations) can be installed every 100-150km to maintain the flow and pressure.

Compressor design will need to be optimised depending upon the range of levels of impurities anticipated. Significant economies could be gained by:

- Improving the compression process, considering the typical large compression ratios required to bring near atmospheric CO2 from the capturing process into dense phase for efficient transportation;

- Capturing waste heat (integrate with power plant or localised CHP);
- Improved models for thermodynamic properties of CO_2 rich mixtures, such that design and operation can be optimized.

Compression and transportation of pure CO_2 have been conducted in North America for over 40 years for enhanced oil recovery (EOR or Enhanced Gas Recovery), in remote areas and at pressures of typically 80 – 180 barg. There is increasing experience in North America related to the transportation of CO_2 containing impurities resulting from the combustion or chemical processing for carbon capture; examples are the Great Plains pipeline to Weyburn and the new capture projects that will come on line in 2016, such as the Kemper County IGCC plant. The future of CO_2 transport needs to take account of the need to transport CO_2 with impurities, in large diameter pipe at lower pressures (between 20 and 150 barg) sometimes near to densely populated regions.

In Europe, and specifically in the North Sea region, the primary drivers for a preference for offshore pipeline transport over transport by ship are that:

1. transportation distances from onshore sources to prospective North Sea storage sites are relatively short;
2. bulk transmission is more economical than individual point to point transportation systems, economies of scale are in developing transportation from clusters of emitters;
3. Pipelines avoid the need for intermediate (near-shore) storage and cryogenic operations as needed at a ship loading point.

4.3.4 Economies of scale

The unit cost of transporting CO_2 by pipeline decreases as scale increases. Both use and scale are important. Optimising location and size of early CO_2 infrastructure can reduce the incremental cost of transportation and storage substantially for later projects and facilitate future CCS deployment. Some examples of projects developing pipelines into networks and the advantage this brings are given in 4.2 above. Examples of cost analyses and economies of scale can be found in Knoope *et al.* [2014ab].

4.3.5 Standards

An international standard is currently in development, PSE/265 Carbon Capture Transportation and Storage - BS ISO 27913 and geological storage - Pipeline transportation systems [31]; the standard is due for release in 2016. The recommended practice formulated by DNV, DNV-RP-J202 [32], was used as the starting point for the ISO standard.

The objective of the international standard is to provide requirements and recommendations on certain aspects of safe and reliable design, construction and operation of pipelines intended for large scale transportation of CO_2 that are not already covered in existing pipeline standards such as ISO

[31] Information about the standard is available at https://www.iso.org/obp/ui/#iso:std:iso:27913:dis:ed-3:v1:en.
[32] The DNV recommended practice is available at http://rules.dnvgl.com/docs/pdf/DNV/codes/docs/2010-04/RP-J202.pdf.

13623, ASME B31.4, EN 1594, AS 2885 or other standards. The International Standard is written to be a supplement to other existing pipeline standards for natural gas or liquids for both onshore and offshore pipelines. The international standard specifies additional requirements and recommendations not covered in existing pipeline standards for the transportation of CO_2 streams from the capture site to the storage site where it is primarily stored in a geological formation or used for other purposes (e.g. for EOR or CO_2 use).

The standard applies to:

- rigid metallic pipelines;
- pipeline systems;
- onshore and offshore pipelines for the transportation of CO_2 streams;
- conversion of existing pipelines for the transportation of CO_2 streams;
- pipeline transportation of CO_2 streams for storage or utilisation;
- transport of CO_2 in gaseous-, and dense-phases.

Issues that are specific to CO_2 transport by pipeline and that need further development include those mentioned in Section 4.2.1. The mechanisms that determine hazards of accidental release from pipelines and associated safety distances for CO_2 pipelines are yet to be fully understood (e.g., Knoope *et al*., 2014; Hébrard *et al*., 2016).

4.4 Transport by ship

4.4.1 Ship transport in operation

Shipping of CO_2 has been established, but experience to date is only limited to smaller carriers. Both Yara (vessels managed & operated by Larvik Shipping AS) and Anthony Veder have been operating small dedicated food-grade CO_2 carriers having a capacity of 900-1250 ton, for decades. Pressurized CO_2 (18 bar(g)) is transported at a temperature of -40°C. For transport of large volumes CO_2 a significant scale enlargement of these carriers is required, which has been established for LNG/LPG shipping. It is rather unlikely that existing gas carriers will be converted for CO_2 transport, as only a limited number of specialised gas carriers for LPG/ethylene meet the pressure and temperature conditions, as required for CO_2. Furthermore it is yet to be studied in more detail how the cold CO_2 can be heated and injected intermittently from the gas carrier into the injection well to optimize the shipping logistics, or whether costly intermediate cold and pressurized storage (and subsequent heating) is required to ensure a more stable injection rate into the well.

4.4.2 Planned projects

Transport by ship is considered to be a cost-effective solution for the full-chain CCS project that is being developed in Norway[33]. This 'Norwegian CCS Initiative' is about capturing CO_2 at one or more onshore emission point(s), transporting it to offshore locations where it is stored in a saline formation or a depleted field. Although pipeline transport could become a viable alternative, depending on such parameters as CO_2 volume and transport distance, ship transport is considered the more cost-effective option, offered as a commercial service by several providers. Some elements

[33] See https://www.regjeringen.no/contentassets/3652c303169e46e7815617adab685710/gassnovas-pre-feasibility-study.pdf.

of the ship transport element in the CCS chain may require technology development, such as offshore offloading and offshore injection.

4.4.3 Potential development

The Norwegian CCS Initiative is currently the only CCS project considering ship transport. However, ship transport has certain advantages over transport by pipeline and could play a key role in the early phases of CO_2 transport. Ship transport could evolve as part of large-scale CO_2 transport in several ways.

1) As a temporary solution, prior to the establishment of a CO_2 pipeline, either one source-one sink, or before an additional connection to an existing offshore pipeline infrastructure. Such a scenario assumes that ship transport could be used during an initial phase when the volumes of CO_2 are relatively small, but where a later phase of larger CO_2 volumes would justify the construction of a pipeline.
2) As a permanent transport solution when distances are too long and/or CO_2 quantities to be transported are too small, or when several storage sites may become necessary during the lifetime of the CO_2 emission source.
3) As part of a mixed system, in which pipelines and ships are combined. This was considered for CO_2 from the industrialised areas in the Netherlands, Belgium and Germany (Global CCS Institute, 2013).

The Norwegian CCS Initiative could perhaps at this moment be regarded as an example of the first scenario. Gassnova has the aim to realize facilities by 2020, although the date of commencement of shipping is not clear. Following this initiative, ship transport may begin to include hubs for loading/offloading of liquid CO_2 either along the North Sea and Baltic coast initially, or even offshore in the future. In case more loading / unloading hubs are developed, a shipping network can start to develop, with ships shuttling between loading and unloading sites.

As CCS progresses from demonstration via early deployment beyond 2020 to widespread deployment beyond 2030, the number and size of ships transporting CO_2 will increase as required, depending on the amount of CO_2 to be transported from coastal areas where no offshore pipeline infrastructure is available. In order to optimize the logistics chain and reduce cost, ships that are capable of transporting both CO_2 and LPG[34] may be relevant to put into operation in cases where it is of interest to transport hydrocarbons back to the area from where the CO_2 is collected.

The NORDICCS project (concluded end of 2015) has conducted CCS case studies of several CO_2 emission points and storage sites in the Nordic region (Iceland, Norway, Denmark, Finland, Sweden)[35]. Regarding CO_2 transport, the overall conclusion is that ship transport is likely to be the most economical solution for transporting CO_2 from individual emission sources in most investigated cases, due to the small CO_2 quantities and in some cases also long transport distances. Also, for CO_2 clusters, CO_2 transport by ship has been found to be the most economical solution, at least in the ramp-up phase of a CCS cluster.

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[34] Or possibly LNG, but then the requirements on CO_2 traces remaining in the tanks will be more stringent.
[35] Recommendations on CO2 transport solutions, NORDICCS deliverable D20.

A Nordic initiative to evaluate the prospects of CO_2 transport by ship is also under consideration. In this scheme, CO_2 from large CO_2 point sources in the Skagerrak / Kattegat region to the south of Oslo is chilled and transported in liquid form to offshore storage locations. There are some minor formations that have been evaluated for CO_2 storage in the Baltic sea (e.g. Faludden, with very limited storage capacity), but it is likely that most CO_2 from the Nordic countries except Iceland but including Finland and Sweden will be transported by ship for storage in the North Sea. In a similar vein, CO_2 captured and aggregated at sea ports in Antwerp, Hamburg, Le Havre or at the mouth of the Thames, Tyne, Humber and Mersey in the UK may be shipped to other ports for transfer to pipelines to offshore storage via buffer storage at the receiving port. A recent study suggests that offshore offloading at the storage site could be feasible (de Kler *et al.*, 2015).

4.5 Status of shipping technology

Much necessary shipping technology can be considered to be well established, but not at the scale/volumes required. Several aspects will need further development.

The shipping technology concept is adequately demonstrated through the operation of LPG tankers although few dedicated liquid CO_2 tankers exist (semi-refrigerated) [36]. Scaling up of these vessels to meet the expected volumes of CO_2 that would be emitted by a typical power station will require a significant effort.

The port to port shipping option could consist of four different elements; 1) the onshore terminal at an onshore collection hub for intermediate storage of the liquefied CO_2 2) loading to the vessel(s), 3) the offloading terminal and intermediate storage facility, and 4) the onshore pipeline which will connect the offloading port facility with the pipeline network.

The implementation of a ship transport chain depends on the location of the loading and unloading sites. In an analysis of the cost of CO_2 transport, ZEP (2011) considers a number of ship transport options; Vermeulen (2011) describes in detail the technical set-up of a ship transport link to an offshore offloading site.

4.5.1 Vessels

The technology to build ships for CO_2 transport is demonstrated and available. In Norway, ammonia producer Yara has a fleet of two ships certified for CO_2 transport (capacity 1800 metric tonnes/ship) in operation today; three more ships are in operation by Larvik Shipping, with a capacity of between 900 and 1200 t. In The Netherlands, Anthony Veder operates a CO_2 vessel with a capacity in the same range. These ships transport food-grade CO_2; the ships are probably too small for the CCS industry.

IM Skaugen is a Norwegian shipping company that operates larger vessels, designed to be able to transport pressurized liquids, such as NH_3, liquefied light hydrocarbons, ethylene and LNG. Typical size is 8000 to 12000 m3. One of the IM Skaugen ships with a capacity of 10,000 m^3 is also certified for ship transport of liquid CO_2. Generally speaking, adapting such liquid carriers (operating typically

[36] A detailed list of existing fleets can be found in http://www.sccs.org.uk/images/expertise/misc/SCCS-CO2-EOR-JIP-Shipping.pdf.

up to 8 bara) for CO_2 transport can be done at relatively low cost. This option offers flexibility in terms of carrier use, reduces owner risk, and implies that when ship transport of CO_2 is envisaged during an initial operation phase of a CCS project, they can be used for other purposes later on if the CO_2 transport is converted to pipeline. Attention must be given to the requirements that will be put on carriers transporting CO_2 with impurities, and whether the steel qualities used can accept such impurities. The EU FP7 IMPACTS project recently provided the data that allow accurate calculations of the effects of the most relevant impurities on the phase behaviour of a CO_2 mixture (see, e.g., Brunsvold *et al.*, 2016).

Design of CO_2 ships may in the future comprise CO_2 heating prior to injection if the CO_2 is delivered to a hub where this is not integrated. A recent study suggested that sufficient heating and compression facilities can be put on board a ship, although a system with offshore temporary storage would be a lower-cost solution (de Kler et al., 2015).

Compressed CO_2 transport (75 bar, 25 °C) has the advantage of requiring little (or no) heating during offloading. However, this technology remains to be demonstrated for large-scale CCS and most studies suggest liquefied CO_2 transport to be the most feasible (Skagestad *et al.*, 2014). In semi-refrigerated ships the CO_2 is kept in the liquid phase on the saturation line by a pressure higher than atmospheric pressure and a temperature lower than the ambient temperature. An additional advantage of transporting CO_2 under these conditions is that it has the highest density possible in these conditions in the liquid state, resulting in a lower unit cost for transportation. Semi-ref ships are usually designed for a working pressure of 5 to 7 bar and operate at low temperatures (-48°C for LPG, -104°C for ethylene and around–50ºC for CO_2). Boil off is reported in the literature at 3-4% per 1000 km; Vermeulen (2011) describes how the boil-off gas can be contained within the tanker, avoiding the need to release to the atmosphere.

The most common type of semi-ref ship is the LPG tanker. The largest semi-ref LPG tankers currently under construction and in operation can transport approximately 20,000 m^3. Such vessels generally have 2 to 6 tanks, and each tank may have a capacity of 4,500 m^3. CO_2 ship transport studies consider ships with capacities in the range of 20 – 50,000 m^3 (Vermeulen, 2014; Byeong-Yong Yoo *et al.*, 2013; De Kler *et al.*, 2015). CO_2 shuttle tankers suitable for offshore offloading need to be built, as there is currently not a market for such vessels. It is believed that existing shuttle tankers for oil transport could be modified to accept limited amounts of CO_2. However, for large scale operation (over 1 Mt/yr), specialized vessels will be required.

4.5.2 Loading and Unloading Facilities at Ports

The loading and unloading facilities consist of the quay/jetty and the loading/unloading system. The loading/unloading system at the quay/jetty transfers liquefied CO_2 from the storage tanks to the ship and vice versa. The storage tanks should have a capacity of at least one tanker. The loading/unloading system includes all the necessary piping between the tanks and the ship, as well as pumps, loading and offloading arms and a return line for CO_2 vapour generated at the ship.

The CO_2 ships currently in operation prove that loading and unloading facilities are commercially available. The step to the scale that is required for large-scale CO_2 transport and storage remains to be demonstrated.

4.5.3 Intermediate Storage Facility

CO_2 is stored as liquid in semi-pressurized storage tanks at -50 °C. Semi-pressurized storage is common for other liquefied gases such as LPG and ethylene. The most common methods are: semi-pressurized spheres, semi-pressurized cylindrical tanks (bullets), or underground storage in caverns (but not as liquid).

Due to the potential for liquid CO_2 to form dry ice, care must be taken in the entire process (process plant, storage and loading and unloading) to avoid this. There is little knowledge regarding the thermodynamics of dry ice formation with impurities present. In the liquefaction of CO_2 at low temperatures, non-condensable impurities like N_2 and Ar will mostly be separated from the liquid, whereas condensable impurities like H_2S or SO_2 can remain.

4.5.4 Gasification, Heating and Compression

In order to transfer CO_2 into long distance transport pipelines, the CO_2 stored in tanks/buffers and/or delivered by ship will require pressurisation (by pumps) and heating.

A recent study into the requirements of heating and compression for ship-based transport suggested that technically and practically feasible solutions could be found, for most offshore storage types, including depleted fields and saline formations [de Kler *et al.*, 2015]. The results suggest that offshore ship-based conditioning of the CO_2, prior to injection, is feasible. However, as mentioned above, the study found that a set-up with temporary offshore storage has advantages for both operations and costs. Further work is needed, such as the detailed design of dedicated systems and ships.

4.5.5 Offshore unloading

Delivering liquid CO_2 offshore in the North Sea and injecting heated CO_2 into wells requires some innovation. Ship to ship transfer with current technology can only take place in relatively calm weather, whereas the industry will require quick offloading turnaround in all weathers if possible. Ship to floating dock or fixed dock is more tolerant of a range of weathers, current and swell. In order to achieve full availability, current mooring and connection systems should be developed and demonstrated in realistic weather and sea state conditions. Vermeulen (2011) and Brownsort (2015) discuss several options that have been put forward in recent studies.

The offloading facility may need a buffering capacity of at least double the size of the visiting tankers. The need for offshore buffering (temporary storage) capacity will depend on the design of the injection system (Brownsort, 2015). Facilities with heaters, compression, filters, meters and monitoring equipment all of a suitable scale have not yet been developed.

Flexible hoses are another element of the offshore offloading system that need testing and verification. Flexible hoses are being used for LPG and LNG in conditions comparable to those expected for CO_2, but their suitability for CO_2 is yet to be tested (Brownsort, 2015).

Ship transport may lead to intermittent injection, with associated thermal and pressure cycles imposed on the injection well. Research is needed into the impact of such batch-wise injection on the well system. There may be a trade-off between avoiding batch-wise injection through local buffer storage and adapting the design of the injection well. Skagestad *et al.* (2014) assign this issue the highest R&D priority.

4.5.6 Benefits and Limitations of Ship Transportation

Some unique benefits of CO_2 transportation using ships include the following.

- Shipping can be a cost-effective transportation option especially for smaller projects with low volumes and projects that are still at an embryonic stage, and/or for projects having large transport distances.
- Short delivery time of CO_2 ships from order can offer a competitive advantage.
- Shipping offers the flexibility of using the ships in several projects and therefore the ship operators can have full utilization of the ship.
- Ships can be certified for transport of several other pressurized liquids in addition to CO_2, (NH_3, light hydrocarbons, LNG, ethylene), which reduces owner's risk.
- Ships offer the ability to collect CO_2 from existing industrial sources with moderate capital costs compared to new pipelines.
- Transportation capacity can be increased at relatively low capital cost by adding further ships to the system.
- Shipping of liquid CO_2 at large scale is feasible with known technologies and can provide a transportation system that is flexible in terms of space and time.

On the whole, ship transport offers an alternative to pipeline transport that has a lower financial risk and that may be more easily investable.

There are some issues that need to be demonstrated for the shipping option; at present no technological showstoppers have been identified.

- The effects of batch-wise injection on the injection system must be investigated. Related to this issue is the need for offshore buffer storage, which could also provide a location for the facilities for conditioning the CO_2 prior to injection.
- Offshore offloading systems are to be demonstrated, especially for more severe weather and sea state conditions.
- The impact from impurities in CO_2 on the selection of steel quality must be verified. For transport of pure CO_2, the technology is at TRL 7. If impurities are present in the CO_2 that is to be transported and stored, the phase behaviour of the mixture may affect the design criteria of the shipping chain elements.

4.6 Transport network

The operation of pipeline networks and hubs for CO_2 is an established technology in the United States within the EOR industry. Therefore, there is not considered to be a technology gap in the development of pipeline networks.

Nevertheless, for pipeline network operation there is a lack of validated modelling experience with CO_2 pipelines; in this respect, the presence of impurities in the CO_2 should be taken into account. Other issues include the ability of the pipeline network to act as a storage vessel (line packing) and the operation for packing and unpacking the pipeline with minimum impact of two-phase flow; the requirement for intermediate storage in the pipeline network; the effect of uncertainties in the geophysical properties of the storage site and the operation of the store under varying CO_2 flow rates and phases.

The availability of well proven tools for modelling of transient CO_2 flow is limited. At least one tool for transient modelling of oil and gas flow has been modified to handle CO_2 [61], however this model is currently not available commercially. Reliable engineering tools for modelling of CO_2 injection will aid in improving the operating envelope, giving better utilization of capacity. This is especially true for concepts which rely on frequent connect/disconnect operations such as ship-based transport, where a good understanding of the transient system response is important.

Another challenge in the operation of pipeline networks is uncertainty surrounding the variation in specifications of CO_2 that may be encountered in the system. Although the importance of CO_2 specification has been mentioned in other sections of this report, with respect to the design of the pipeline, the variation that could be accommodated in the specification should be considered and the restrictions that these could place on 'late entrants' into a pipeline network. In this respect the on-line metering and monitoring of the CO_2 stream entering the transportation system becomes critical. Technologies will need to be developed to monitor the variations in CO_2 composition for a number of critical components (*e.g.* water, hydrogen, nitrogen, oxygen) to ensure the integrity and operability of the transport and storage system. It has been concluded that current capture systems provide CO_2 of sufficient purity for CO_2 pipeline systems with standard carbon steel, provided that dehydration at the system inlets ensures the absence of free water at all times (Brunsvold *et al.*, 2016); it is noted that oxyfuel systems form the exception, as these produce the least pure CO_2. Brunsvold *et al.* (2016) suggest that in general it is more cost-effective to remove impurities at the source, rather than to deal with downstream effects. The purity of CO_2 from current capture systems is already sufficiently high for transport systems with standard carbon steel pipelines to allow some variation in CO_2 composition in the system. The EU FP7 IMPACTS project has contributed to the database of CO_2 mixtures properties that is maintained at NIST[37], with which the properties and behaviour of real CO_2 mixtures in transport and storage systems can be predicted.

If at high pressure to avoid two-phase flow, CO_2 pipelines do not need a minimum flow rate, although higher flow rates have better asset utilisation. It is important to maintain flow in a single phase, but this can already be achieved by effective control systems.

4.7 Summary

As noted in Section 4.1, CO_2 transport is well-established technology, with significant development required only for large-scale ship transport. The sections above list a number of technological gaps that are summarised in Table 4.1, with an indication of need, cost and agent for delivery or cooperation.

[37] Available at www.nist.gov.

Table 4.1 Transport challenges and R&D gaps.

Section	Technology	Must have / Nice to have	Development Cost	Who
4.3.1	Contaminants affect CO_2 phase behaviour and reactions with materials	Must have	Low	Research and Industry
4.3.2	Alternative pipeline materials	Nice to have	Low to medium	Multi-industry and research organisations
4.3.2, 4.5.6	Measurement of constituent components – real time measurement of contaminants	Must have	Low to medium	Research and Industry
4.3.2	Extract samples in dense phase - new sampling technique or gas chromatograph at high pressure	Nice to have	Low	Research and Industry
4.3.3	Compressor design – optimise for range of CO_2 duties and CO_2 quality	Ongoing	Medium	Industry share experience and research
4.3.4	International standard in development	Happening	Low	Research and Industry cooperate
4.5.1	Scaling up CO_2 ships	Must have	High	Shipping industry
4.5.1	Optimise design of ship and of offshore buffer storage (if any)	Must have	Low	Shipping industry
4.5.2	Loading/unloading facilities at ports for liquid CO_2 – confirm safe range of operation and build into design	Must have	High	Shipping and HC industries
4.5.3	Dry ice formation with impurities – range of specific lab studies	Must have	Low	Research and gases from air industry
4.5.5	Offshore unloading – ship to platform or to satellite in rough sea: mooring, flexible hoses	Must have	Very high	Shipping and HC industries
4.5.5	Offshore buffering, pre- injection heating, compression	Must have	Very high	HC industry and research
4.5.5	Understand impact intermittent injection on injection system	Must have	Very high	HC industry and research
4.5.6	Modelling and operating with transient flow in complex pipeline network	Must have	Low	Transfer from natural gas industry and liquid transport

5 CO_2 injection and storage technologies

5.1 Storage technology needs

The projected development of CCS, as described in Section 4.1 implies that large-scale storage is required to store the CO_2 from a wide range of capture projects. Similar to transport, benefits from economies of scale can be by obtained by linking several sinks of CO_2 in a network, ensuring continuity of storage capacity and decreasing the risk for capture facility operators. While today's one-on-one type of CCS projects represent the proving ground for CCS technologies, new developments will be required for the storage networks of the future.

Section 5.2 describes the set-up and performance of existing CCS projects, which have already proven CCS as a feasible and commercially available technology. Section 5.3 discusses the potential to develop current CCS technologies, to match the needs of future CCS infrastructures.

5.2 Performance of existing (and planned) storage projects

The IPCC Special report on CO_2 capture and storage [21] already stated that CO_2 injection and storage technology largely thrives on the experience built up from oil and gas exploitation, including long experience with natural gas storage and with injection of CO_2 for enhancing the recovery of oil. The IPCC report refers to two large-scale CO_2 storage projects offshore, in the North Sea and the Barents Sea and one onshore, in Algeria, demonstrating that CO_2 storage technology is available. Since the 2005 IPCC report, several new projects have provided additional evidence of the operational status of CCS as emission reduction technology [3]. Next to the Sleipner and Snøhvit projects several smaller scale transport and/or storage projects are or were operating in Europe. Some of their design and operational characteristics are listed in Table 5.1.

5.2.1 Dedicated CO_2 storage pilots and demos

The first large-scale CO_2 storage activity (TRL8), the offshore Sleipner CO_2 storage project, started injection in 1996 and is still ongoing offshore Norway. This commercial scale project with an annual storage volume of about 0.85 Mt, which is injected via one well, has the longest track record of CO_2 storage globally. In this project CO_2 is captured from the natural gas produced from the Sleipner gas reservoirs and is re-injected in a deep saline aquifer, the top of which is at a depth of 800 m. The reservoir properties are excellent with exceptionally high permeability-height (Kh – a measure of injectivity) and good pressure connectivity within the aquifer (see also Figure 5.1).

Two more large-scale CO_2 storage projects started up in 2004 in Algeria and in 2008 in the Barents Sea, known as the In Salah CO_2 storage (TRL9) and Snøhvit CO_2 storage projects (TRL8), respectively. In both projects, like in the Sleipner project, CO_2 is captured from the natural gas production stream and is re-injected in a deep saline aquifer. Predictable and reliable pressure management in aquifer storage structures is a critical requirement. For In Salah a configuration with three horizontal injection wells was chosen. After lowering the injection pressure in 2010, injection at In Salah was suspended in 2011 [64]. Injection at Snøhvit was originally into the Tubåen formation, halted when pressure built up faster than predicted. Injection was diverted into the Stø Formation from 2011. A second Stø Formation injection well is being evaluated. In November 2015 CO_2 injection operations started as part of the QUEST project in Canadian province Alberta. About 1 Mt CO_2 is to be injected annually through 3 wells in a deep saline aquifer (see also Figure 5.2).

Table 5.1 Overview of operational CO_2 transport and injection projects in Europe.

	OCAP (NL)	Ketzin (GE)	K12-B (Offshore NL)	Sleipner West (Offshore NO)	Snøhvit (Offshore NO)	Lacq (FR)
Operational	2005	2008	2004	1996	2008	2010
Source of CO_2	Shell/ Abengoa	Linde/ Schwarze Pumpe	Engie K12-B	Statoil Sleipner	Statoil/ Snøhvit/ Melkoya	Total/Gas oxycom-bustion
Compression at source	Yes	N/A	N/A	N/A	Yes	Yes
Pipeline inlet pressure (bar)	20	N/A	N/A	N/A	150-210	27
Pipeline inlet temp (°C)	Ambient	N/A	N/A	N/A	Liquid	-
Distance (km)	85	0	0	0	153	27
Flow rate kT/yr	400	15	up to 20	1000	650	Up to 43
Cumulative CO_2 (kT)	~3000	67	100	>16000	>2000	51
Compression at site	N/A	Yes	Yes	Yes	No/choke	Yes
Wellhead pressure (bar)	N/A	60	50 - 55	~65	80-150?	>40
Wellhead temp (°C)	N/A	35	60 - 80	25	-	40
Injection well	N/A	Ktzi201	K12-B6	16/9-A-16	7121/4F-2H	RSE-1
Formation/Field	N/A	Stuttgart	Rotliegend	Utsira	was Tubaen now Sto	Mano/ Rousse
Storage depth (m)	N/A	640	3800	>800	2500	4500
Info	OCAP	KETZIN	K12-B	SLEIPNER	SNOHVIT SNOHVIT2	LACQ
Reference	[500]	[62]	[501]	[510]	[510, 511]	[63]

A few more large-scale storage projects are expected to be on stream in the next two years. The Illinois Industrial CCS project in the USA is planned to be on stream early 2016 and will inject on

average 1 Mt CO_2 per annum in a deep saline aquifer. This storage project is a scaled up version of the large pilot injection in the Illinois Basin Decatur Project. This pilot started in 2011 and has injected more than 1 Mt by the end of 2014. A major step forward in scaling up will be the Gorgon CO_2 Injection Project which is expected to start up in 2017. 3.4 to 4 Mt of CO_2 is captured annually from a gas production stream and will be injected via 8 to 9 wells in a deep saline aquifer under Barrow Island off the coast of Australia. Next to the injection wells three pressure management production wells have been planned.

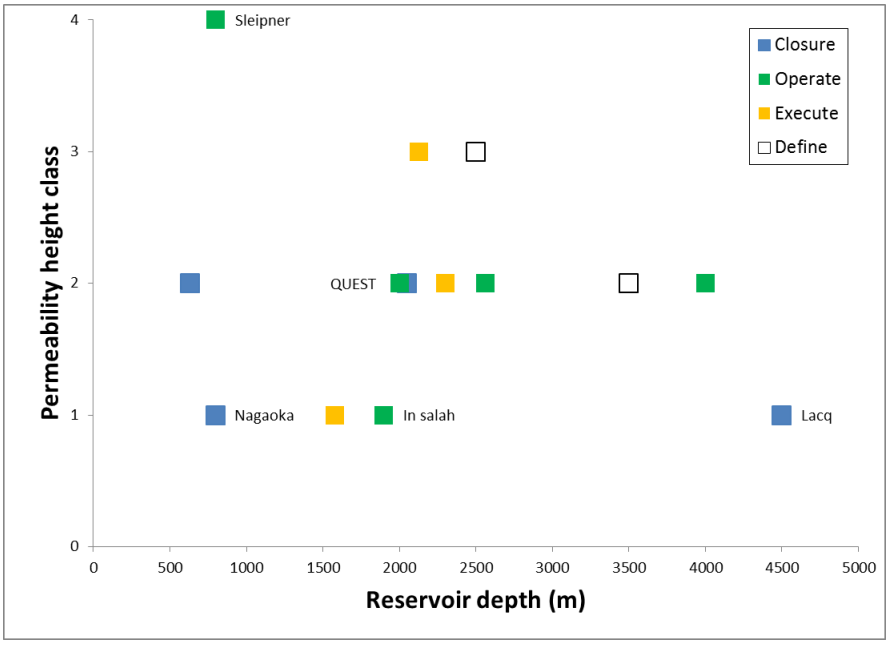

Figure 5.1 Depth of reservoirs versus reservoir permeability-height (k·h) for selected storage pilots and demos; k·h classes: 1 = Low (< 10^3 mD·m), 2 = Medium (10^3 – $5*10^4$ mD·m), 3 = High (> $5*10^4$ – 10^5 mD·m), 4 = Very high (> 10^5 mD·m) (see Appendix 2 for used data). Storage projects cover a wide range of values of permeability-height (which is a measure of the injectivity of the reservoir).

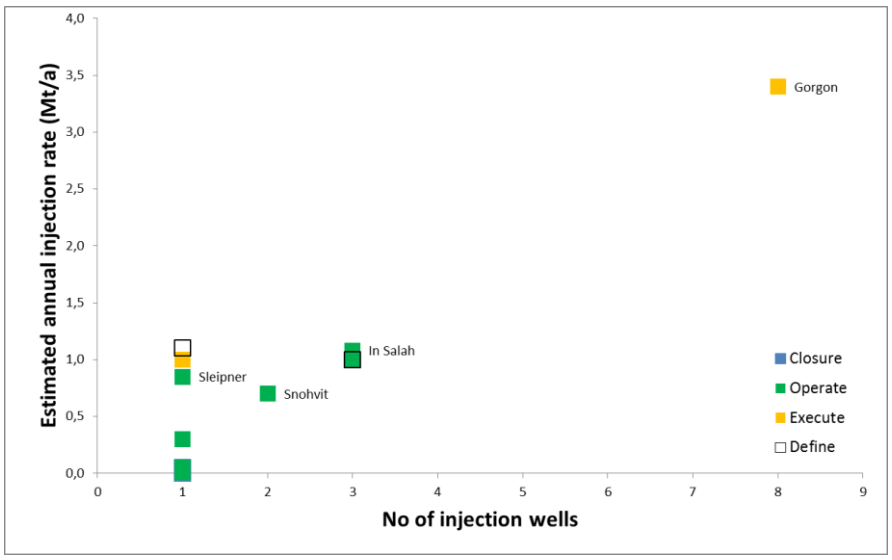

Figure 5.2 Relation between number of wells and estimated annual injection rate for selected storage pilots and demos and their lifetime stage in 2015 (see Appendix 2 for used data).

All of the mentioned large-scale dedicated CO_2 storage activities are in deep saline sandstone aquifers. Several pilot projects have been developed in other storage media, e.g. in depleted gas reservoirs in sandstone (K12-B [501]) and in carbonate rock (Lacq, [63, 502]), in a carbonate aquifer (Hontomin, [503]) and in basalt rocks (Carbfix-Sulfix projects and the Hellisheidi industrial project[38]). Storage in basalt is an emerging technology which is based on mineralisation of the injected CO_2. These pilot projects have TRLs between 5 and 7 (Table 2.2). A few pilot projects already have ceased injection and are now in the phase of evaluation before dismantling and abandonment, like the Ketzin Pilot project in Germany.

Storage costs are highly variable, depending on the type of reservoir, geographical location and re-use of well infrastructure [19, 20]. The ZEP study [19] showed that the costs of onshore storage range from 1 to 12 EUR/tCO2 whereas offshore storage costs vary between 2 and 20 EUR/tCO_2. More recent studies on storage costs onshore resulted in a smaller range of costs between 6 and 13 EUR/tCO2 [20].

The time taken to start storing in a reservoir from site characterisation to first injection will be at least 5 years and on average 10 years, each site appraisal requiring substantial investment partly depending on available legacy data (e.g., SiteChar, 2011). Depleted oil and gas fields may have shorter lead times because of the existing data from HC exploitation. On the other hand legacy wells may need more attention to ensure integrity. A study for the UK offshore showed that the lead time from identification to FID could be reduced to 2 to 4 years for storage prospects with a high level of already existing information [504].

5.2.2 EOR projects

CO_2-EOR is a mature technology in the onshore USA since the mid-seventies, however it has been deployed and operated with a focus on hydrocarbon extraction not CO_2 storage. CO_2-EOR is also deployed in Eastern Europe and Turkey. CO_2 is injected to mobilise remaining oil by reducing viscosity and changing relative permeability. The CO_2 will break through at production wells and is produced with the oil, separated and reinjected. Natural gas produced with the oil and CO2 may be separated and then used as fuel or sold provided the concentration and volume are large enough, otherwise it is reinjected with the CO_2. Onshore CO_2-EOR involves a large number of wells, kilometres of flow lines and significant processing equipment for the treatment of produced fluids.

Studies have shown that over the project's lifetime, CO_2-EOR operations store about 90% of the acquired CO_2 [505, 506]. seldom release CO_2 from their facilities or wells. Operating EOR projects provide an opportunity to develop monitoring programmes that verify CO_2 storage [e.g. 507]. In the USA two of the DOE partnerships are now studying EOR projects as if they were dedicated CO_2 storage projects in saline aquifers and they are providing the evidence to show that emissions have not occurred. Also the Weyburn project in Canada has undergone an extensive storage demonstration programme [e.g. 508].

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[38] See, for the Carbfix-Sulfix and Hellisheidi projects, see http://www.globalccsinstitute.com/sites/www.globalccsinstitute.com/files/content/page/122975/files/The CarbFix-SulFix Project.pdf

Some differences between CO_2-EOR and aquifer storage mean that monitoring techniques need to be modified and adapted. Storing CO_2 will always equate to waste disposal and costs will need to be minimised. Learning from CO_2-EOR operations has the potential to drive cost reduction in CCS. In the North Sea CO_2-EOR can act as a springboard for the deployment of CCS by providing investment in infrastructure which can be re-used or co-used for CO_2 storage.

5.2.3 Summary

The development of a wide range of CCS projects proves that CCS technology is available. In principle, no technology development is necessary, as solutions exist for the entire CCS chain of capture, transport and storage. Technology development is currently ongoing, through the same CCS projects, as operational issues are encountered and solved, and as new solutions are deployed and proven. New projects help to bring down costs through learning and knowledge sharing.

This is the main conclusion from the overview of current projects: CCS is an available and proven technology. However, to meet the needs of future, large-scale capture, transport and storage operations that connect multiple capture plants with large-scale storage reservoirs or clusters of reservoirs, new solutions will be required. The next section discusses those needs and the developments needed.

5.3 Development potential for injection and storage technology

Even though injection and storage technology for CO_2 stored in aquifers and oil reservoirs for EOR is proven, technology improvements are required to apply the technology on a large scale, to reduce the cost and to making the processes more efficient.

The first generation of storage systems are characterised by point-to-point projects developed using conservative assumptions and oil industry technologies. The scale is small from a commercial point of view, generally less than 50 Mt CO_2 stored. Follow-on capture projects will include both power and industry emission sources. In a power market that will increasingly be dominated by renewable energy sources, CO_2 supply from fossil-fueled power is expected to be strongly intermittent; industry-based CO_2 supply will also have varying rates, depending on the industrial sector. When applied at large scale, storage technology will be applied in networks of linked storage sites and will have to be able to deal with intermittent supply of CO_2.

The following sections address potential technology development to meet the needs of future large-scale, linked storage and storage networks.

5.3.1 Storage portfolio management

Whilst investigations by a number of countries around the North Sea, e.g UK[39], Norway[40] and the Netherlands[41] indicate that abundant storage is available, efficient exploitation of this theoretical pore space will require site investigations to be undertaken in a timely manner to ensure the stores

[39] See http://www.co2stored.co.uk/home/index.
[40] See http://www.npd.no/Global/Norsk/3-Publikasjoner/Rapporter/PDF/CO2-ATLAS-lav.pdf.
[41] See http://www.globalccsinstitute.com/sites/www.globalccsinstitute.com/files/publications/35621/independent-assessment-high-capacity-offshore-co2-storage-options-opt.pdf.

are available when needed. The time from the start of appraisal of individual storage sites and first injection is in the range of five to ten years; the recent study of the development of five potential storage sites offshore UK also came to this conclusion.[42] The long development time of operational storage reservoirs suggests that some de-risking (testing, permitting) of storage reservoirs is needed to promote the development of CO_2 capture and transport projects. **Pre-commercial characterisation of effective storage capacity and of sustainable injection rates** is crucial for wider deployment of CCS following the first demonstration projects, as already suggested [e.g. 509].

In the case of depleted hydrocarbon reservoirs the available information and knowledge from the production period provides the basis for storage appraisal. In the case of large virgin saline aquifers, storage appraisal is not fully possible due to the extensive properties of storage (compared to the intensive properties of oil). In hydrocarbon deposits the size of the accumulation is appraised by drilling wells which are also required for the extraction of the hydrocarbons. For CO_2 storage in saline aquifers it is necessary to understand the connectivity within the store over long distances, however cost constraints preclude the drilling of many wells during evaluation/appraisal (huge up front cost). Technological developments, potentially redeploying techniques from groundwater reconnaissance and other similar subsurface activities, have the potential to reduce the cost of appraising storage capacity.

The capacity of a CO_2 store often relies on understanding the connectivity over long distances and the related pressure build-up: the CO_2 might eventually only occupy 1% of the pressure-affected pore space (see, e.g., IEAGHG, 2014). In this case the appraised storage pore space needs to be 100 times the volume of the CO_2 to be injected. The areal extent of a saline storage aquifer might be many times larger than the areal extent of even the largest known hydrocarbons reservoirs.

Therefore, for saline aquifers in particular, technologies are needed for the **management of large areal extent aquifers** and stacked reservoirs to ensure their optimal use as a strategic resource both for individual MS and for Europe as a whole. In some large areal extent formations further optimisation is possible through development of integrated injection schemes across multiple injection locations. Aquifers will cross boundaries and thus subjected to different regulatory regimes, ownerships and liabilities. In short, experience should be gained with **developing and using saline formations for CO_2 storage**, as these hold the largest storage capacity in Europe [65].

Additionally, the optimal time to use a depleted pressure hydrocarbon field is at the end of production or earlier where enhanced hydrocarbon production might be utilised. At this point knowledge of the field behaviour is at a maximum and infrastructure that may be converted for CO_2 injection is available. However, once a field has ceased production it is likely that infrastructure will be quickly decommissioned and wells plugged, reducing the opportunity for CO_2 storage at reduced costs. This requires defining **cost-efficient ways of mothballing wells and facilities**, maintaining their capacity for future re-use.

[42] See http://www.eti.co.uk/project/strategic-uk-ccs-storage-appraisal.

5.3.2 Drilling, completing and operating wells

Well drilling and completion technology is the most important cost driver in the offshore oil and gas industry. Increased subsurface understanding with integration of multiple disciplines and real time data support is key to secure best possible drainage strategy and for optimised well construction.

The key will be **to develop low cost drilling techniques** to step out from a location adding additional wells and subsea/surface manifolds/well pads plus water extraction on an as needed basis. Here the experience in the oil and gas industry with identifying HC prospects and developing them in a portfolio of producing HC fields will be of great use. Innovative drilling technologies such as steerable casing and liner drilling solutions and managed pressure drilling (MPD) are being introduced for the extension of the drilling envelope. Revolutionary technologies such as "fishbones" or multi-laterals installed as an integrated part of the bottom hole design have been developed to increase the drainage area in tight formations.

If CO_2 is being injected into a low pressure environment, like a depleted pressure reservoir, CO_2 injection cools well tubulars and annulus fluids [66]. In addition if a well is allowed to back flow, or when CO_2 is produced with enhanced production of oil, CO_2 expansion can cause significant cooling at surface. Most oil and gas field equipment has been designed with high temperatures in mind – as a result there is R&D potential to extend the operating envelope and improve current equipment to sustain lower temperatures for specified time intervals and activities. Specific research is needed in order to design **injection wells serving low pressure reservoirs**.

Transported and injected CO_2 will need as much water to be removed as practically possible to minimise corrosion. Most projects are likely to use corrosion resistant steel but this will increase the capital cost of the project. Seals at valves and joints will need specific materials. One specific area is the well bottom hole casing materials in contact with brine/ CO_2 and other chemicals and materials in the formation. Another technology development area is specific CO_2 well tubular materials where the industry can build on the extensive knowledge in the O&G industry and the CO_2 EOR industry. Material research is required to **expand the operational envelope of well completions for CO_2 injection**.

Well plugging and abandonment (P&A) of offshore wells has been conducted for many decades but is always a hot topic for the industry and new technologies are being developed for more cost efficient operations. The Norwegian Oil and Gas Association has developed a roadmap for new P&A technologies which include drillpipe conveyed tools for optimised casing milling and rigless solutions for offline well work with use of wireline and coiled tubing. Examples are optimised perforation, well washing and cementing technologies to avoid pulling or milling of tubulars. Improved verification and logging methods for well diagnostics are also under constant development. Alternatives to cement for annular isolation such as creeping shale are being investigated. High energy solutions for melting downhole components and tubulars to effectively create a volcanic type rock as a well barrier are being studied. CO_2 storage RTD on plugging and abandonment should line up with programmes for the oil and gas industry.

The Snøhvit project is thought to have experienced halite precipitation blocking the pores in the Tubåen formation. This was countered by injection of a water based fluid. Testing of well productivity by water injection has the potential to damage the formation – clays can swell blocking

the pores. CO_2 has the ability to swell certain types of clay. Hence specific research is required to evaluate each potential storage reservoir.

5.3.3 Pressure management for increasing capacity and injectivity

CO_2 injection can be divided into 1) saline formation injection or CO_2 injection for EOR where the pressures may be increased above initial formation pressure and 2) depleted pressure fields where the initial storage pressures are below that of the adjacent water saturated formation, but pressures steadily rise as CO_2 is injected. The common theme here is that CO_2 creates an increase in subsurface pressure in the storage zone; ultimately, the storage capacity is limited by pressure limits dictated by safety of storage in the reservoir.

In the case of saline aquifer storage using water production wells in order to manage pressures and minimise formation pressure increase may lead to better exploitation of the theoretically available pore space and, hence, lower overall storage cost. In CO_2 EOR and CO_2 storage with water extraction like in the Gorgon CCS project[43] the areal size of the pressure plume is constrained or controlled by water/oil extraction. In saline aquifer storage (like in Quest, and Sleipner) without water production wells the pressure plume is only constrained by the geology and selection of an aquifer with a large areal extent will lead to a small or negligible pressure increase.

The deployment of water extraction wells opens up questions related to (i) development of strategies for the location and operation of water production wells, (ii) preventing breakthrough of CO_2 at the water production wells, (iii) monitoring of produced water qualities (iv) The disposal or cost-effective treatment of the produced water and potential re-use [67]. Finding the optimum configuration of injection wells and production wells (if any) is likely to be strongly case specific.

The common theme in the above is subsurface **pressure management**. Research is needed to operate in large extent storage formation and to manage clustered storage sites.

5.3.4 Low-cost monitoring and mitigation technology

Monitoring is a regulatory and operational requirement to demonstrate that an injection operation is performing appropriately and that there is no evidence of significant irregularities that might lead to the need to make changes in operation or take remedial actions. Many of the technologies used in CO_2 storage to establish baseline conditions (which may themselves evolve during the lifetime of the project) are mature and benefit greatly from continuous development in other sectors, notably the oil and gas industries. A large body of evidence has now been obtained from several key storage demonstrations of the wide portfolio of technologies available to monitor storage site performance. The applications of these technologies are described in detail in IEAGHG's monitoring selection tool (available online[44]). However, storage operation will benefit from greater experience of optimal and efficient integration of a selection of the most appropriate tools in future projects.

Current CCS projects deploy oil field technology, such as time-lapse seismic surveys and pressure and temperature monitoring. The In Salah project showed how satellite interferometry can be used to

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[43] See, e.g., https://www.globalccsinstitute.com/projects/gorgon-carbon-dioxide-injection-project.
[44] http://ieaghg.org/ccs-resources/monitoring-selection-tool1.

monitor the CO_2 plume (see, e.g., [64]). **There is large potential for cross over, learning and co-development from many other fields in monitoring technology to construct site-specific monitoring systems.** Recently, the first CO_2 storage permit obtained under the EU CCS Directive proved that a monitoring system using current technology can be relatively simple [68].

Another key aspect for the improvement of monitoring technology lies in **minimising the impact on stakeholders.** Oil and gas technology – such as 3D seismic surveying – is often very intrusive onshore. For example vibroseis necessitates the driving of trucks across the country side, through fields and crops. This is potentially acceptable for hydrocarbon exploration where it happens once – to locate the fossil hydrocarbons– but for CCS in aquifers this is required multiple times as the CO_2 plume expands. New techniques such as continuous source seismic (being piloted in Japan and Canada[45]) have the ability to increase the frequency and extent of seismic data collection (especially when coupled with permanent fibre-optic distributed acoustic sensors) while also dramatically reducing the stakeholder impact.

Monitoring groundwater quality is a mature technology and can be automated at low cost. Similarly, whilst techniques for monitoring atmospheric CO_2 concentrations are relatively mature, further technological developments are needed to **develop efficient low-cost integrated monitoring systems that can track CO_2 migration in the shallow subsurface and quantify the rate of atmospheric emissions** in the unlikely situation of CO_2 leakage. Technologies for detection of elevated atmospheric CO_2 concentrations include eddy covariance, laser-based atmospheric CO_2 concentrations, permanent monitoring of soil gas compositions and fluxes, which have been demonstrated as being useful at a number of pilot sites but would require further improvements in terms of efficiency, robustness and integration for wider deployment [69]. However, these techniques have no application offshore. Improvements in monitoring efficiency can also be found in dedicated, 'on-demand' monitoring [70], that measures discriminating characteristics of CO_2 seeping into or out of the near-surface zone to prove its origin.

Monitoring technologies have been demonstrated in a number of large scale demonstration projects globally to be effective at the detection of CO_2 in a range of storage types such as saline formations and operating and depleted hydrocarbon fields. Nevertheless, **opportunities still exist to reduce costs, improve detection limits and resolutions**, particularly through the use of permanent installations on the seabed or down well. Conceptually, detection of CO_2 escape at the seabed can be considered easier than at the surface onshore since natural variations underwater are not as large. The use of mature technologies such as sonar and multi-beam systems for bubble detection require further demonstration of their applicability in a range of credible leakage scenarios. Similarly, whilst the use of AUVs offers significant potential for the detection of CO_2 leakage in seawater columns, further demonstration under prolonged operation in the North Sea is needed. Other permanently installed monitoring technologies should also be tested to develop low-cost but robust offshore leakage quantification technologies. Quantification of the flux of CO_2 from a leak still requires further technological development and demonstration. Technologies for the detection of proxy or pre-cursor indicators of leakage (including novel tracers and displaced fluids) should also be

[45] See http://rmc.usc.edu/assets/002/96013.pdf.

demonstrated. Most of these techniques can only be effective if they can detect against often naturally highly variable background fluctuations [70], A research challenge is to develop monitoring techniques which do not require extensive measurement of natural background fluctuations, viz. t find indicators which are unique to the injected CO2 stream.

A promising approach is to develop advanced methods for time lapse seismic acquisition and potentially the development of **combined techniques** such as seismic and gravity or seismic and controlled source electromagnetics (CSEM). IEAGHG [69] also suggest that the improvements in monitoring are to be found in combining individual techniques.

Recent developments, as shown by the Shell Quest commercial scale project in Canada, which is injecting over 3,000 tonnes per day, include fibre optic sensing down the whole length of the well and line-of-sight surface CO_2 detection using laser absorption[46]. The technologies employed by Quest have further development potential, for example the sensitivity of optical fibres for seismic acquisition is increasing rapidly. In time it should be possible to use these for micro-seismic detection as well as vertical seismic profiles. Quest has a suite of MMV technologies for demonstration from which future projects can select the most effective and efficient to satisfy their MMV requirements[47].

As with monitoring technologies, mitigation technologies can be applied from other sectors, most particularly from the oil and gas production industry. Here well workover technologies are continuously improving from which future CO_2 storage operations will naturally benefit. Future technology development can be expected in the areas of plume steering and management of 'thief' zones and high permeability zones to control migration. A particular area of future technology development is the optimisation of trapping mechanisms and the potential for reducing reservoir permeabilities in locations where this might be needed. An overview of mitigation techniques can be found in Gerdes [71], while Steeghs *et al.* [68] describe the corrective measures (mitigation) plan that is part of the P18-4 storage permit, mentioned above.

A well with a leak of CO_2 can benefit from the technologies used in oil and gas to fix a blowout, such as relief wells. There is potential for less invasive techniques like the injection of calcite precipitating microbes.

The closure of a CO_2 site and the subsequent monitoring period before transfer of responsibility to the competent authority depends on a thorough understanding of the storage performance. The techniques for closure at present are adopted from the oil and gas industry. Better understanding of the risk can lead to a shortening of the post closure periods – reducing the exposure of operators and hence the cost of "insurance" or "liability provision". Cost effective methods of closing wells permanently and also of monitoring post closure will also reduce the unit cost of storage; examples of the former include natural sealing techniques, which use, for example, subsurface salt or clay layers to permanently close the well bore.

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[46] See http://www.energy.alberta.ca/CCS/pdfs/CCSQuestReport2014.pdf.
[47] Information available at http://www.energy.alberta.ca/CCS/3848.asp.

5.3.5 Reducing costs and footprint of installations

CO_2 pipelines and CO_2 injection installations differ markedly from a hydrocarbon production facility. When hydrocarbons are produced oil, gas and water have to be separated. Because of this all the monitoring equipment has been designed to work on large manned facilities. The monitoring equipment is a small portion of the total cost.

When CO_2 is injected for EOR this means additional equipment on old oil production platforms to handle the injection wells, compression, distribution and more separation equipment to remove any produced CO_2 for reinjection. Much of the old production system will need to be replaced with corrosion resistant material. To address the issue of limited space on existing platforms for new equipment, work is underway in Norway in developing and demonstrating subsea compression and gas separation systems.

When dry CO_2 is injected in an aquifer structure the range of equipment required, new wells, compression, distribution, monitoring, measuring is likely to be much less than for a hydrocarbon facility for EOR. There may be a desire to make most or even all facilities normally unmanned, which further reduces the technical scope of the facilities. Monitoring equipment may make up a larger proportion of the total cost. If water production wells are required for pressure management more well slots will be needed and equipment to detect CO_2 in the produced water, but provided the water does not need treatment and can by dumped to the sea, the complexity of the installation is minimal.

When dry CO_2 is injected into depleted pressure fields, the original platforms and wells may be available for use and the deck space may be adequate for the incremental equipment required. In some cases compression and CO_2 heating may not be required, depending mainly on the injection temperature, the injection rate required, the number of wells and the final reservoir pressure desired and the reservoir depth.

Subsea wellheads for injection wells will also reduce the complexity of the offshore facilities, although well entry requires a rig which may limit the opportunity for several monitoring techniques to be employed. **The challenge for CCS is to reduce operational cost of CO_2 storage facilities:** develop minimal facilities, preferably unmanned, which could lead to lower operating cost, compared to Oil and Gas industry facilities.

5.3.6 Need for flexibility of CO_2 throughput

The key question is where to build capacity and redundancy into a system, which copes with volatility in supply and demand for CO_2. For example, should the storage have 100% availability in order to ensure that a connected power plant can always export CO_2 and sell clean electricity? How much does this additional capacity cost – potentially requiring networked storage across more than one site? Is it better for the power plant to either stop generating or potentially emit CO_2 for a short period? What delivers the lower system cost and how should commercial agreements and grid supply rules be structured so that additional cost can be driven out of the system? And how can these agreements evolve as a network grows and the consequence of interruption of a single source or sink has less effect on the whole?

Injection wells can, in general, take varying flow rates – from very low to a physical maximum, often dictated by the onset of strong vibrations. At times a relatively low injection rate is enforced because

of the high degree of Joule-Thompson cooling of the injected CO_2. Strong intermittency, for example system shut-ins on a daily basis, might lead to concerns about expansion and contraction on the injection tubing, on the casing, and on the cement bonds between the casing and the rock formation. Owing to the high cost of offshore well interventions operators take a conservative approach and try to minimise on/off cycles. **Research into the effects on the well construction of intermittent injection** could inform operators of the reliability envelope and has the potential to increase the ability of a single point-to-point system to adapt to changing rates.

For subsea equipment, the foreseen operating pressures and temperatures of CO_2 injection wells are within the range of current systems. Still, it is likely that some technical modifications will be required, to be able to handle the CO_2 stream. For intermittent injection with a large number of cycles, additional development may be required in order to ensure reliability of subsea installations. Valves, which would be operated for a higher number of cycles compared to during typical oil and gas service, may require some development.

Some types of storage system are more likely to experience down time than others. In general the more complex the system the more likely it is to trip or to require maintenance. As a result an EOR storage system might suffer more down time than an aquifer storage system with continuous supply of CO_2.

How to manage daily fluctuations from practices like 'two shifting' operating regimes have also been discussed and elements like buffer CO_2 tanks, or rich amine tanks debated. At this point in the development of the industry such measures are probably immature. The moment a power station has more than one unit on capture, or two or more emissions sources are captured, the ability exists to alter commercial constructs to allow operators to manage the CO_2 export to all but eliminate periods of zero flow – rather going from low flow to high flow. This removes the need for additional infrastructure.

There is an opportunity for research into identifying the best or complementary combinations of captured emission sources and how to manage these to create the lowest cost of capture, transportation and storage infrastructure – taking full cognisance of the external constraints like wind power variability, cement plant work practices, and even public holidays or extreme weather conditions.

Currently the performance of well construction materials is not tested under daily thermal cycling. First generation projects are assuming steady injection. Materials science research can extend the operating envelopes of well materials and increase the responsiveness of storage systems.

5.3.7 Summary of development potential

For storage the question is mainly of an economic nature rather than technical, however there are several areas where further developments are required to prepare for future, large-scale storage, as well as for the transition period between demonstration and large-scale deployment of CCS.

Portfolio management

- Support pre-commercial storage appraisal
- Develop storage sites in saline formations
- Develop mothballing strategies for depleted hydrocarbon fields

Wells

- Develop and deploy lower-cost drilling technologies
- Investigate the impact of intermittent flow on the well system
- Develop dedicated well abandonment technology

Pressure management

- Develop a knowledge base on subsurface pressure management

Monitoring and mitigation technology

- Develop strategies leading to lower-cost, integrated monitoring systems
- Improve leakage detection and quantification of monitoring techniques

Cost reduction

- Reduce operational costs CO_2 storage sites
- For offshore sites, develop and test subsea technology

Flexibility of storage

- Develop approaches to ensure flexibility of storage

5.4 Discussion and summary

The discussion in the previous sections show that there is a need for further developments in the area of storage, to progress from the current demonstration phase into the transition to large-scale deployment of CCS.

Table 5.2 provides a summary of the main technology improvements for CO_2 injection and storage which have been brought forward in this report. They are grouped in two main categories: technology improvements for existing storage media and a smaller group with development of novel CO_2 storage media. The impact of each development for cost reduction, improving conformance and safety and expansion of the storage portfolio has been indicated. Also involved technology customer and providers have been mentioned.

Table 5.2 Improving technology for CO2 injection and storage; Category (i) Cost, Conformance, Confidence and Safety of existing storage media and Category (ii) Expansion of the range of storage options with novel storage media. Low investment = 106-107 EUR; High investment = 108-109 EUR

Area of main impact	Technology development	Cross reference	Investment need	Main actor(s) Buyer/provider
Improving performance for current CO_2 storage media				
Cost, Confidence	Improve well construction materials for low temperatures, different fluids & dynamic loading		Low-High	HC well service Co/ material research
Cost, Conformance	Improved metering technology for CO_2 mixtures and CO_2 mass balance, e.g. for EOR	5.3.4	Low	Oil OPCo, service Co
Cost, Confidence	Improve (transient) fluid dynamic modelling of CO_2 mixtures, e.g. for low T & well backflow		Low	Storage OPCo/ flow modelling research
Expansion, Confidence	Modelling and management of water extraction aquifers	5.3.3	Low-high	Flow modelling & water treatment research
Expansion	Regional characterisation of aquifer injectivity & management of multi user storage formations under acceptable overpressure constraints	5.3.3	High	OPCo, storage org, geoscience & modelling
Expansion, Cost, Confidence	Governance and financing of multi-store locations, e.g. evolution, time-variable CO_2 streams, liability, CCS chain and risk profile		Low	EU & MS regulators/ economics & business school research
Cost, Confidence, Safety	Improvement of well drilling ('smart drilling') & intervention, e.g. offshore CO_2 cooling effects dissolution into elastomers		Low	OPCo, drilling service Co; synergy with HC exploitation and mining / drill rig simulator research
Cost, Conformance, Expansion	Improvement of marine environmental monitoring, e.g. sensors, autonomous under water vehicles for seabed profiling & characterization of natural fluxes		Low	OPCo, storage org/ environmental research
Cost, Confidence, Conformance, Expansion	Development of wireless long term pressure monitoring in plugged wells		High	OPCo, storage org, well service Co/ technical research

Cost, Expansion, Conformance, Confidence	Improvement of (spatial seismic) monitoring and data transmission techniques, e.g. lower cost, less intrusive and higher detectability of microseismics		Low-High	OPCo, storage org, geophysical service Co; synergy with HC exploitation / geophysical research
Confidence, Expansion	Improved modelling, characterization & management of microseismic risk, e.g. understanding fault behaviour		Low	OPCo, storage org; synergy with HC exploitation/ geomechanical and geoscientific research
Cost, Conformance	Field trials of CO_2 tracer injection – especially noble isotopes of Xe		Low	OPCo, well service Co/ fluid dynamic modelling research
Cost, Expansion	Improved well leakage assessment, monitoring & management – e.g. shale squeeze & legacy wells		High	OPCo, storage org/regulatory bodies/ well and geoscientific R&D
Cost, Expansion	Governance and financing of mothballing HC wells and installations	5.3.1	Low	Mining authorities
Conformance, Confidence	Improving well plugging and abandonment, e.g. securing annular isolation	5.3.1	Low	Synergy with HC exploitation
Cost, Expansion	Minimizing compression costs for aquifers and EOR, e.g. offshore		Low	Synergy with HC exploitation
Developing novel CO_2 storage media				
Expansion	Shale storage – including pilots		High	
Expansion	Basalt storage pilots		High	
Expansion	Formations with non-standard caprocks – e.g. multiple baffles		Low	

6 Conclusions & Recommendations

CCS is known to be important in most UNEP scenarios targeting 2 °C and essential in scenarios with long term targets of 1.5 °C as agreed in COP 21. In such scenarios, CCS is expected to compete and co-exist with other low carbon technology options in the power generation sector. In addition, about a quarter of global emissions stems from energy-intensive industries like steel, cement, refineries and other industrial sectors. These industries may be unable to reduce significantly their GHG emissions within the next 2-3 decades without CCS. Non-fossil alternatives are not yet commercially available and newly developing processes have to be brought in line with the lifecycle of the existing assets in order to prevent additional economic burden.

The assessment of future CCS technologies carried out in this report has embraced not only the changing market conditions for fossil power plants caused by an increasing share of intermittent renewable power, but also the emerging importance of CCS for non-power industries. Furthermore, the assessment criteria of CCS technologies has been deliberately enlarged beyond typical cost and efficiency criteria to incorporate in qualitative form key factors like operational flexibility, retrofitability, HSE issues, materials availability, etc., that will determine the economic viability and acceptability of the different process options in a future CCS technology market.

As far as transport and storage is concerned, requirements for improvement of currently available technologies and, where the need was identified, the development of new technologies were derived from the projected growth of CCS. This growth will lead from current demonstration and early commercial projects that can be typified as one-on-one projects, to increasingly interconnected transport and storage systems, in which economies of scale are obtained by sharing transport and storage structures.

Although this assessment of technology prospects and status has only been done qualitatively, it allowed us to highlight many common R&D priority areas for the coming years, as described below.

6.1 CO_2 capture

6.1.1 R&D Challenges & recommendations for CO_2 capture

Conclusions following the assessment of emerging capture technologies are listed below. New power cycles or enabling technologies to the power or industrial sectors have been left out of the scope of this report.

- To enable quantitative, more precise cost and performance assessments of emerging capture technologies, it is important that these reach a sufficiently credible pilot scale testing at TRL level 5-7.
- Capture technologies which have already achieved high TRL levels under certain boundary conditions, e.g. for power applications, cannot necessarily be classified with the same TRL under different boundary conditions, or for other industrial applications. However, it should be possible to build on existing pilot infrastructures experience and quickly adapt them to new, modified boundary conditions of different industrial sectors.
- Technology improvements arising from R&D efforts need to be assessed on system (plant) level, rather than focusing on isolated improvements with uncertain impact on the overall efficiency penalty and cost of CCS.

- An open R&D challenge is the continuous development of new functional materials (solvents, sorbents, membranes, oxygen carriers for CLC) which:
    - are less sensitive to the most abundant impurities in flue or process gases, e.g., steam, SO_x, NO_x, and to degradation/attrition (decreasing OPEX),
    - could enable fast adsorption/absorption kinetics or transport (permeance, diffusion) to reduce residence time, allowing for more compact capture equipment (decreasing CAPEX).
- Many new materials show apparently good results in CO_2 separation on a lab scale. Testing under real process conditions, real flue gas conditions and compositions should be a R&D priority to confirm the actual potential of such materials, e.g. testing of capture technologies in steam free environment is artificial.
- R&D efforts should aim at fast up-scaling of promising lab-scale capture technologies (TRL<3), in order to speed up their development and avoid stagnation on low TRL status. For example, many new materials are synthesized in labs and lack any commercial supply chain which makes their up-scaling costly.
- The types of application and fuel (coal or biomass vs natural gas) is known to favour some capture technologies with respect to others, for both power generation and industrial systems. Despite a recent shift in interest towards natural gas in some regions, emerging technologies for solid fuels should remain in the portfolio of R&D priorities, as the CO_2 capture technology market is of global nature.
- Current solvent based capture processes are commercially available but there is a substantial scope to reduce their relatively high cost and efficiency penalty. They also display limited operational flexibility, which is increasingly required by power plants today. The development of capture processes allowing for (higher) operational flexibility (load following operation) without additional cost is therefore a key R&D challenge, as is the adaption of the transport and storage elements of the CCS chain to higher operational flexibility (i.e., intermittent gas flow).
- Flexibility during operations of power plants is a major requirement that may alter substantially the viability of a particular CO_2 capture process. This has only recently been addressed for first-generation technologies. Therefore, much has to be learned by sustained R&D on how flexibility requirements will impact the efficiency and cost prospects of emerging CO_2 capture technologies. Synergies of CCS systems, hybrid systems of capture technologies currently classified in different generations, as well as combinations with energy storage concepts at wider system level need to be investigated.
- Finally, the sequence of generations in capture technologies is based on the assumption that first-generation technologies are deployed. The natural progression towards currently emerging technologies will only occur after the realisation of this deployment. Therefore, solving specific R&D challenges closely linked to large demonstration projects will remain an important R&D priority.

6.1.2 Benchmarking of emerging technologies for CO_2 capture

Table 3.3 compares in a qualitative way the various emerging capture technologies according to the different assessment criteria introduced in this report.

- Nearly all emerging capture technologies claim a reduction potential with respect to CAPEX required by first-generation capture technologies. The current status of many emerging capture technologies still includes too many uncertainties to come to quantitative and precise conclusions. Nevertheless, under this premise chemical looping shows currently the highest CAPEX reduction perspective.
- Technologies involving solid sorbents, looping processes and polymeric and metallic membranes show a legitimate potential to improve operational cost (OPEX) compared to first-generation solvents, due to the avoidance of co-evaporation of large amounts of water. Solvent alternatives currently being developed focus on the improvement of particular parts within the capture process that show disadvantages or trade-offs with other parts of the capture/plant process. Therefore, the anticipated improvements on overall plant level might be marginal and related to better process integration.
- With respect to process efficiency, most of the technologies assessed show potential for improvement. Quantitative assessments are difficult and the possible outcome ranges from "better than existing first-generation solvents" to "indifferent", thus equally good or bad (green/yellow colour in Table 3.3). Chemical looping appears most promising and polymeric membranes show potential, as they are already commercially applied in natural gas processing. Polymeric membranes might be a good alternative for natural gas or other clean flue gas post-combustion applications, eventually compromising on other process parameters, such as CO_2 capture rate; they could also be applied or in combination with other technologies (hybrid systems).
- Degradation of functional material appears to be a problem of almost all emerging technologies over time, with calcium looping being the only exception.
- Operational flexibility gained much importance in the power sector over the last years. Many gas and coal plants have to compensate for the intermittency of growing renewable electricity generation, stabilizing the grid and matching demand. This causes less annual operational hours, faster operational load change of power plants, including fast ramp-ups and shut downs. Hence, there is a need in the power sector for capture technologies that can follow load change at zero additional capture cost. Promising emerging capture technology in this regard are polymeric membranes and solid sorbent processes (VPSA, PSA), conditional to the integration of these technologies in the overall process configuration.
- With respect to HSE and waste disposal, solid sorbents, calcium looping and membranes have an advantage over current aqueous amine solvents. This is due to the volatility of amines that requires additional efforts/technical equipment to prevent amine emissions.
- Chemical looping cannot be retrofitted as it is a new concept substituting a boiler or gas turbine. Calcium looping, in contrast, is applied as post-combustion capture technology. Oxy-combustion related processes, such as oxy-ceramic membranes, require the recirculation of flue gas and are difficult or too complex to be integrated into existing configurations.
- Finally when it comes to availability, chemical looping as well as oxy-ceramic and metallic membranes might be the technologies that face the most critical challenges today.

6.2 Transport and Storage R&D challenges & recommendations

In contrast to capture technologies, transport and storage technologies rely to a high degree on commercially available equipment used in the oil and gas industry. Future development of transport and storage technology will mostly be of incremental nature, leading to improved performance

and/or lowered costs of existing technology. There are some exceptions, which relate to transport by ship and storage in basalts which are both at low TRL levels today and can be considered as emerging technologies.

6.2.1 CO_2 transport

Transport of CO_2 by pipeline.

- This is a well-established technology and is commercially available.
- Minor issues exist around the modelling of transient flow in pipelines, across platforms and into wells, especially to account for the effects of impurities in the CO_2. With recent developments in databases of physical CO_2 mixture properties, advancements are required in software that is capable of performing transient flow calculations.
- In more complex transport networks, the quality of CO_2 becomes a management issue, taking into account mixing of streams of different quality and maintaining control over the performance of the system. In principle, the knowledge about the relation between CO_2 quality and the behaviour of the CO_2 in the system is available.

Transport of CO_2 by ship.

- This is well established but for large-scale CCS ship transport needs to be scaled up. CO_2 carriers exist, but larger ships will be required; the same can be said about loading and unloading facilities at ports. Offloading offshore, near the injection location requires some technology development and demonstration, such as flexible hoses and mooring systems.
- Ship transport to offshore storage locations may lead to batch-wise injection. The effect of intermittent injection, with pressure and temperature cycling, on injection wells needs to be investigated. An on-site buffer storage could remove some of the intermittency.
- The design of CO_2 carriers and that of a possible buffer storage remains to be optimised and demonstrated; the optimisation relates to the location of and power source for facilities to condition the CO_2 prior to injection.

6.2.2 CO_2 storage

- The required operational flexibility holds for the whole CCS chain including CO_2 injection and storage, in particular in the early stages of CCS development from demonstration to early deployment where the dependence on single sources for a reliable continuous supply will dominate availability of CO_2. Systems analysis of the whole chain is necessary to evaluate where the capacity for flexibility is to be built most cost-effectively, e.g. flexible, cost-effective capture technology, in buffering and in networking to stabilize transport grid and storage load.
- Research including full-scale demonstration is required on expanding the operational envelope of injection wells and subsea equipment under repetitive cycles of pressure and temperature changes, particularly for injection into low pressure stores like depleted pressure gas fields.
- Approaches for effective storage portfolio management are necessary to efficiently exploit the available pore space, e.g. in large areal extent aquifers, to shorten the appraisal lead time and to timely expand the infrastructure for injection of CO_2 including mothballing of existing infrastructure.
- Sufficient storage capacity must be assured before investors can decide on financing CCS. A good starting point for tackling this research item is the work done for the UK sector [504].

- Pressure management for increasing the capacity and injectivity, e.g. by using water production wells; research is to be directed to strategies for water production, the breakthrough of CO_2 and water treatment. In 2016 US DoE has selected two projects on technologies for the production of usable water from CO_2 storage sites (EWR).[48]
- Lower-cost monitoring and mitigation technologies which are cheaper than current technologies from the oil and gas industry. Combined techniques such as seismic with gravity or seismic with controlled source electromagnetics (CSEM) with less impact on the earth's surface; for tracking CO_2 in the shallow subsurface and atmosphere and water need further development. Technology development should also be directed to less invasive leakage mitigation techniques and cost-effective methods for closing wells.

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Annex I

List of Commercially Available Solvent (Amine) for Post-Combustion CO_2 Capture

Table A.0.1 List of Commercially Available Solvent (Amine) for Post-Combustion CO_2 Capture

Developer	Solvent Name / Trademark	Types	Reported KPIs (based on coal PP - flue gas)	Comments	TRL
Aker Solution	Just Catch Process	Mix Amine		• Performance evaluated at TCM Mongstad (~250 TPD) pilot plant. • Mobile pilot plant test completed or on-going at NCCC (AL, USA), Brevik (Norway) and Klemenstrud (Norway). • Assessed in SSE's Longannet (UK), Norcem's Brevik (Norway), Enel's Porto Tolle (Italy) FEED study	7-8
Flour	Econamine FG+	MEA		• Licensed to several plants worldwide. • Significant operational experience in capturing CO_2 from GT flue gas (i.e. Bellingham CHP) • Performance evaluated at TEPCO's Kawasaki (~120 TPD), EOn's Wilhelmshaven (~70 TPD), ENEL's Federico II (~60 TPD) pilot plants, etc… • Assessed in the ROAD's Maasvlakte (Netherlands) FEED study	7-8

Developer	Solvent Name / Trademark	Types	Reported KPIs (based on coal PP - flue gas)	Comments	TRL
GE (Alstom)/Dow Chemicals	Advance Amine Process (AAP) based on Dow's UCARSOL FGC 3000 solvent	MEA/ Chilled ammonia	2.3 – 2.4 GJ/t[49]	• Development based on other Dow's solvent for CO_2 removal used in the NG processing industry. • Performance evaluated at EDF's La Havre (~25 TPD) pilot plant • Assessed in the PG&E's Belchatow (Poland) FEED study	7-8
Hitachi	H3 family of solvent	Mix Amine	H3-1 Solvent:[50] 2.5 -2.8 GJ/t	• Performance evaluated at Saskpower's Shand (120 TPD) pilot plant • Mobile pilot plant test completed or on-going at various Electrabel's and EOn's power plants in Europe (6 MWt slip stream).	7-8
HTC Pure Energy	Thermal-Kinetics Optimisation (TKO) CO_2 capture process based on RS Family of Solvent	Mix Amine	RS2 Solvent: ~2.4 GJ/t	• Based on University of Regina's solvent development programme using the pilot plant at Boundary Dam (now decommissioned). • Performance recently evaluated at SSE's Ferrybridge (~100 TPD) pilot plant • Assessed in the BEPC's Antelope (Dakota, USA) FEED study	7-8

[49] http://pennwell.sds06.websds.net//2014/cologne/pge/slideshows/T2S3O20-slides.pdf

[50] http://www.psa.mhps.com/supportingdocs/forbus/hpsa/technical_papers/Technology%20Option%20For%20Clean%20Coal%20Power%20Generation%20with%20CO2%20Capture.pdf

Developer	Solvent Name / Trademark	Types	Reported KPIs (based on coal PP - flue gas)	Comments	TRL
MHI	KM-CDR Process based on KS family of solvent	Hindered Amine	2.4 – 2.8 GJ/t	• Licensed to several plants worldwide. • Performance recently evaluated at TCM Mongstad (~250 TPD) and Plant Barry (~500 TPD) pilot plants. • Assessed in EOn's Kingsnorth (UK) FEED study • Plant under construction – NRG's WA Parish Petra Nova (TX, USA) Power Plant with flue gas slip stream - equivalent to 240MWe. Expected to be in service by 2017/2018.	8-9
Shell Cansolv	Cansolv Solvent based on DC103 / DC201 solvent	Tertiary Amine with Promoter	Design Basis for BD aims to achieve ~2.5 GJ/t[51]	• Capable of selective or sequential SOx, NOx and CO_2 removal • Performance recently evaluated at TCM Mongstad (~250 TPD), EOn's Heyden (~100 TPD), RWE's Aberthaw (~50 TPD) pilot plants • Assessed in the SSE's Peterhead (Scotland) FEED studies. • Large scale demonstration plant in operation – Saskpwer's Boundary Dam (Sask. Canada) – capturing CO_2 from flue gas of 110MWe lignite fired power plant	8-9

[51] http://www.platts.com/IM.Platts.Content/ProductsServices/ConferenceandEvents/2014/pc465/presentations/18DevinShaw_SHELLCANSOLV.pdf

Annex II

Data used in Figure 5.1 and Figure 5.2.

Project name (click on project name for link to full description)	Project lifecycle stage	Country	Operation start date	Status 2016	On-/offshore	Storage medium	Reservoir lithology	Reservoir depth (m)	Reservoir thickness (m)	Permeability (mD)	Permeability height*	No of injection wells	Estimated annual injection rate (Mt/a)	Injection volume (Mt)	TRL
Nagaoka CO2 Storage Project	(Post-)closure	JAPAN	2003	CEASED 2005	ON	SAQ	Sandstone	800	60	6	LOW	1	0,0050	10 kt	6
Carbfix & Sulffix CCS Pilot Project	(Post-)closure	ICELAND	2012	CEASED 2012	ON	MIN	Basalt	400	400			1	0,0003	0.3 kt	5
Lacq CCS Pilot Project	Closure	FRANCE	2010	CEASED 2013	ON	GAS	Carbonate	4500	130	5	LOW	1	0,0150	51 kt	7
Ketzin Pilot Project	Closure	GERMANY	2008	CEASED 2013	ON	SAQ	Sandstone	630	40	750	MEDIUM	1	0,0160	67 kt	7
CO2CRC Otway Project Stage 1	Closure	AUSTRALIA	2008	CEASED 2009	ON	GAS	Sandstone	2050	31	50-1600	MEDIUM	1	0,0500	65 kt	7
Don Valley Power Project	Define	UNITED KINGDOM	2020	FEASIBILITY	OFF	SAQ	Sandstone						1,5		9
Rotterdam Opslag en Afvang Demonstratieproject (ROAD)	Define	NETHERLANDS	2019-20	LICENSE	OFF	GAS	Sandstone	3500	24	207	MEDIUM	1	1,1000		9
Spectra Energy's Fort Nelson CCS Project	Define	CANADA	2019 (Institute estimate)	FEASIBILITY	ON	SAQ	Carbonate	2100					2,2		9
White Rose CCS Project	Define	UNITED KINGDOM	2020-21	FEED/ON HOLD	OFF	SAQ	Sandstone						2,0		9
Peterhead CCS Project	Define	UNITED KINGDOM	2019-20	FEED/ON HOLD	OFF	GAS	Sandstone	2500	82	790	HIGH	3	1,0000		9
Gorgon Carbon Dioxide Injection Project	Execute	AUSTRALIA	2017 (Institute estimate)	CONSTRUCT	ON	SAQ	Sandstone	2300	500	20-30/ 30-100	MEDIUM	8	3,4000		9
Illinois Industrial Carbon Capture and Storage Project	Execute	UNITED STATES	2016	CONSTRUCT	ON	SAQ	Sandstone	2130	300	225	HIGH	1	1,0000		9
CO2 Capture, Transport & Storage TDP	Execute	SPAIN		TESTING	ON	SAQ	Carbonate	1580	133-165	0.015-1.8	LOW	1		<100 kt	6
In Salah CO2 Storage	Operate	ALGERIA	2004	ON HOLD	ON	SAQ	Sandstone	1900	29	5	LOW	3	1,0000	3.8	9
Sleipner CO2 Storage Project	Operate	NORWAY	1996	ONGOING	OFF	SAQ	Sandstone	800	250	5000	VERY HIGH	1	0,8500	15.5	8
Snøhvit CO2 Storage Project	Operate	NORWAY	2008	ONGOING	OFF	SAQ	Sandstone	2560	60	450	MEDIUM	2	0,7000	3	8
Quest	Operate	CANADA	2015	ONGOING	ON	SAQ	Sandstone	2000	46	20-50	MEDIUM	3	1,0800		9
K12-B CO2 Injection Project	Operate	NETHERLANDS	2004	ONGOING	OFF	GAS	Sandstone	4000	350	20	MEDIUM	1	0,0100	90 kt	6
Illinois Basin Decatur Project	Operate	USA	2011	ONGOING	ON	SAQ	Sandstone	2130	300	225	HIGH	1	0,3000	1 Mt (2015)	8
Shenhua Group Ordos CCS Demonstration Project	Operate	CHINA	2011	ONGOING	ON	SAQ		2500				1	0,0500	155 kt (2013)	7
Hellisheidi industrial scale gas capture and injection project	Operate	ICELAND	2014	ONGOING	ON	MIN	Basalt						0.005		6