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Carbon Sequestration Leadership Forum SUPPORTING DEVELOPMENT OF 2ND AND 3RD GENERATION CARBON CAPTURE TECHNOLOGIES: Mapping technologies and relevant test facilities

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Executive summary

Results

This report describes efforts to identify emerging technologies $(2^{nd} \text{ and } 3^{rd} \text{ generation})$ for CO₂ capture and identify potential testing facilities that can help bring the technologies out of laboratoryand pilot-scale testing to demonstration-scale testing, i.e. capture rates in the order of 100 tonnes per day and more.

The study is based on a literature and web review of the status of emerging (2^{nd} and 3^{rd} generation) CO₂ capture technologies and existing test facilities. It was performed jointly by the CSLF Policy and Technical Groups. Neither the inventory of emerging technologies nor of test facilities can be regarded as complete.

Around 30 groups of 2^{nd} and 3^{rd} generation CO₂ capture technologies have been identified. Most are 3^{rd} generation, i.e. currently at Technology Readiness Level (TRL) 1 - 3(4) and must be classified as tested at laboratory- or bench-scale only. A minority is classified as 2^{nd} generation, i.e. currently at TRL 4(5) – 6. The results are summarized in Table 1 below.

In Table 1, the potential for energy consumption reductions vary from "very small" to "significant". However, it is important to note that the numbers are based on a literature survey and may not have been derived in a consistent manner. Furthermore, the technologies are at different levels of maturity, which will influence the uncertainties of the estimates. Factors that contribute to the uncertainties in energy consumption estimates include:

- Comparison to different baselines (old, new, unfavourable, etc. in addition to different; assumptions and battery limits);
- Discrepancies in reporting efficiency changes (% relative some baseline) or energy requirements (GJ/tonne CO₂);
- The relative value of electricity vs. thermal energy;
- $\circ~$ Discrepancies in converting the thermal energy required for CO₂ capture to useful work; and
- \circ Limited information and testing of emerging technologies.

Cost reduction potential is not included in Table 1. In addition to the uncertainties in energy consumption estimates (energy consumption is an important operational cost) factors that will contribute additional uncertainties to cost estimates include:

- \circ Cost unit (e.g. cost of electricity (COE), levelized cost of electricity (LCOE), cost per tonne of CO₂ captured or abated;
- Whether a technology is assessed as a first-of a kind (FOAK) processor nth of a kind (NOAK), e.g. how and to what extent capital cost reductions are included; and
- Unfamiliar production methods and materials.

It is important to be conscious of these uncertainties when choosing technologies for further development and testing.



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Table 1. Identified emerging $(2^{nd} \text{ and } 3^{rd} \text{ generation}) \text{ CO}_2$ capture technologies. Note that the spread in TRL for some groups reflects variations of individual technologies within the group. ?=Uncertain estimates that are not quoted

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Technology	Generation/TRL	Potential for energy savings	Applications
Precipitating solvents	$2^{nd} - 3^{rd} / 4 - 6$	10-20% rel. MEA (2.3- 3.6 GJ/t CO ₂)	Power, steel, cement
Two-phase liquid system	$2^{nd} - 3^{rd}/4 - 5$	2.0-2.3 GJ/t CO ₂	Power, steel, cement
Enzymes	$3^{rd/}$ 1-2(3)	30-35% rel. MEA (?)	Power, steel, cement
Ionic fluids	$2^{nd} - (3^{rd})/1 - 4$	15 -20 % rel. MEA	Power, steel, cement
Encapsulated solvents	3 ^{rd/} 1-2	?	Power, cement
Electrochemical solvents	3 ^{rd/} 1-2	Uncertain	Power, cement, steel, aluminium
Calcium looping system	2 nd /5-6	Coal: Efficiency penalties 5-10% Gas: no benefits	Power, cement
Other looping systems	$2^{nd}-3^{rd}/1-6$?	Power, steel, cement
Vacuum Pressure Swing (VPS)	$2^{nd}-3^{rd}/2-5$	Uncertain, could be good	Power, cement
Temperature swing (TS)	$2^{nd}-3^{rd}/1-4$	Uncertain, appears limited	Power, cement
Polymeric membranes	2 nd /5-6	Fuel consumption: 50% down rel. MEA?	Power, cement, steel
Polymeric w/cryogenic	2 nd /2-6	Better than above	Power, cement, steel
MoltenCarbonateFuelCells(electrochemical)	$2^{nd} - 3^{rd}/3-4$	Could result in efficiency higher than base power plant	Power, cement, steel
Cryogenic (low temp)	$2^{nd} - 3^{rd}/3 - 5$	Competitive MEA	Power
Supersonic	$3^{rd}/1-2$?	Power
Hydrates	$3^{rd}/1-3$?	Power
Algae	3 rd /1-3	?	Power and most other industries
CO ₂ -enriched flue gas	2 nd /5-6	?	Power
Pressurized post- combustion	$2^{nd} - 3^{rd} / 2 - 5$?	Power

Table 1A. Post-combustion capture technologies



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Table 1B Pre-combustion decarbonisation technologies

Technology	Generation/TRL	Potential for energy savings	Applications
Sorption Enhanced Water Gas Shift (SEWGS)	2 nd /4-5	Efficiency gain 3-4 %- points	Power, refinery, H ₂ production, blast furnaces
Sorption Enhanced Steam- Methane reforming (SE- SMR)	3 rd /1-2	Appears limited in NGCC	Power, refinery, H ₂ production
Metal and composite membranes	$2^{nd} - 3^{rd}/3 - 5$	Efficiency gain 3 %- points	Power, refinery, H ₂ production
Ceramic membranes	$2^{nd} - 3^{rd}/2 - 4$	As above?	Power, refinery, H ₂ production
Cryogenic (low temperature)	3 rd /1-3	Efficiency gain 3-4 %- points; 1 GJ/t CO ₂	Power, refinery, H ₂ production
Concepts with fuel cells	$2^{nd} - 3^{rd}/3 - 6$	Efficiency gain up to 30 %-points rel. IGCC and gas w/MEA	Coal and biomass power, refinery, H ₂ production

Table 1C Oxy-combustion capture technologies

Technology	Generation/TRL	Potential for en savings	ergy	Applications
Chemical looping combustion	2 nd /4-5	Efficiency gain 2-4 %-points (?)	Coal p	ower
Oxygen transporting membranes (OTM) power cycle	3 rd /2-3	Efficiency gain 5 %-points over NCCC w/MEA(?)	Power	
Pressurized oxy- combustion	3 rd /2-4	~35- 40% - efficiency	Coal a	nd biomass power

The study has identified 11 test facilities for CO_2 capture technologies that are or will be independent of technology providers and that may be used to speed up the development of emerging capture technologies. Only two of these are sufficiently large to allow the next step in the technology development to be full-scale. The others must be classified as small-scale testing facilities, i.e. < 10,000 tonnes CO_2 /year or the equivalent of $2MW_{th}$ coal-fired power plant. These are often operated on simulated flue gas. Testing at these smaller facilities will require at least one intermediate step before going to full scale. The majority of the identified test facilities are designed for postcombustion capture of CO_2 .

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There are also several test or demonstration facilities for CO_2 capture technologies that are owned by technology providers to test specific proprietary technologies. These are, in general, not available for testing of other technologies. Some of these facilities are briefly described in the report.

The study revealed that the literature uses a range of definitions for technology maturity and test scales and sometimes inconsistent use of terms. For example, although it is difficult to avoid a sliding scale between the terms "pilot-scale" and "demonstration-scale" facilities, the difference in terms of captured CO_2 has been found to vary with almost three orders of magnitude and at least one order in terms of power generation.

Recommendations for follow-up by the CSLF

Many technologies are developed by universities or small R&D companies that do not have the facilities, financial resources, and competence, to develop technologies beyond the lab or small bench scale without external support by others and access to larger test facilities. To progress the 2^{nd} and 3^{rd} generation CO₂ capture technologies further in a cost efficient manner CSLF should consider the following:

- Implement mechanisms that allow developers of emerging technologies and operators of test facilities to co-operate in mutually beneficial and cost-effective ways, e.g. help to establish biand/or multi-lateral agreements and funding mechanisms that allow emerging technologies to be tested at another nation's facilities. The International Test Centre Network (ITCN) and the European ECCSEL network initiatives are examples of how governments co-operate to increase testing capacities;
- Promote co-operation between facilities with different capabilities, both below and above $2MW_{th}$ or $(10^4 \text{ tonnes } CO_2/\text{year}, \sim 30 \text{ tonnes } CO_2/\text{day})$. This would increase the range of test opportunities and facilitate and accelerate knowledge sharing and exchange of experiences among CSLF member countries and between two or more test facilities;
- Based on the successful model of the ITCN and ECCSEL, the CSLF should encourage and facilitate enhancing the networks to cover additional regions, sectors, and levels of scale. This would help to lay the ground work to accelerate the development and testing of technologies in additional environments and facility configurations / conditions. As well, with increased membership, costs can be spread across a larger number of participants.;
- Enhance opportunities for researchers and developers to participate in extended visits and staff exchanges to other demonstration projects and test centres (six months or more) as well as training opportunities, much along the lines of the European initiative ECCSEL. This item should be co-ordinated with the re-established CSLF Academic Community Task Force;
- \circ Contribute to the derivation of a consistent terminology for new CO₂ capture technologies, maturity (2nd and 3rd generation vs. emerging or transformational; consistent use of TRLs) and for different testing scales (bench-, laboratory-, pilot- and demonstration-scale); and
- Contribute to the derivation of consistent performance indicators, e.g. common methododology for cost and energy consumption as well as test conditions that need to be represented during pilot testing that will simulate steady state, process upsets, and dynamic load following.



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1. Background and Objectives

At the CSLF Ministerial Meeting in Washington, DC, in November 2013, the Exploratory Committee of the CSLF Policy Group identified the following topics of great interest to the CSLF that should be moved forward in Task Forces:

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- 1. Communications;
- 2. Global collaboration on large-scale CCS project(s);
- 3. Financing for CCS projects;
- 4. Supporting the development of 2^{nd} and 3^{rd} carbon capture generation CCS technologies; and
- 5. Transitioning from CO₂-EOR to CCS.

The fourth task is the topic of this report. More specifically, the Policy Group stated that: "Efforts should be taken to better understand the role of 2nd and 3rd generation technologies for CCS deployment, and policies and approaches identified among individual CSLF member countries that can stimulate 2nd and 3rd generation CCS project proposals to improve the outlook for successful Large Scale Integrated Project deployment in the 2020 to 2030 timeframe. Development of these technologies will benefit from the CCS Pilot Scale Testing Network, which is in the process of being stood up. "

2. Scope and Approach

To achieve this fourth task, the following activities were agreed to be performed jointly by the CSLF Policy and Technical Groups:

- 1. Map initiatives and funding mechanisms for 2nd and 3rd generation technologies in CSLF member countries. US DOE/NETL Advanced Carbon Dioxide Capture R&D Program, Norwegian CLIMIT and UK Innovation Fund for Carbon Capture Projects are examples that should be summarized for the benefit of CSLF members. Provide perspective on how these initiatives run parallel with market mechanisms which would drive the adoption of these technologies. The effort should also include:
 - 1.1 Mapping/exploring the criteria that industry around the world may use to adopt technologies, i.e., market pull;
 - 1.2 Identifying the specific financial challenges associated with scale-up and deployment of 2nd and 3rd generation capture technologies; and
 - 1.3 Exploring the understanding of what those challenges might be, particularly if government funds are used, as well as the interest in joint funding/international collaboration

Responsible: Policy Group;

2. Map/identify 2nd and 3rd generation technologies under consideration in CSLF member countries, and identify technologies that may mature in the 2020-2030 timeframe, their development plans to scale from current readiness levels to prepare for demonstration, and the major challenges facing technology development. Good starting points are technology updates from DOE/NETL Advanced Carbon Dioxide Capture R&D Program, report from the UK Advanced Power Generation Technology Forum (APGTF), projects and reports from the IEA Greenhouse Gas R&D Programme (IEAGHG), CLIMIT projects and reports from SINTEF on behalf of the CSLF and TCM. Responsible: Technical Group;



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- 3. Use existing networks, e.g. the established International CCS Test Centre Network and ECCSEL, to map the potential for testing 2^{nd} and 3^{rd} generation technologies at existing test facilities. There is knowledge from a limited number of test facilities (e.g. NCCC, CanmetENERGY and TCM) on the possibilities to test 2^{nd} generation technologies in scale 1 5 MW_{th}. The list of test facilities needs to be expanded. Responsible for liaising with the networks: Technical Group; and
- 4. Prepare a Policy Document on how to achieve an accelerated implementation of 2^{nd} and 3^{rd} generation CO₂ capture technologies. Responsible: Policy Group.

2.2 Approach

This report answers points 2 and 3 above by compiling and summarizing information that is already available but spread on several publications. It summarises several review papers and is NOT an original work. The first version of the report was prepared for the CSLF Technical group meeting in Regina, Canada, June 15n- 19, 2015. At that time, the draft report and the grouping of capture technologies as well as the descriptions relied heavily on reports by SINTEF (2013)¹, DOE/NETL (2013)² and IEAGHG (2014)³. Other review documents at that time included ZEP (2013)⁴, CSLF (2013a)⁵, GCCSI (2014)⁶ and APGTF (2014⁷) as well as presentations at the 2014 NETL CO2 Capture Technology Meeting, Pittsburgh, PA, USA, July 29 – August 1, 2014,⁸ and the 2014 Transformational Carbon Capture Technology Workshop, Arlington, VA, USA, September 23⁹, 2014.

Additional review papers as well as updates on particular emerging CO2 capture technologies became available between the June and November 2015 meetings of the CSLF Technical Group. In particular, several review articles on recent development of CO2 capture technologies appeared in the Special Issue of the International Journal of Greenhouse Gas Control (IJGGC)¹⁰. The review article by Abanades et al (2015)¹¹ have been most relevant for this work. In addition, The 2015 NETL CO₂ Capture Technology Meeting June 23-26 in Pittsburgh, PA, USA¹² provided useful updates on capture technology development funded by the US Department of Energy (DOE). The NETL (2015)¹³ document on CO2 capture technology maturity was also included post-Regina.

⁵ http://www.cslforum.org/publications/documents/CCSTechnologyOpportunitiesGaps_FinalReport.pdf

¹³ http://www.netl.doe.gov/File%20Library/Research/Coal/Reference%20Shelf/DOE-NETL-20151710-2014-Technology-Readiness-Assessment-Comprehensive.pdf

¹ http://www.tcmda.com/PageFiles/1544/SINTEF%20report.pdf

²<u>http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/handbook/CO2-Capture-Tech-Update-2013.pdf</u>

³ IEAGHG (2014) Assessment of emerging CO_2 capture technologies and their potential to reduce costs.

^{2014/}TR4, December 2014. Note that the version used here is an interim version, issued before external review ⁴ http://www.zeroemissionsplatform.eu/library.html

⁶ GCCSI (2014) Global Status of CCS 2014. http://www.globalccsinstitute.com/publications/global-status-ccs-2014-summary-report

⁷ http://www.apgtf-uk.com/index.php/publications/publications-2014

⁸ http://www.netl.doe.gov/events/conference-proceedings/2014/2014-netl-co2-capture-technology-meeting

⁹ http://www.netl.doe.gov/research/coal/carbon-capture/workshop-2014

¹⁰ International Journal of Greenhouse Gas Control 40 (2015)

¹¹ J.C. Abanades, B. Arias, A. Lyngfelt, T. Mattisson, D.E. Wiley, H. Li, M.T. Ho, E. Mangano, S. Brandani (2015) Emerging CO2 capture systems. International Journal of Greenhouse Gas Control, 40, 126–166

¹² http://www.netl.doe.gov/events/conference-proceedings/2015/2015-co2-capture-technology-meeting



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References to these documents or presentations at the conferences are usually not given in the general descriptions, nor are references to papers and articles used by the mentioned references. The reader is referred to the above references for more details.

Rather than delving into each single technology provider and its technology, this report groups the technologies according to the classic post-, pre- and oxy-combustion process schemes. Where relevant, each scheme is further attempted to be divided into sub-sub-groups by the gas separation principle, e.g. by type of solvents, sorbents and membranes. A common template is used to describe each technology sub-group by including a brief general description, maturity, potential for improvements, key challenges, list of some players (not at all intended to be exhaustive), pathway to technology qualification, infrastructure required, potential environmental impact and possible applications.

Note the objective of the report is to give an objective as possible overview of emerging CO_2 capture technologies, NOT to pick winners. That will require a much more detailed and consistent assessment of the technologies than is available in the literature.

2.3 Organisation of report

Chapter 3 of the report provides the definitions of 2^{nd} and 3^{rd} generation capture technologies and Chapters 4 to 6 give summaries of the identified 2^{nd} and 3^{rd} generation technologies, sorted by technology approach/route and groups. Chapter 7 provides brief summaries of novel technologies of which detailed descriptions are not yet available in the open literature, and Chapter 8 presents summary descriptions of the capabilities of identified test facilities to perform bench-, pilot- and, in a few cases – demonstration-scale testing of 2^{nd} and 3^{rd} generation CO₂ capture technologies.

Appendix A provides a summary of how CO_2 capture technologies can be applied in industries other than power generation, in support of the possible applications given for each identified technology.

3. What are 2nd and 3rd generation capture technologies?

3.1 Definitions of technology maturity

Different definitions and/or classifications of emerging capture technologies are in use, see e.g. APGTF $(2011)^{14}$, CSLF (2013a, 2013b¹⁵), SINTEF (2013), US DOE/NETL (2013), ZEP (2013), GCCSI (2014), IEAGHG (2014) and Horizon 2020^{16} (used by Abanades et al ,2015). One way to define the maturity of technologies is using Technology readiness Levels (TRL), The first approach to this appears to have been made by NETL(2012)¹⁷, using the definitions in Table 2.

¹⁴ http://www.apgtf-uk.com/index.php/publications/publications-2011

¹⁵ http://www.cslforum.org/publications/documents/CSLF_Technology_Roadmap_2013.pdf

¹⁶ http://ec.europa.eu/research/participants/data/ref/h2020/wp/2014_2015/annexes/h2020-wp1415-annex-g-trl_en.pdf

¹⁷ http://www.netl.doe.gov/File%20Library/Research/Coal/Reference%20Shelf/TRL-Comprehensive-Report_121112_FINAL_1.pdf



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Others have different definitons of TRL. Table 3 shows how IEAGHG (2014) and Abanades (2015) have defined the nine TRL levels and Table 4 the definitions according to GCCSI (2014).

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SINTEF (2013) does not use TRL and defines technology maturity according to the five groups:

- Idea/theoretical investigations only;
- Proof-of-concept/laboratory-scale testing;
- Pilot-scale testing;
- Demonstration; and
- Commercial.

DOE/NETL (2013) uses similar maturity descriptions in the capture technology sheets but add whether the tests imply slip-streams with real flue gases, syngas or simulated flue gases.

TRL	DOE-FE Definition	DOE-FE Description
1	Basic principles observed and reported	Lowest level of technology readiness. Scientific research begins to be translated into applied R&D. Examples include paper studies of a technology's basic properties.
2	Technology concept and/or application formulated	Invention begins. Once basic principles are observed, practical applications can be invented. Applications are speculative and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytic studies.
3	Analytical and experimental critical function and/or characteristic proof of concept	Active R&D is initiated. This includes analytical and laboratory-scale studies to physically validate the analytical predictions of separate elements of the technology (e.g., individual technology components have undergone laboratory-scale testing using bottled gases to simulate major flue gas species at a scale of less than 1 scfm).
4	Component and/or system validation in a laboratory environment	A bench-scale prototype has been developed and validated in the laboratory environment. Prototype is defined as less than 5% final scale (e.g., complete technology process has undergone bench-scale testing using synthetic flue gas composition at a scale of approximately 1–100 scfm).
5	Laboratory-scale similar-system validation in a relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Prototype is defined as less than 5% final scale (e.g., complete technology has undergone bench-scale testing using actual flue gas composition at a scale of approximately 1–100 scfm).
6	Engineering/pilot-scale prototypical system demonstrated in a relevant environment	Engineering-scale models or prototypes are tested in a relevant environment. Pilot or process-development-unit scale is defined as being between 0 and 5% final scale (e.g., complete technology has undergone small pilot-scale testing using actual flue gas composition at a scale equivalent to approximately 1,250–12,500 scfm).
7	System prototype demonstrated in a plant environment	This represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Final design is virtually complete. Pilot or process-development-unit demonstration of a 5–25% final scale or design and development of a 200–600 MW plant (e.g., complete technology has undergone large pilot- scale testing using actual flue gas composition at a scale equivalent to approximately 25,000–62,500 scfm).
8	Actual system completed and qualified through test and demonstration in a plant environment	The technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include startup, testing, and evaluation of the system within a 200–600 MW plant CCS/CCUS operation (e.g., complete and fully integrated technology has been initiated at full-scale demonstration including startup, testing, and evaluation of the system using actual flue gas composition at a scale equivalent to approximately 200 MW or greater).
9	Actual system operated over the full range of expected conditions	The technology is in its final form and operated under the full range of operating conditions. The scale of this technology is expected to be 200–600 MW plant CCS/CCUS operations (e.g., complete and fully integrated technology has undergone full-scale demonstration testing using actual flue gas composition at a scale equivalent to approximately 200 MW or greater).

Table 2. TRL Definitons by NETL (2012)

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Maturity	TRL	Definition IEAGHG (2014) Horizon 2010 (used by Abanades et al		
Demonstration 9		Normal commercial service	Actual system proven in operational environment (competitive manufacturing of full system)	
	8	Commercial demonstration, full- scale deployment in final form	System complete and qualified (system demonstrated at industrial scale)	
	7	Sub-scale demonstration, fully functional prototype	System prototype demonstration in operational environment (industrial pilots operating at over 10 MW_{th})	
Development	6	Fully integrated pilot tested in a relevant environment	Technology demonstrated at in relevant environment (steady states at industrially relevant environments; pilots in the MW _{th} range)	
	5	Sub-system validation in a relevant environment	Technology validated in relevant environment (pilots operated at industrially relevant conditions at $0.05 - 1 \text{ MW}_{\text{th}}$)	
	4	System validation in a laboratory environment	Technology validated in laboratory (continuous operated pilot at lab scale $< 50 \text{ kW}_{\text{th}}$	
Research	3	Proof-of-concept tests, component level	Experimental proof of concept (pilot testing of key components at small bench scale)	
	2	Formulation of the application	Technology concept formulated (basic process design)	
	1	Basic principles observed, initial concept	Basic principles observed	

Table 3. TRL definitions according to IEAGHG (2014) and Horizon 2020

Table 4. TRL definitions according to GCCSI (2014)

Maturity	TRL	Definition
Demonstration	9 8	The process is implemented at full or reduced scale but is representative of a commercial plant in performance and complexity. The process is engineered in the same manner as a commercial project and fully integrated with the flue gas source process. Flue gas is derived from a source representative of the commercial application. The plant operates over the full range of operating conditions.
Pilot/demonstration	7	The overlap between pilot and demonstration
Pilot	6	The main parts are integrated and tested in a complete process to conduct performance tests and sensitivity analyses. First engineering design takes place. Real flue gas e.g. derived from a new or existing source, conditioned to meet actual characteristics if necessary (e.g. dedicated burner).
Lab/bench/pilot	5	The overlap between lab/bench and pilot
Lab/bench	4	The core process components are tested in a lab facility or at bench-scale to
	3	demonstrate the working principle on single components or limited integration (main parts of the process). Flue gas is artificial.
Concept/lab-bench	2	The overlap between concept and lab/bench
Concept	1	The idea is demonstrated using theoretical calculations and/ or observation of basic principles in laboratory.



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Several factors contribute to an inevitable degree of subjectivity when evaluating the maturity level of technologies. These include:

- The reviewers (and vendors) will have different views on how far a technology has come or how promising it is. For example, among the post-combustion capture technologies, temperature swing adsorption (TSA) and pressure swing adsorption (PSA) are classified by GCCSI (2014) at TRL 5-7, whereas IEAGHG (2014) classify them as, respectively, TRL 1 and 3;
- Reviewers use different definitions of technology maturity, as described above. The terms 2nd and 3rd generation technologies are generally not used in the reviewed documents;
- Reviewers are not always precise as to which maturity level a technology is and indicate a maturity between two categories; and
- The boundary between "pilot-scale" and "demonstration" is indeed floating and imprecise, in terms of quantity as well as units. SINTEF (2012) may be interpreted to group technologies with CO_2 capture rates of a few kg/hour to several tonnes/hour as pilot, whereas GCCSI (2014) mentions both technologies with 1 2 MW_{th} and 35 MW_{th} as pilots. The former indicates that the 'pilot' designation would cover three orders of magnitude, which is too large to be meaningful.

3.2 Definitions used in this report

This report will use the following definitions, basically adapted from DOE/NETL (2013), to describe the maturity of the technologies:

- 2nd generation technologies—include technology components currently in R&D that will be validated and ready for demonstration in the 2020–2025 timeframe; and
- 3rd generation technologies, or "Transformational" technologies in DOE/NETL, —include technology components that are in the early stage of development or are conceptual that offer the potential for improvements in cost and performance beyond those expected from 2nd generation technologies. The development and scale-up of 3rd generation technologies are expected to occur in the 2016–2030 timeframe, and demonstration projects are expected to be initiated in the 2030–2035 time period.

It should be noted that DOE/NETL (2013) has cost targets of less than \$40/tonne of CO₂ captured for 2^{nd} generation technologies and less than \$10/tonne of CO₂ captured for 3^{rd} generation, or transformational, technologies. These unit costs translate to approximately 20% and 30% reductions in levelized cost of electricity (LCOE)¹⁸, respectively.

A difficulty for a review paper like this is that the referenced papers and reports do not necessarily use the same grouping of technologies. SINTEF (2013) and IEAGHG (2014) use very similar grouping and the NETL reports allow technologies to be categorised using the same groups. Abanades et al (2015) use a different grouping when showing changes in TRL from 2005 to 2015 (their Table 1), making direct comparisons of estimated technology maturity difficult,

Table 5 shows how the classifications of four of the reviewed reports correspond to the definition of 2^{nd} and 3^{rd} generation used here.

¹⁸ See also: <u>http://energy.gov/downloads/chapter-4-advancing-clean-electric-power-technologies</u>

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Table 5. Maturity definitions in relation to emerging (2nd and 3rd) generation capture technologies

Classification used in this report, generation	SINTEF (2013)	DOE/NETL (2013)	IEAGHG (2014)	GCCSI (2014)
2^{nd}	Pilot-scale testing	Pilot-scale testing (real and	Development (TRL	Pilot (TRL 5-
		simulated gases)	4 – 6)	7)
3 rd	Proof-of-concept/lab	Proof-of-	Research (TRL 1 -	Concept and
	scale testing;	concept/laboratory-scale	3)	lab/bench
	Idea/theoretical	testing;		(TRL 1 – 5)
	investigations only	Idea/theoretical		
		investigations only (real		
		and simulated gases)		

The term "emerging" will be used to include both 2nd and 3rd generation technologies.

In Chapters 4 - 6 technologies are classified according to estimated TRL, basically using the IEAGHG (2014) definitions in Tables 2 and 4. A balance has been sought when there are different views among the referenced sources, realizing that some of the classifications may be open to interpretation.

NOTE: The TRL grading is based on technical status, not on feasibility or whether this approach is CCS or CCUS.

3.3 **Potential for improvements**

Any summary of emerging technologies would be incomplete without assessment of the potential for improvements compared to some selected baselines. The choice of appropriate baseline is an important issue and ideally, one would prefer a common baseline. However, this is not always possible and the choice varies between technology developers. Thus, fair and direct comparisons of the potential for improvements may not always be possible. Numbers presented here should be used with extreme care.

Two factors that are usually considered when assessing improvements are potential for reduced energy consumption of the capture process and the LCOE.

Factors that may contribute to different estimates for energy consumption include:

- Comparison to different baselines and operating conditions in addition to different assumptions and battery limits;
- Reporting in efficiency changes (% vs. some baseline) or energy requirements (GJ/tonne CO₂);
- Electricity vs. thermal energy;
- Work vs. thermal energy; and
- Limited information and testing of emerging technologies.

Improvements in energy consumption are mainly based on IEAGHG (2014) and SINTEF (2013). The baselines for the IEAGHG(2014) numbers are as for cost reductions. The reporting of energy



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reduction potential in the SINTEF (2013) report includes qualitative assessments, absolute energy consumption and references to MEA based post-combustion capture.

Numbers for the potential for reduction of energy consumption given in this report are subjective syntheses and summaries of numbers found in the referenced documents.

In addition to the uncertainties in energy consumption estimates (energy consumption is an important operational cost) factors that will contribute additional uncertainties to cost estimates include:

- $\circ~$ Use of different cost unit (e.g. cost of electricity (COE), LCOE, cost per tonne of CO₂ captured or abated;
- Whether a technology is assessed as a first-of a kind (FOAK) processor nth of a kind (NOAK), e.g. how and to what extent capital cost reductions are included; and
- Unfamiliar production methods and materials.

For these reason cost reduction numbers are not given here.

3.4 Excluded from this report: Overall process development and integration, and materials

Several retrofit measures to improve technologies and reduce energy penalties and costs will be common to all types of CO_2 capture technologies. Such measures include but are not limited to:

- General energy efficiency measures, e.g. for turbines;
- Optimized integration a CO₂ capture system with the power or processing plant, e.g. heat integration;
- Improvement of other environmental control systems (e.g. for SO_X and NO_X emissions);
- Part-load operation and daily cycling flexibility;
- Impacts of CO₂ composition and impurities, for 'new-build' plants as well as for retrofits;
- Materials choice and improvements; and
- Improved process equipment like heat exchangers, pumps fans and other auxiliary equipment.

These measures are not connected to any particular CO_2 capture technology or technology generation but improving them are processes that need to be going on continuously. They are not considered here.

3.4 Excluded from this report: Overall process development and integration, materials

Several retrofit measures to improve technologies and reduce energy penalties and costs will be common to all types of CO_2 capture technologies. Such measures include but are not limited to:

- General energy efficiency measures, e.g. for turbines;
- Optimized integration a CO₂ capture system with the power or processing plant, e.g. heat integration;
- Improvement of other environmental control systems (SO_X, NO_X);
- Part-load operation and daily cycling flexibility;



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- Impacts of CO₂ composition and impurities, for 'new-build' plants as well as for retrofits;
- Materials choice and improvements; and
- Improved process equipment like heat exchangers, pumps fans and other auxiliary equipment.

These measures are not connected to any particular CO_2 capture technology or technology generation but improving them are processes that need to be going on continuously. They are not considered here.

3. Summary of Identified Technologies - Post-combustion

In post-combustion CO_2 capture, the CO_2 is removed from the combustion or industrial process flue gases. CO_2 concentration in the flue gases varies from 3-4% for gas-fired power generation to well above 20% for some industrial processes. Note, howvere, that there are challenges associated with capturing CO_2 from iron and steel gas streams that make them different from 'post-combustion flue gases', as both have significant amounts of CO and H₂, in addition to CO2, N₂ and H₂O.

The principle of the post-combustion capture process is illustrated in Figure 1.



Figure 1. Schematic illustration of the post-combustion process

The separation process itself can be achieved by using solvents, sorbents or membranes, with each of these alternatives being offered through a variety of options. Presently, the use of solvents is the most mature approach. For solvents and sorbents two reactors are required: one for absorption/adsorption process in which the CO_2 is captured, and one for the reverse process in which the CO_2 is released. A main hurdle is the energy required for the release.

An alternative to solvents and sorbents is the use of membranes which selectively let the CO_2 pass through. Hybrid solutions and solutions that cannot be classified as either of the three above also exist and are briefly described in the report.



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4.1 **Post-combustion capture solvents**

Solvent-based CO_2 capture involves chemical or physical absorption of CO_2 from combustion flue gases into a liquid carrier. Chemical solvents rely on a chemical reaction of CO_2 in the solvent whereas physical solvents absorb molecular CO_2 without a chemical reaction. Chemical solvents are most attractive for post-combustion capture with dilute low-pressure flue gases. The absorption liquid is re-generated by increasing its temperature or reducing its pressure.

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Solvents for use in post-combustion CO_2 capture are commercially available from several vendors. The world's first commercial-scale capture plant, SaskPower's Boundary Dam Unit #3, Saskatchewan, Canada, is the best example, using Shell's Cansolv process. Other vendors that have tested their commercial solvents at scale of several MW and above, include:

- Aker Solutions (earlier Aker Clean Carbon);
- Alstom (now part of GE Power);
- Fluor;
- Linde-BASF;
- Mitsubishi Hitachi; and
- Toshiba.

A majority of these vendors offer proprietary solvents that typically involve amine-based solutions. Alstom's technology is based on chilled ammonia. These vendors all continue R&D to improve the solvents and associated processes.

Others that have announced their intention to test proprietary solvents at the CO_2 Technology Centre Mongstad (TCM) are

- Carbon Clean Solutions Pvt. Ltd (CCS), an India-based company that has developed a solvent in which amine-based compounds are combined with salts, the CDRMax solvent. The proprietary solvent was tested at Solvay Chemicals' 7,700 tonnes per annum CO₂ capture plant at Vishnu Barium, India in 2012; and
- GE Global Research has developed a solvent based on amino silicone compounds that at various temperatures capture and release CO₂. GE researchers are preparing (fall 2015) a demonstration of it's CO₂ capture solution in a 0.5MW_{th} power system the US National Carbon Capture Center (NCCC).

Important objectives for the improvement of post-combustion capture solvents, including those that are commercially available, are the development of low-cost, non-corrosive solvents that have a high CO_2 loading capacity, high absorption rate, low regeneration energy, improved reaction kinetics, low environmental impact and are resistant to degradation. Such ongoing research by vendors, research institutes and universities is excluded from this summary, which focuses on new concepts not yet at the demonstration stage.

4.1.1 Precipitating solvents

Certain solvent systems form a precipitate when absorbing CO_2 . Amino acid salts and inorganic carbonate (e.g. K_2CO_3) solvent systems are among the examples, in which precipitation of neutral amino acid or bicarbonate salts occur. The precipitation leads to a concentrated slurry of salts, which is sent to re-generation, while part of the solvent is sent back to the absorber. The use of precipitating



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solvents has potentially several advantages over traditional solvents. As the equilibrium CO_2 pressure remains constant when the CO_2 loading continues to increase the absorption can be maintained, potentially leading to improved absorber performance such as increased stability and absorption capacity, increased kinetics, higher cyclic loading, and reduced energy consumption during regeneration (can be regenerated at higher pressure) compared to amine systems.

- **Maturity**: 2nd to 3rd generation; TRL 4-6 (Laboratory-scale testing to small pilot-scale with real flue gases; depending on solvent)
- Potential for improvements:
 - Energy savings: 10 20% (energy consumption 2.3 3.6 GJ/t CO₂)
- **Challenges:** Novel contactors for optimal gas-liquid-solid contact need to be designed and tested (there is limited operational experience in operating conventional packed column absorbers with slurries at power planscales; liquid-solid separation, or slurry concentration require additional equipment, which may increase capital costs and auxiliary load); the impact of SO₂ and NO_x; the need for reclaiming of solvent needs further investigation; the operation of packed absorbers with precipitation requires some development; optimization of packing materials; and tendency for solids to build up and slowly block the process will need to be checked by long pilot plant runs; solid liquid separation is an additional process step and needs to be optimised
- Some players: Shell Global Solutions, Alstom, CO2CRC, SINTEF/NTNU, TNO, GE Global Research/University of Pittsburgh
- **Pathway to technology qualification**: On-site testing with real flue gas at e.g. a few tens of tonnes of CO₂/hour. Further research on packing materials and optimization of liquid/gas ratios is recommended
- **Infrastructure required**: Further lab and pilot testing is recommended. This requires basic equipment for characterization of crystals formation. Equipment for solid-liquid separation, slurry pumps, extruders, and heat exchangers is also needed. Needs access to real flue gases, water, electricity and other utilites
- Environmental impact: Low impact if inorganic carbonates are used. Potential Health, Safety and Environment (HSE) issues must be addressed if NH₃ is used
- Applications: Power generation, cement industry, steel industry, other small industries.

4.1.2 Two phase liquid phase solvents

Biphasic mixtures consist of two immiscible phases. In the case of CO_2 capture certain solvents form two liquid phases at absorption or when heated. Examples are blends of amine with different dissolution between the components. When two liquid phases are formed, the lower phase will contain most of the bound CO_2 at very high concentration. This lower phase is separated out and sent for desorption.

The two-phase liquid systems studied show a great degree of flexibility in operation and have advantages over working with solids/precipitates, e.g. it is believed that a re-boiler energy requirement of 2.0 GJ/tonne CO_2 is within reach and that the CO_2 can be released at higher pressures.

• Maturity: 2nd -3rd generation; TRL 3 - 4 (Proof-of-concept with material testing at lab-scale, some testing planned or carried out in pilots)

• Potential for improvements:

- \circ Energy savings: Energy consumption 2.0 2.3 GJ/t CO₂
- **Challenges:** Tailoring and characterizing the system to minimize the energy requirement; firmer validation



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- Some players: IFPEN with partners in the Octavius Project, SINTEF/NTNU, Technical University of Dortmund, University of Illinois
- **Pathway to technology qualification**: Further lab and pilot testing should be performed in terms of optimizing solvent formulation and composition based upon operability, degradation and emissions. For firmer validation of process Pilot-scale tests were planned for ENEL plant at Brindisi in 2015 but have been cancelled
- **Infrastructure required:** The concept utilizes a similar infrastructure as in conventional absorption/desorption cycles, i.e. access to real flue gases, water, electricity and other utilities, but requires some additional equipment like gas/liquid and liquid-liquid separators
- Environmental impact: Very limited evaluation so far. Use of amines with low aqueous solubility may potentially lead to high emissions and might require special mitigation steps
- Applications: Power generation, cement industry, steel industry.

4.1.3 Enzymes

The enzyme carbonic anhydrase (CA) is known to accelerate the hydration of neutral aqueous CO_2 molecules to ionic bicarbonate species. CA is amongst the most well-known enzymes, since it operates in most living organisms, including human beings. By adding a soluble enzyme to an energy efficient solvent one may be able to achieve a lower cost process for c CO_2 capture by mimicking nature's own process. Increasing the kinetic rates of the hydration of CO_2 and dehydration, as CA does, results in enhanced absorption and desorption of CO_2 into and out of a CO_2 solvent and/or in various membrane processes with immobilized CA. Novozymes applies ultrasonic energy to increase the overall driving force of the solvent re-generation reaction.

- Maturity: 3rd generation; TRL 1 2 (Bench-scale testing with real flue gas)
- Potential for improvements:
 - \circ Energy savings: 30 35 %
- **Challenges:** Understanding the level of enzyme activation; increasing the chemical and physical stability of the enzymes (mainly thermal stability); advancing the limited cyclic capacity (for carbonates); finding the optimal enzyme type and concentration to achieve sufficiently high reaction rate
- Some players: CO₂ Solutions, Novozymes, Carbozymes, Akermin, University of Illinois
- **Pathway to technology qualification**: Further basic research to understand the level of enzyme activation and to increase the chemical and physical stability of the enzymes (mainly thermal stability). In addition, the limited cyclic capacity (for carbonates) needs further advancements. Scale-up to laboratory and small pilot
- **Infrastructure required**: The concept can utilize the existing infrastructure for post-combustion capture as found at many larger test facilities, such as access to real flue gas, water, electricity and other utilities. Some modifications may be required, depending on the need for recycling enzymes to avoid high temperature exposure
- Environmental impact: Potentially low impact. If inorganic carbonates are use as main component and there are no other activators than the enzyme, there should be no emissions
- Applications: Power generation, cement industry, steel industry.

4.1.4 Ionic liquids

Ionic liquids (ILs) are inorganic or organic salts in a liquid state, with low melting usually below 100 °C. Ionic liquids are largely made of ions and short-lived ion pairs. The physical and chemical properties of ILs can be tuned to achieve high physical and chemical solubility for CO_2 to reduce the

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energy demand, increase stability, and to lower the losses of aerosols compared to standard amine solvents (they are non-volatile), thereby reducing the costs of capture while also reducing the environmental impact. They are often termed "designer solvents". In reversible IL neutral molecules react with CO_2 to form a liquid that dissolves additional CO_2 by a physisorption mechanism. A modest rise in temperature reverses the reaction and releases pure CO_2 . Another type of IL, polyionic liquids, made from ionic liquid monomers, have enhanced CO_2 sorption capacities and achieved fast sorption/desorption rates compared with room temperature ionic liquids.

 CO_2 binding organic liquids (BOLs) are switchable ionic liquids that convert a non-polar liquid to a polar ionic liquid with CO_2 as the chemical trigger. If coupled with the newly discovered polarity-swing-assisted regeneration (PSAR) process CO_2BOLs are estimated to provide more than 42 percent energy savings over aqueous alkanolamine systems due to significantly lower temperatures and energy requirements for CO_2 separation relative to conventional technology, making appreciable cost savings possible.

IL have also been proposed for use in liquid membranes, supported on a porous alumina membrane.

- Maturity: 2nd to 3rd; TRL 1 4 (Laboratory-scale testing with simulated flue gas to small pilot-scale with real flue gases. Pilot-scale testing at 0.5 MW_e) with slipstream was completed late 2015
- Potential for improvements:
 - \circ Energy savings: 15 20%
- **Challenges:** Optimization of chemical/physical properties to overcome high viscosity problems, lowering the thermal energy requirements for CO₂ desorption and reduce costs of ILs
- Some players: ION Engineering, Dupont, Xcel Energy, Evonik, Eltraon R&D, University of Notre Dame, University of Alabama, Georgia Tech Research Corporation, University of Colorado, Batelle Pacific Northwest Laboratories, University of Melbourne and many Chinese research groups (materials development)
- **Pathway to technology qualification**: Pursue an active research to optimize physical and chemical properties of ILs by expanding the lab-scale units to pilot scale. In addition, more work is needed on lowering the thermal energy requirements for desorption of CO₂ and investigations on the stability and regeneration of the solvent
- **Infrastructure required**: The concept utilizes a similar infrastructure as in conventional absorption/desorption cycles, i.e. access to real flue gas, water, electricity and other utilities, and is usually described as a drop-in replacement for aqueous amine solvent systems
- Environmental impact: More work is needed to evaluate toxicity, "green label" is not straight forward due many unknowns related to effects of long-chain ILs and cations/anions. The non-volatile nature of ILs indicates lower exposure risk than for volatile solvents. ILs are non-flammable at ambient and higher temperatures
- Applications: Power generation, cement industry, steel industry.

4.1.5 Novel solvent systems – encapsulated and electrochemical systems

These are processes that use amine-based solvents with novel system designs that should minimize the known disadvantages of standard amine systems. This can be done through solvent development and/or novel process configurations. Two examples are encapsulated solvent and electrochemically-mediated amine regeneration systems.

Encapsulated solvent involves encapsulating the solvent, e.g. an amine or a carbonate, in thin polymeric membrane or shell, forming beads of size $200 - 400 \mu m$, thereby given a large increase in

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contact surface area between flue gases and solvent. The inner solvent will perform the selectivity role. The shell must be highly permeable to CO_2 and strong enough to survive capture, and presumably release pure CO_2 via heating, over thousands of cycles. With the capacity of liquids and the physical behaviour of solid sorbents, encapsulated solvents may be useful in both conventional-style capture applications, as well as new approaches. The liquid, as well as any degradation products or precipitates, remains encapsulated within the beads.

In electrochemically-mediated amine regeneration (EMAR) systems, the heat exchanger and stripper is replaced with an electrochemical cell. As integration is required with the plant steam cycle this concept offers the advantage of easier retrofitting than traditional amine or other solvent systems. It may also achieve lower CO_2 lean loading. The process has the potential to improve the overall process economics by reducing absorber size and lowering system energy penalty.

- **Maturity**: 3rd generation; TRL 1 2 (Encapsulated solvents: Proof-of-concept; Electrochemicallymediated amine regeneration: Bench-to-laboratory-scale testing)
- Potential for improvements:
 - Energy savings: Uncertain
- Challenges: Scale-up from laboratory
- Some players:
 - Encapsulated solvents: Lawrence Livermore National Laboratory, University of IL Urbana-Champaign, Babcock and Wilcox Co., University of Notre Dame, Columbia University
 - Electrochemically-mediated amines: Mass. Institute of Technology, Siemens, Topchiev Institute of Petrochemical Synthesis, Russia
 - o Addition of organic acid: NTNU
- Pathway to technology qualification: On-site testing with real flue gases at e.g. a few tens of tonnes of CO₂/hour. The impact of SO₂ and NO_x and the need for reclaiming of solvent needs further investigation. Further research on packing materials and optimization of liquid/gas ratios is recommended
- **Infrastructure required**: The concept can utilize the existing infrastructure for post-combustion capture as found at many larger test facilities i.e. access to real flue gas, water, electricity and other utilities. Some modifications will be required, such as cathodic systems. Sufficient electricity must be secured
- **Environmental impact**: For the encapsulated solvent concept, leakage of amines degradation products to the surroundings may be reduced if the encapsulated amines remain structurally intact. This will require further research. In general, an improved efficiency may reduce the environmental foot-print
- Applications: Power generation, cement industry; EMAR also steel and aluminium industries.

4.2 **Post-combustion capture sorbents**

4.2.1 Metal organic frameworks (MOFs)

MOFs are a class of crystalline porous materials that consists of organic ligand molecules that are able to bind metal ions that hold some promise to improve cost and performance of CO_2 capture technologies based on sorbents. Their advantages include

• High tunability with respect to surface chemistry and pore size, i.e. a very large number can be synthesized from different metal ions and different linkers



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- Very high surface area, up to $5000 \text{ m}^2/\text{g}$
- Thermal stability and operated at higher presuures; and
- Potentially high concentration of adsorption sites

Challenges connected to MOFs include

- Synthesizing and fabricating novel MOF materials with exceptional CO₂ separation capacities at affordable cost
- Developing MOF materials with catalytic abilities for CO₂ conversion into usable products
- Scale-up and fabrication of membrane-based devices for integration of MOFs into industrial platforms; and
- Modelling, prediction and advanced characterization of these new materials.

Many academic and research institutions are working on MOFs. Due to many combinations of different metal ions and different linkers, they are not described further.

Important players include RTI and Lawrence Berkeley National Laboratory.

4.2.2 Calcium looping systems

In this process flue gases are fed to a carbonator with calcium oxide (CaO) that reacts with the CO₂ in the flue gases to form calcium carbonate (CaCO₃). The CaCO₃ is transferred to a calciner in which CaCO₃ is converted back to CaO and CO₂ under the addition of air or oxygen, heat and fuel. CO₂ can thereafter be captured. Temperatures in the carbonator are 600 - 650 °C and in the calciner 850 – 1000 °C. Advantages of the calcium looping process are that the output from the calciner is high purity CO₂; that the exothermic heat of the CO₂ absorption reaction can be recovered for use in steam generation, which reduces the energy penalty; and that the raw material (CaO/CaCO₃ found in e.g. dolomite and natural gypsum) is abundant and inexpensive.

The calcium looping process has mainly been studied for post-combustion application in coal fired power plants but to some extent also for gas fired power plants and cement plants. In coal fired plants there are good opportunities for heat integration for both carbonator and the steam leaving the calciner. In gas fired plants, one loses the good heat integration that can be obtained for coal fired plants. Cement plants utilize a calciner for materials production but it would need to be converted to oxygen fired to facilitate carbon capture.

- **Maturity**: 2nd generation; TRL 5 6 (Pilot scale):
 - $\circ~$ At $1-2~MW_e$ on real flue gases from coal-fired power plant (Darmstadt, smaller one in Stuttgart and China;
 - 8000 9000 tonnes CO₂/year at cement plant by Taiwan Cement Group)
- Potential for improvements:
 - Energy savings: 5 -10 % for coal-fired; small for gas-fired
 - **Challenges:** The rapid degradation of the sorbent, CaO, requires continuous substitution of CaCO₃ (which also degrades). As the CO₂ from the "fresh" CaO also must be captured, the degradation leads to an increased amount of CO2 that must be captured, compressed and transported. This, in combination with the low residual activity, may require studies on more advanced sorbents but the additional cost of advanced sorbents may not be justified by the improved performance. Further, the design and operation of the solid-solid heat exchanger required between the carbonator and calciner to recuperate heat and improve energy efficiency



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must be improved

• Some players: Foster Wheeler, Alstom, SINTEF, IFE, TU Darmstadt, University of Stuttgart, INCAR (Oviedo, Spain), CSIC, SINTEF, IFE, Chalmers University of Technology, other universities in Europe, North America, Australia and China

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- Pathway to technology qualification: Scale-up to large pilot-scale in the order of 10MW_e is needed
- Infrastructure required: CO₂-containing flue gases are required. Infrastructure is required for continuous supply and makeup of CaCO₃ sorbent as the sorbent deactivation rate is high, and for disposal of degraded CaO
- Environmental impact: CaO and CaCO₃ can be safely stored at atmospheric conditions (CaO is also a saleable product) since they are stable and non-volatile materials. The impact of the calcium looping process regarding the fine dust emission must be evaluated
- Applications: Power generation, cement industry, steel industry.

4.2.3 Other sorbent looping systems

Due to the rapid degeneration of CaO/CaCO₃ and the large need for make-up, one will seek to find other options. This can be done in several ways, including:

- By improving the lifetime of natural Ca-based minerals by promoting the minerals with other elements or processing with other inorganics;
- By preparing supported Ca-based sorbents by wet impregnation of calcium-containing solutions onto a porous substrate followed by calcination;
- By developing sorbents based on nano technology, such as nanoparticles of e.g. CaO, LiO, Na₂O, K₂CO₃ and Na₂CO₃ that are stabilized by other nano-sized particles made from e.g. ZrO, CeO₂, TiO₂, SiO₂, Al₂O₃;
- By loading CO₂-philic polymers onto high surface area nanoporous materials ("molecular basket sorbents", MBS): and
- By modifying mesoporous carbon material with surface functional groups that adsorb CO₂.
- **Maturity**: Demonstration to 2nd or 3rd generation; TRL 1 6 (Depends on adsorbent: From labscale testing on simulated flue gases via 1 MW pilot on slipstream of actual flue gases (ADA-ES at Southern Company Miller Plant, amine based adsorbent) to 10 MW_e with K₂CO₃ based sorbent on slip-stream of KOSPO's Hadong coal-fired power plant, South Korea

• Potential for improvements:

- Energy savings: Uncertain
- **Key Challenges**: Increase stability and reduce degradation while at the same time have high CO₂ absorbing/desorbing capacity and heat requirements; large-scale manufacturing
- Some Players: Toshiba, CanMet, Imperial College Londom, ECN, SINTEF, Mitsubishi, ETH, ADA-ES, TDA Research, RTI International, University of North Dakota, SRI International, KEPCO RI, Korea and KIER in South Korea
- **Pathway to technology qualification**: Depends on sorbent. Once qualified in lab the possibilities of larger scale testing in facilities as used at NCCC for the SRI sorbent, at Southern Company Miller Plant for ADA-ES sorbent and at the Hadong plant in South Korea should be explored.
- **Infrastructure required**: Slipstream of flue gases from full-scale power plant and possibilities for make-up and disposal of deactivated sorbent. Possibilities to analyze for potential emissions or hazardous waste



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- Environmental impact: Sorbent dependant
- Applications: Power generation, cement industry, steel industry.

4.2.4 Vacuum pressure swing adsorption (VPSA)

VPSA is a version of pressure swing absorption (PSA) that uses vacuum to desorb the adsorbed gas. Two or more columns, which are filled with adsorbent pellets, are needed to achieve a continuous process. In each column a sequence of adsorption, rinse, evacuation and purge to desorb the adsorbed gas is carried out. The adsorbent is a high surface area material with moderate adsorption energy with the adsorbing gas and high selectivity for CO_2 compared to gases like NO_X and O_2 . The energy required in this process is the electric power for the vacuum pumps and the valves as well as the energy needed to compress the CO_2 from below atmospheric pressure. There is no need for steam. One hypothesis is that the energy requirement will be lower than that for amine solvent solutions. The VPSA (vacuum pressure swing adsorption) process is best suited for flue gases with a CO_2 content >10%, i.e. for coal-fired power plants and several industrial processes.

Zeolites are often used as adsorbents in the VPSA process but MOFs and other tuneable materials with high surface area may result in significantly improved performance provided they have high cyclic capacity and can work at high relative humidities.

- **Maturity:** 2nd-3rd generation; TRL 2 5 (Laboratory-scale testing with real flue gases for postcombustion; TRL 5-8 have been achieved for VPSA used in pre- and oxy-combustion, exemplified by, respectively Air Products at Port Arthur, Texas, USA, and Air Liquide at a steel plant in Luleå, Sweden)
- Potential for improvements:
 - Energy savings: Uncertain
- Key Challenges: Need to investigate the impact of water, SO₂ and NO_x and achieving high recovery of CO₂ at high purities; as well as further development of optimised adsorbents; the costs of MOFS, which are a concern
- Some Players: Engineering companies: Air Products, Linde, UOP, Wärtsilä Hamworthy, Zeolite producers: UOP, Grace, Zeolyst. Academic and research institutions: SINTEF and University of Oslo, CO2CRC, Monash University/CSIRO, University of Ottawa, Georgia Tech, ETH, RTI International
- **Pathway to technology qualification**: Scale-up to pilot-scale on-site testing with real flue gases at e.g. a few tens of tonnes of CO₂/hour. Further research on adsorption materials and optimization of operating cycles is recommended
- Infrastructure required: Access to real flue gases with CO₂ concentration >10%
- **Environmental impact**: No specific impacts are expected as the sorbents are stable non-volatile solid materials that contain no trace-metals
- Applications: Power generation, cement industry, steel industry, refineries, other small industries.

4.2.5 **Temperature swing adsorption (TSA)**

In a TSA process, CO_2 is adsorbed on a high surface area material at low temperature (40-60°C) in an adsorber. Two solutions exist for the desorption process:

• The adsorbent is in a contained in two or more columns and each column undergoes a cycle with adsorbing and desorbing that leads to the release of CO₂. Energy for the desorption step is usually heat in the form of steam but electric current can also be used. The latter is referred to as electric



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swing adsorption (ESA).

• Adsorption and desorption are performed in the same column by first absorbing CO₂, followed by heating (to 80-150°C) to desorb the CO₂.

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Several materials are being tested as adsorbent for the TSA process. These include zeolites, sorbents based on sodium, silica- and alumina-based sorbents, activated carbon and polymeric hollow fiber contactors filled with CO_2 adsorbent.

An amine-impregnated sorbent developed by RITE and NAIST of Japan has been tested successfully in a moving-bed system utilizing low-temperature steam. The system (KCC) has been designed by Kawasaki Heavy Industries and tested with promising results on exhaust gas from a 7800 kW gas engine, producing 3.2 t/h of CO₂.

TSA can be combined with a PSA)in a PTSA process where both reduced pressure and increased temperature are used to regenerate the adsorbent.

- **Maturity**: 2nd to 3rd generation; TRL 1 4 (TRL 4: the amine impregnated sorbents in a TSA moving-bed system; other sorbents mainly TRL 1-2, i.e. bench scale with real flue gases, lab scale with simulated flue gases)
- Potential for improvements:

• Energy savings: Uncertain

- Key Challenges: Depends on the sorbent but include: Increasing the CO₂ adsorption capacity of some sorbents; reducing the impact of contaminants, particularly SO_x; reducing heat of adsorption
- Some Players: RITE; NAIST and Kawasaki Heavy Industries, Japan, Adsorption Research Inc (SRI) and Inventys (Veloxotherm[™]), adsorbent producers Grace, UOP, and Zeolyst, Georigia Institute of Technology, CO2CRC/The University of Melbourne, InnoSepra, TDA Research and ETH
- **Pathway to technology qualification**: On-site testing at pilot scale with real flue gases at e.g. a few tenths of tonnes of CO₂/hour
- Infrastructure required: A CO₂ containing real flue gas preferably with CO₂ concentration < 10%. Some moving-bed concepts need the flue gas at at > 200 °C (for regeneration). The KCC system may use steam at 60 °C
- Environmental impact: No specific impacts are expected as the sorbents are stable non-volatile solid materials that contain no trace-metals
- Applications: Power generation, cement industry, steel industry.

4.3 **Post-combustions Membranes**

4.3.1 Polymeric and hybrid membranes, general

Membrane-based post-combustion CO_2 capture uses permeable or semi-permeable materials that allow for the selective separation of CO_2 from flue gas. While membranes are more advantageous for separating CO_2 in high-pressure applications, such as coal gasification, there is also significant work going on in developing highly selective and permeable membrane systems designed specifically for CO_2 separation from low partial pressure, post-combustion flue gas streams. Membranes potentially could be a more energy efficient and cost-effective technology option for post-combustion CO_2 capture than solvents or sorbents

Membranes for post-combustion capture come as polymeric, glassy as well as rubbery membranes; as



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hybrids of polymeric membranes and nano-particles; electrochemical membranes; as ceramic membranes; and as composites. Polymeric membranes have long been used in a number of industrial gas separation processes including air separation; hydrogen recovery from ammonia; dehydration of air; and CO_2 separation from natural gas. Of the polymeric membranes, rubbery membranes have higher permeability and lower selectivity, while glassy membranes have higher selectivity and lower permeability. Improvements of polymeric membrane performance may be achieved by use of chemical reactions, in which a CO_2 -reactive functionality is attached to the polymer.

Liquid membranes (LMs) are a prospective separation system consisting of a liquid film through which selective mass transfers of gases, ions, or molecules occur via permeation and transport processes. LMs can be both non-supported and supported. In the latter microporous films are used as the solid support and they are either flat sheet or hollow fiber LMs. Post-combustion membranes can be in the shape of both sheets and hollow fibers. They can be used as a contactor between the CO_{2} -containing flue gases and an absorption liquid.

The process and material design research focuses on ensuring a large driving force for sufficient flux across the membrane and membrane selectivity.

Membranes have advantages that include:

- Simple passive operation with no moving parts;
- Energy-efficient with low operating costs;
- No hazardous waste streams;
- Modular design that makes them suitable for retrofit and scale-up; and
- Simple and easy maintenance provided sufficiently long lifetime.
- Maturity:
 - $\circ 2^{nd}$ generation; TRL 5 6 (Polymeric membranes for separation of CO₂ from natural gas are commercially available but are still in need of pilot and demonstration-scale testing for post-combustion capture)
 - \circ 3rd generation; TRL 2 4 (Other membranes range from bench scale with synthetic flue gases to small-scale pilot (1 MW) stage testing with real flue gases)
- Potential for improvements:
 - Energy savings: May be up to 50%
- **Key Challenges:** Increase and prove long term membrane stability; increase selectivity and permeability for the low partial pressure of CO₂ in the flue gas from power production to reduce compression work and need for multi-stage membrane design may be required; optimize process design
- Some Players: Membrane Technology and Research Inc., RTI International, NTNU, SINTEF, University of Twente, New Jersey Institute of Technology, FuelCell Energy, General Electric, Ohio State University, Gas technology Institute, American Air Liquide, University of New Mexico, Carbozyme, CO2CRC
- **Pathway to technology qualification**: Continue material development and better understanding of membranes other than polymeric. Scale-up to pilot and thereafter small-scale demonstration on-site with real flue gases at e.g. a few tonnes of CO₂/hour
- **Infrastructure required**: The concept can utilize the existing infrastructure for post-combustion capture as found at many larger test facilities. Some modifications will be required
- Applications: Power generation, cement industry, steel industry, other small industries.



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4.3.2 Polymeric membranes combined with low-temperature separation

This is a hybrid system where the stream with a high concentration of CO_2 from a polymeric membrane is sent to a low temperature "cryogenic" unit to obtain high capture rates and CO_2 transport specifications. Another concept operates also the membrane at low temperature (-25 °C to - 45 °C), as membrane selectivity and permeance increases significantly at these temperatures.

- Maturity:
 - $\circ 2^{nd}$ to 3^{rd} generation; TRL 3 5 (Hybrid concept, membranes at somewhat higher level).
- Potential for improvements:
 - Energy savings: 50% or perhaps more
- **Key Challenges**: For membranes as described in 4.3.1; for the refrigeration system bringing down energy requirements and improve membrane performance (peremance and selectivity)
- Some Players:
 - Membranes: Membrane Technology and Research Inc (MTR), RTI International, Air Liquide, NTNU, University of Twente, NJIT, Monash University.
 - Low-temperature CO₂ purification: Air Liquide, Air Products and Chemicals Inc., Praxair, Linde Engineering
- **Pathway to technology qualification**: Perform pilot tests on the membrane systems at 1 10 MW. As the low-temperature systems have been are being tested at the pilot scale, the hybrid system will/can be tested at pilot scale once the membranes are qualified at pilot scale
- Infrastructure required: The concept can utilize the existing infrastructure at TCM but cooling possibilities down to 130 °C must be added
- Environmental impact: None is expected as there are no chemicals involved
- Applications: Power generation, cement industry, steel industry.

4.3.3 Molten carbonate fuel cells

Although molten carbonate fuel cells (MCFCs) are not, strictly-speaking, membranes, they are addressed in this section for ease of classification. MCFCs use carbonate salt suspended in a porous ceramic matrix as the electrolyte.Salts commonly used include lithium carbonate, potassium carbonate and sodium carbonate. They operate at high temperature, around 650 °C, and there are several advantages associated with this. MCFCs can be used to capture CO_2 . When flue gases are supplied to the cathode side of the fuel cell, rather an air, the CO_2 in the exhaust gases is transferred to the anode side if the cell. There it is concentrated, separate and liquefied for transport.

Advantage of MCFCs is that produce power while capturing the CO_2 and is scalable to the need for capture and power production.

- **Maturity**: 3rd generation/TRL 3-4 (Small scale lab)
- Potential for improvements:
 - Energy savings: Could result in efficiency increase for treated facility
- **Key challenges**: Obtain better cost end efficiency estimates;long-term operations to assess impacts of impurities on performance and operational costs; . Disadvantages associated with MCFC units arise from using a liquid electrolyte rather than a solid and the requirement to inject carbon dioxide at the cathode as carbonate ions are consumed in reactions occurring at the anode. There have also been some issues with high temperature corrosion and the corrosive nature of the electrolyte but these can now be controlled to achieve a practical lifetime.
- **Some players**: FuelCell Energy (FCE). Others work on MCFCs but generally for other applications than CCS
- Pathway to technology qualification: First step is tests at larger scale



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- Infrastructure required: Foot print for units; natural gas onsite
- Environmental impact: Probably limited
- Applications: Power production, cement, steel.

4.4 Post-combustion low temperature (cryogenic) CO₂ separation from flue gases

Low-temperature separation is also known as anti-sublimation, cold separation, cryogenic separation, freeze-out separation, and frosting separation. Low-temperature separation is possible since the flue gas constituents have different freezing temperatures. The process includes the freeze-out of CO_2 and separation of the solid particles from other flue gas components through solidification on cold surfaces or through expansion of pressurized and cooled gas into the CO_2 freeze-out region. While low-temperature separation is physically possible, its cost-effectiveness is limited due to the large quantity of energy necessary to accomplish the flue gas cooling. The energy consumption is inversely proportional to the CO_2 concentration in the flue gases. Thus, cryogenic separation is not well suited for gas-fired power generation. However, using hybrid technologies, e.g., along with membrane and/or adsorbent to increase the CO_2 concentration in the feed gas looks a better possibility as explained above (4.3.2). Under any circumstances, tight heat integration is necessary to keep the energy penalty low. However, some simulations claim lower specific capture work than the conventional MEA-based capture processes.

- Maturity: 2nd-3rd generation; TRL 3-5 (Large laboratory-/small pilot-scale at 240 kg CO₂/day)
- Potential for improvements:
 - Energy savings: Competitive with MEA
- **Key Challenges**: Pilot testing is needed to determine the specific capture work and efficiency; develop hybrid technology approach
- **Some Players**: GE, Shell Global Solutions, Alstom, Eindhoven University of Technology, MINES ParisTech, CO2CRC/Curtin University, Brigham Young University
- **Pathway to technology qualification**: Process equipment is available for larger scale that hitherto tested, thus scale-up will be the natural next step
- Infrastructure required: Real flue gases are needed, power and refrigeration possibilities down to -130 °C
- Environmental impact: None is expected as there are no chemicals involved
- Applications: Power generation, cement industry, steel industry, refineries.

4.5 CO₂ enrichment in flue gases from gas turbines

The basic idea behind this concept is to recirculate part of the flue gas prior to the CO_2 capture unit to increase the CO_2 content in the flue gases, which will facilitate post-combustion CO_2 capture. Concepts with oxygen-enriched air are also envisaged for producing flue gases with a further increase in CO_2 concentration.

- **Maturity**: 2nd generation; TRL 5-6 (process optimization may be validated by 2020, turbine by mid-2020s)
- Potential for improvements:
 - Energy savings: Uncertain
- **Key challenges**: Develop optimal process configuration; obtain stable and complete combustion in CO₂- and/or oxygen-enriched atmosphere by adaptation of gas turbines



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- Some players: Turbine manufacturers
- Pathway to technology qualification: Further testing on large existing gas turbines
- Infrastructure required: None special
- Environmental impact: None
- Applications: Power production.

4.6 Hydrates

Gas hydrates are crystalline materials composed of water and gas under suitable conditions of low temperature and high pressure. When gas hydrate is formed from a mixture of gases, the component that forms hydrate most easily might be enriched in the hydrate phase. Due to hydrates having the capacity to store a large amount of gas and to separate a gas mixture, hydrate technology has attracted much attention as a potential means of capturing CO_2 . One advantage of the technology is the modest energy penalty, thus hydrate technology for gas separation seems to be cheap compared to other postcombustion capture alternatives in case of a CO_2 rich source gas. It may be competitive in application fields where the inlet gas has a high pressure such as the oil and gas industry. However, this technology is at an early stage of development and an indication of the modesty of energy penalties would be welcome.

- **Maturity**: 3rd generation; TRL 1-3 (Concept studies to bench-scale)
- Potential for improvements:
 - Energy savings: Uncertain
- **Key challenges**: Further reduction of energy consumption; increasing hydrate formation rate; improving separation efficiency; reducing induction time before hydrate production start
- Some players: IFE, University of Peruga, several research institutions in China, Technical University of Denmark, Los Alamos National laboratory, Curtin University
- **Pathway to technology qualification**: Improve computation models; improve additives; Much laboratory work is still needed
- Infrastructure required: Too early
- Environmental impact: To be investigated
- Applications: Power production.

4.7 Algae

Algae are found in fresh as well as salt water. Like plants, they draw energy from photosynthesis, using light from the sun and CO_2 from the air. They efficiently capture carbon by taking it out of the air and locking it away in solid biomass. Thus, they are considered suitable for taking the CO_2 out of flue gases. Two types of microalgae can be envisaged: (1) One type that grows rapidly and puts on sufficient weight to sink to the sea bed; and (2) a second type that can be used as a raw material for making products or as a renewable fuel itself.

Algae technologies use planktonic algae in water solution in vertical bioreactors (VBs) or in algae farms with large ponds. However, most are currently not economically viable, especially on a large scale. Limitations to these systems include: sub-optimal productivity, expensive installation, large footprint (surface area), low concentration of algae biomass, energy-intensive extraction and processing steps, high water demand and the requirement for a highly trained end-user.

• Maturity: 3^{rd} generation/TRL 1 – 3 (Small units exist for both bioreactors and open ponds, but

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amount CO₂ captured is very small)

- Potential for improvements:
 - Energy savings: Uncertain
- **Key challenges**: Reducing the need for water during production and for space; collecting the CO₂, as it is released through bubbling in the liquid phase and harvesting is difficult, time consuming and inefficient. In addition, the present operation is difficult to scale-up, leaves a large foot print, may have problems with light supply at night (open outdoor ponds), understanding impacts of trace contaminants (e.g. heavy metals) is required
- Some players: University of Bergen, University of Kentucky, CESFAC (Confederación Española de Fabricantes de Alimentos Compuestos Para Animales), partners in EU project ALGADISK, Macquarie Generation (Australia), Seambiotic, Israel, MiroBio Engineering Inc., Natural Live Plankton (NLP, www.nlp21.co.kr, South Korea)
- **Pathway to technology qualification**: Develop systems with lower water and space needs and in which CO₂ would be captured either from the gas phase directly or from the liquid phase after bubbling and with automatic and continuous harvesting. Scale-up up from small pilot to large demonstrations
- Infrastructure required: Flue gas with CO₂, water supply and, for ponds, space
- Environmental impact: Open ponds have high risk of contamination. Using lakes or ocean areas may be controversial. Open ponds require large amounts of water and land. To be investigated more for bioreactors. Ethical, esthetical, legal and societal aspects must be analysed.
- Applications: Power generation, industry.

4.8 Supersonic post-combustion inertial CO₂ extraction system

This process, inertial CO_2 extraction system (ICES), is based on the principle that aerodynamic expansion to high velocity converts potential energy contained in the form of pressure and temperature into kinetic energy. The conversion results in condensation of undesirable constituents of flue gas including the desublimation of CO_2 . The high density of the solid phase constituents of the flow allows for inertial separation by centrifugal forces induced by flow path curvature.

ICES does not require external media or chemical processes and, due to high flow velocity, will have a very small system volume compared to membrane systems. It also has the ability to achieve steady capture conditions very rapidly after start-up. The ICES has a footprint approximately 25 percent the size of an equivalent amine system, is readily scalable, reduces parasitic plant load from capture and compression, and includes steps for capture, purification, and highly efficient pressurization.

- Maturity: 3rd generation; TRL 1 2 (Concept stage for CCS but commercialized in another application)
- Potential for improvements:
 - Energy savings: Uncertain
- Key challenges: To generate CO₂ particles greater than approximately 2.5 µm in effective diameter to ensure efficient inertial migration; verify CO₂ particle growth to a size that permits them to migrate to a compact layer adjacent to one wall where they can be readily removed by a boundary layer capture duct. Confirm the feasibility of the inertial CO₂ separation in a compact device without any moving parts or consumables
- **Some players**: Alliant Techsystems Operations, ACENT Laboratories, the Electric Power Research Institute and Ohio State University
- **Pathway to technology qualification**: A detailed laboratory-scale investigation and analysis of the mechanisms underlying CO₂ condensation, nucleation, and particle growth. A bench-scale testing



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of the complete ICES incorporating the selected particle growth method with the optimized capture duct and diffuser systems to enable the integrated testing of CO_2 condensation, migration, removal, and flow diffusion

- Infrastructure required: Flue gases with CO₂
- Environmental impact: Needs to be investigated
- Applications: Power generation.

4.9 Pressurised post-combustion capture

It may be possible to use a coal-fired pressurised fluidised bed boiler in post-combustion capture applications to take advantage of much higher partial pressures of CO_2 . Energy would be expended in compressing air into the boiler and would be recovered by re-expanding the flue gases after CO_2 capture. Efficiencies increase with increasing starting temperature for this expansion.

A similar process could work for a gas turbine-based power plant whereby the capture of CO_2 would occur at high pressure prior to expansion. The proposal is to use hot potassium carbonate as the absorption medium. The hot flue gases have first to be cooled to about 100°C before entering the capture plant but is reheated using heat exchange so that most of the heat is recovered. The pressurised gas, scrubbed of CO_2 , is then expanded to generate power.

- Maturity: 2nd 3rd generation; TRL 2 5
- Potential for improvements:
 - Energy savings: Uncertain
- Key challenges: Further work is needed to demonstrate it as a commercially competitive technology to conventional pulverised coal combustion. Also further work needs to be done to establish the overall energy efficiency of the systems with CO₂ capture. Operating the boiler at higher pressure also increases air leaks, leading to losses. Further, there might be a maximum pressure after which there is no real improvement in efficiency or the parasitic load of CO2 capture because a lot of the CO2 will be removed before the turbine. If potassium carbonate is used to capture CO₂, materials of construction will have to compatible. Alternatively, other sorbent/membrane technologies could be used.
- Some players: Sargas and GE; PFBC-FET
- Pathway to technology qualification: Testing at pilot scale
- Infrastructure required: Access to a power station
- Environmental impact: Needs to be investigated
- Applications: Power generation (new built, not retrofit).

It is mentioned that the pressurized fluidized bed combustion and other advanced combustion technologies which facilitate the use of alternate CO_2 capture technologies such as hot potassium carbonate or some advanced sorbents or membranes designed for high pressure and temperature.

5 Summary of identified technologies - Pre-combustion decarbonisation

In pre-combustion decarbonisation the carbon and hydrogen in the fuel are separated before combustion, i.e. the fuel is effectively decarbonised before combustion. In the case of coal or biomass, a gasification process followed by gas clean-up is necessary, in the case of gas, the fuel is reformed.



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In both cases the product is a syngas consisting mainly of hydrogen (H₂), carbon monoxide (CO) and minor amounts of other gases. A water gas shift (WGS) reaction, where steam is added to the syngas, produces a mixture mainly of hydrogen and CO₂ and the two are separated in a separation process. The process is shown schematically in Figure 2.

One advantage of the pre-combustion decarbonisation process over post-combustion CO_2 -capture, is that the CO_2 produced is released at significantly higher pressure and the CO_2 concentration is higher, thus potentially reducing the energy demand. However, energy is required for the air separation and the gasification or reforming processes, so the lowered energy demand is counteracted. The hydrogenrich gas is fed to a gas turbine for power production. Pre-combustion decarbonisation is well suited for combined production of power, liquid fuel and hydrogen.



Figure 2. Schematic illustration of the pre-combustion decarbonisation process

The CO_2 capture becomes an integrated part of the combustion process, which adds to the complexity of the system. The system integration itself is a challenge. Thus, existing power or industrial plants are not easily retrofitted with pre-combustion CO_2 capture. Due to the complex system integration pre-combustion CO_2 capture is primarily an option for new built plants.

Research and development in pre-combustion decarbonisation involves warm gas clean-up technologies; better sorbents and membranes for the water gas shift and separation processes; combined processes of sorbents and membranes, including the combination of the WGS and separation processes into one stage; a more energy-efficient air separation process; and turbines that can also be used for hydrogen-rich fuel without de-rating or fuel dilution.

Improvement in pre-combustion decarbonisation technologies will also benefit industrial applications where hydrogen production is an important element, e.g. fertilizer plants and refineries.



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5.1 **Pre-combustion capture solvents**

Solvents are commercially used to remove CO_2 (and other acid gases) from syngas (e.g. SelexolTM, based on dimethyl ether of polyethylene glycol (DEPG); Coastal AGR[®], based on DEPG; Purisol[®], based on n-methyl-2-pyrrolidone (NMP); Rectisol[®], based on methanol; and Flour SolventTM, based on propylene carbonate). Solvents for pre-combustion capture applications can be considered mature technology, e.g. used in hydrogen production for refineries and the fertilizer industry. However, these applications are often complex and may involve separation in more than one stage if hydrogen sulphide (H₂S) is present. Adequate separation of CO_2 and H₂S in the regeneration step is still a challenge, as is reduction of operation costs.

Thus, there is ongoing research and development to improve existing pre-combustion decarbonisation solvents. Identified players include CO2CRC in co-operation with the University of Melbourne, SRI International (an aqueous ammoniated solution containing ammonium carbonate, tested in pilot-scale on actual syngas) and a Japanese group from Kawasaki Heavy Industries and Research Institute of Innovative Technology for the Earth (RITE), who co-operate on the developments of a capture process with a chemical solvent called RH-x, which RITE developed for high-pressure conditions^{19,20}. RH-x is suitable for pre-combustion decarbonisation because of its capability of CO₂ regeneration at a high pressure which inlet gases have. This high-pressure regeneration will lead to lower energy consumption in CO₂ compression for transportation to a storage site and, consequently, to cost reduction in CCS operations.

5.2 **Pre-combustion capture sorbents**

5.2.1 Sorption-enhanced water gas shift (SEWGS)

The process is a multi-column process in which the columns are filled with a mixture of hightemperature WGS catalyst and CO₂ adsorbent. Syngas (containing H₂, CO₂, CO, H₂O, CH₄, and inert gases) is fed at high pressure and temperature and CO₂ is removed by the sorbent. The process almost completely converts the CO and maximises the production of H₂. CO and CO₂ are effectively removed from the feed gas, producing a high-pressure, hydrogen-rich product stream. When the adsorbent is saturated and CO₂ begins to show up in the product stream (breakthrough), the bed is taken off-line and regenerated. Regeneration is based on PSA and produces a low-pressure byproduct stream rich in CO₂. By using multiple beds and properly staggering the process cycle, the inherently dynamic process can mimic a continuous one, with essentially constant feed and product/by-product streams.

- Maturity: 2nd generation; TRL 4 5 (Pilot-scale 50 100 kg CO₂/hr)
- Potential for improvements:
 - Energy savings: Efficiency gain 3 4 % -points

 $^{^{19}}$ Nakamoto, T., T. Muraoka, S.Yamamoto, T. Higashii (2014) Study on high-pressure
 $\rm CO_2$ capture process. Energy Procedia 63 (2014) 1940 – 1943

²⁰ Yamamoto, S., H.Yamada, T.Higashii (2014) Development of chemical CO_2 solvent for high-pressure CO_2 capture (2): Addition effects of non-aqueous media on amine solutions. Energy Procedia 63 (2014) 1963 – 1971

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- **Key challenges**: Prove or long term stability of sorbents with high volumetric cycling capacity, develop alternative sorbent system operation, providing steady stream of H2 for use
- Some players: ECN (Netherlands), TDA Research, URS Group, Air Products, Korea Electric Power Corporation Research Institute (KEPCO RI) and Korea Institute Of Energy Research (KIER)
- Pathway to technology qualification: Scale-up to demonstration
- **Infrastructure required**: SEWGS is a pre-combustion decarbonisation technology working at elevated pressures (30-40 bar). A (synthetic) syngas containing CO is needed, as well as steam
- **Environmental impact**: Probably very low, as SEWGS utilizes solid adsorbents that are non-volatile and stable materials without known negative environmental consequences. Deposition of used materials should also be non-problematic (i.e. better than for cracking catalysts that contain traces of metals)
- Applications: Power generation, refineries, hydrogen production.

5.2.2 Sorption-enhanced steam-methane reforming (SE-SMR)

This technology is also called sorption-enhanced reforming (SER) or chemical looping autothermal reforming (CLR). Its purpose is to enhance the well-known steam-methane reforming process used industrially for natural gas-based H₂ production, and to simultaneously capture CO₂. The principle has much in common with calcium looping systems, where a solid sorbent, typically CaO, continuously adsorbs the CO₂ that is generated in the steam-methane reforming process, thus shifting the equilibrium of the process towards a higher hydrogen yield, while CaCO₃ is formed. CO₂ can be captured when CaCO₃ is converted back to CaO in a calciner. The CO₂ adsorption is exothermic, but the calciner process is highly endothermic, i.e. heat must be supplied, typically through direct combustion of oxygen and natural gas in the calciner. The result is an overall process that is slightly endothermic, meaning that heat must also be supplied to the reformer/carbonator. SE- SMR could enable the steam-methane reforming reaction to be carried out at lower temperatures than with conventional technology, which could lower investments and operational costs.

Studies indicate varying degree of potential for cost reductions.

- Maturity: 3rd generation; TRL 1 2 (Bench-scale)
- Potential for improvements:
 - Energy savings: Uncertain
- **Key challenges**: Further development of sorbents. Avoidance of contamination of Ni-based catalyst by sorbent and development of separation method of Ni-catalyst and deactivated sorbent. Assess where the technology can be a viable option
- Some players: IFE (ZEG Project), SINTEF, NTNU, Chalmers, Vienna University of Technology, Instituto de Carboquímica (CSIC), Spain
- Pathway to technology qualification: Scale-up to small pilot
- **Infrastructure required**: For stand-alone testing of the SE-SMR process at a pilot scale, steam is required, as well as methane or natural gas + pre-reformer. In addition, supplies of sorbent and catalyst, and disposal possibilities for deactivated sorbent is required
- Environmental impact: Ni-catalyst that is required for steam-methane reforming is poisonous, and must be handled carefully
- Applications: Power generation, refineries, hydrogen production.



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5.3 **Pre-combustion capture membranes**

Gas separation membranes use differences in physical or chemical interactions between gases and a membrane material, allowing one component to pass through the membrane faster than another. Two types of pre-combustion capture membranes are: 1) Hydrogen membranes, in which H₂ selectively passes through the membrane; and 2) carbon dioxide membranes, in which CO₂ selectively passes through the membrane. Membranes are used commercially for CO₂ removal from natural gas at high pressure. However, for CO₂ capture further development is required.

Membranes currently available for pre-combustion capture include porous inorganic membranes, metallic membranes, polymeric membranes, zeolites and carbon membranes acting as molecular sieves (i.e., H₂-permselective membranes). The membranes can be used in a range of configurations, e.g. related to where they are placed regarding the shift process.

Only metallic and ceramic membranes are described below. There are, however, a number of membranes made of other materials (e.g. polymers), which are in general at the same stage of development as metallic and ceramic membranes. Outstanding developments of highly CO₂-permselective polymeric membranes include poly(amidoamine) dendrimer / poly(vinyl alcohol) hybrid membranes being developed in Japan.

5.3.1 Metal and composite membranes

Metal-based membranes are usually based on palladium or palladium alloys that are uniquely selective to hydrogen, and they can therefore be integrated in pre-combustion capture processes to separate hydrogen from shifted syngas. The hydrogen-selective membranes have been studied for integration in membrane reactors for water-gas shift membrane reforming (WGS-MR) or steam reforming (SR-MR) reactions, allowing simultaneous high CO or methane conversion and production of pure H_2 . Advantage include the production of a high pressure CO_2 stream, reducing the need for compression energy, and high-purity H_2 for power generation. This can greatly facilitate the economics of power generation with CCS.

- Maturity: $2^{nd} 3^{rd}$ generation; TRL 3 5 (Tested using slip-streams, CO₂ capture > 100 kg/hour)
- Potential for improvements:
 - Energy savings: Efficiency gain 3 %-points
- **Key challenges**: Long-term performance and stability of membrane in real gas streams, in particular when applied in coal-derived sulphur-containing syngas. Reducing sensitivity to impurities. Production methods for reduced Pd thickness (giving lower cost and higher permeability)

Membrane and membrane reactor manufacturing equipment is required on a adequate scale
Some players: Shell, BP, Chevron, Linde Gas, Plansee, Tecnimont KT, Reinertsen AS, Pall

- Corporation, HEF, GKN, NGK Japan, MTR USA, Mitsubishi Heavy Industries Japan, ECN, SINTEF, ENEA, Worchester Polytechnical Institute, Dalian Institute, SINTEF
- Pathway to technology qualification: A test infrastructure on 1/100 scale of full-scale (membrane area 10 50 m², 1-5 MW_{th}, or 1000- 5000 t/year of CO₂ captured) could be the next step. An industrial site with realistic operating conditions is needed for validation
- Infrastructure required: Syngas, steam and nitrogen for sweep gas are required on site. Furthermore, systems for handling the CO₂-rich retentate and the H₂/N₂ stream are probably required
- Environmental impact: No known emissions issues related to membrane technology



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• Applications: Power generation, refineries, hydrogen production.

5.3.2 Ceramic-based hydrogen transport membranes

The ceramic-based membranes have the same potential applications as metallic membranes but they are made of ceramics. Important criteria for ceramic and porous inorganic membranes are selectivity, diffusion rate and tolerance to impurities. They typically operate at higher temperature than Pd membranes.

- Maturity: 2nd 3rd generation; TRL 2 4 (Laboratory-scale to very small pilot testing)
- Potential for improvements:
 - Energy savings: Efficiency gain 3 %-points
- **Key Challenges**: High flux vs. long-term stability in operation. Sealing technology and robust and low cost fabrication routes. Membrane manufacturing and assembly at large scale: ceramic processing with extrusion; coating techniques (dip-coating, spray-coating)
- Some Players: Saint Gobain, Praxair, AirLiquide; Technip, CNRS in France, Fraunhofer IKTS and Eifer in Germany; DTU-Risoe in Denmark, SINTEF; CO2CRC in cooperation with UQ ;University of Oslo and NTNU
- Pathway to technology qualification: Verify stability of membranes in contact with sealing materials and, depending on integration under real operating conditions, including exposure to various gases and contaminants (e.g. H₂S, CO₂) and sufficiently high temperatures (around 850 °C). Up-scaling of the membranes toward commercial scales is also needed
- **Infrastructure required**: On short- to medium-term time-scales, mainly laboratory- and very small pilot-scale:
 - Furnace facilities for low-temperature de-binding and high-temperature sintering of ceramics
 - Module testing: high-pressure gas infrastructures to produce and supply a hydrogen-rich gas at suitable temperatures (700-900 °C); gas chromatography for analysis; furnace for module testing at high temperature
- Environmental impact: No known emissions issues related to membrane technology
- Applications: Power generation, refineries, hydrogen production.

5.4 Low-temperature CO₂ separation from syngas

In low-temperature syngas separation CO_2 is separated from the syngas as a gas-liquid separation by cooling pressurised and dehydrated syngas to temperatures around $-50^{\circ}C$. The CO_2 -rich fluid and the H₂-rich gas are then separated by gravitational or rotational gas-liquid separators.

The advantages of this process include that it is simple, there are no chemicals involved and it produces a liquid that can be pumped to high pressures, thereby avoiding the high energy consumption and high cost of compression. A disadvantage is that the percentage capture of CO_2 is limited by phase equilibria.

Variations of the process involve combination with CO_2 recirculation (Timmins process²¹) and combination with an upstream hydrogen membrane, the latter being better suited for pre-combustion capture in natural gas-fired power systems.

²¹ http://gtr.rcuk.ac.uk/projects?ref=130767



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Low temperature separation is different from cryogenic separation for post-combustion, which occurs at around -150° C and separates CO₂ as solid particles.

- **Maturity**: 3rd generation; TRL 1 3 (Laborstory-scale as a CO₂ capture process, but most required components are commercially available, except for multistage expanders for H₂-rich gas which have been designed and tested)
- Potential for improvements:
 - Energy savings: Efficiency gain 3 4 %-points
- Key Challenges: Capture ratio depends on partial pressure of feed to low-temperature process, CO₂ freeze-out. Some H₂ will potentially dissolve in the CO₂ stream due to high pressures. High cost.
- Some Players: BP, Mitsubishi Heavy Industries, SINTEF and Eindhoven University of Technology, CO2CRC in cooperation with Curtin University
- **Pathway to technology qualification**: Laboratory- and pilot-scale tests of parts and complete process.
- **Infrastructure required:** Natural gas reformer and shift reactor. Possibilities for gas dehydration, auxiliary refrigeration (propane, ethane, CO₂ or other); insulated coldbox; power; optionally generator or turbine brake
- Environmental impact: Potentially significant advantages with respect to the environment. Since no chemicals are involved, issues and unknowns regarding emissions of chemical by-products can be completely avoided
- Applications: Power generation, refineries, hydrogen production.

5.5 Concepts for pre-combustion using fuel cells

Use of fuel cells has the potential for higher efficiency power generation. Fuel cell technologies are being improved by many companies and countries but units for large-scale power generation are not yet available. Certain types of solid oxide fuel cells (SOFC) have high energy efficiencies and they are also able to inherently capture CO_2 , which means that the incremental cost of including CCS could be low.

Some other fuel cells are designed to use hydrogen, which could be produced in plants with precombustion capture. Hydrogen fuel cells could be attractive particularly for distributed combined heat and power production, which would make hydrogen production with pre-combustion decarbonisation a more favoured technology if their cost and efficiency were better than those of combined cycle plants.

- Maturity: 2nd to 3rd generation; TRL 3 6 (Concept study, small-scale sub-system validation in relevant environments)
- Potential for improvements:
 - Energy savings: Efficiency gain up to 30 %-points relative to post-combustion capture with MEA and IGCC w/capture (assumes improved fuel cell, up to 20% %-points with baseline fuel cell)
- **Key Challenges**: Integration of SOFC with gasifier. Reduce degradation of SOFC with respect to voltage
- Some Players: NETL
- **Recommended pathway for technology qualification:** Validate all sub-systems, test SOFC with a gasifier
- Infrastructure required: Gasification facilities



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- Environmental impact: None identified so far
- Applications: Coal and biomass based power.

Another solution could be to feed hydrogen from a reforming process of natural gas (or syngas) to a solid oxide fuel cell (SOFC). One such solution is the ZEG (Zero Emission Gas,

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http://www.zegpower.no), where hydrogen is produced by sorption-enhanced steam-methane reforming (SE-SMR) using a CaO/CaCO₃ process with inherent CO₂ capture. The SOFC provides the heat required for steam methane reforming. Both electricity and hydrogen can be provided to users. Estimates show that this could be a high potential process, with more than 70% energy efficiency, if successful.

- **Maturity:** 2nd -3rd generation (Pilot-scale testing)
- Potential for improvements:
 - Energy savings: May achieve > 70% when heat and H2 production and utilization are included
- **Key Challenges**: As for SE-SMR described above plus SOFC and high-temperature heat transfer from the SOFC to the SE-SMR process. Scale-up of SOFC subject to appropriate material development
- Some Players: IFE and Prototech (ZEG Power AS)
- **Recommended pathway for technology qualification:** Must be verified at a pilot scale before considering any further up-scaling. Also the high-temperature heat transfer between the SOFC and the SE-SMR needs to be demonstrated
- **Infrastructure required:** Probably natural gas supply, handling systems for fresh sorbent and produced mixture of sorbent and Ni-catalyst, make-up water of power plant quality, and receivers of the produced electricity (and hydrogen)
- **Environmental impact:** If Ni-catalyst is employed for the SE-SMR, the handling of the mixture of deactivated sorbent and Ni must be given attention, due to the poisonous character of Ni
- Applications: Power generation, hydrogen production.

5.6 Improved pre-combustion decarbonisation technologies that do not require CO₂ capture test facilities

Several improvements can be made to elements of pre-combustion decarbonisation that do not particularly require access to capture test facilities. These include:

- **Hydrogen turbines**. The most modern high-class turbines developed for natural gas (up towards the H-class) needs to be modified so that they can operate on the hydrogen-rich fuel gases produced in the pre-combustion decarbonisation processes. The aim is to use as high hydrogen-content as possible without dilution with nitrogen or steam;
- **Gasification**. The gasification process, which produces syngas from solid fuels (i.e. coal, lignite, biomass) can be improved but this is outside the scope of this report;
- **Oxygen production for pre-combustion decarbonisation applications**. Use of oxygen rather than air in gasification and reforming has potential for improving efficiency and cost of the processes. Air separation is expensive and energy consuming, cryogenic separation being most commonly used. Using oxygen transporting membranes has the potential to improve the process. This is described in the chapter on oxy-combustion below; and
- Warm gas clean-up technologies.



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6 Summary of identified technologies - Oxy-combustion

In oxy-combustion processes the fuel is burnt in pure or almost pure oxygen rather than air. This avoids handling all the nitrogen contained in air and the exhaust is mainly CO_2 and water, which provides for a relatively simple separation by dehydration. The combustion process takes place with recycled flue gas (CO_2) or a CO_2 /steam mixture to avoid very high temperatures of oxy-combustion. The process is shown schematically in Figure 3. Depending on the fuel and its contaminants, an additional step may be needed to purify the CO_2 before compression.

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Figure 3. Schematic illustration of the oxy-combustion process

The CO_2 separation in the oxy-combustion process is straight forward, and the challenges lie within air separation and combustion. In this case the development may be along these paths:

- 1. Improve the efficiency of oxygen production;
- 2. Improve the boiler for oxy-combustion;
- 3. Improve the gas turbine for oxy-combustion; and
- 4. CO₂ processing and clean-up are also areas where improvements can be made.

These paths will not necessarily involve CO_2 capture facilities, although in some cases that will be advantageous, and are only briefly summarized at the end of this chapter. It should be noted, however, that improved efficiency of oxygen production is relevant also to pre-combustion decarbonisation.

Here we focus on a path to oxy-combustion that involves solid looping processes.

An interesting potential of oxy-combustion technologies is that it allows for CO_2 recovery of nearly 100%.

6.1 Chemical Looping Combustion (CLC)

Chemical looping combustion (CLC) is a technology that relies on combustion or gasification in an N_2 -free atmosphere. In principle this is an oxy-combustion technology with an unconventional way of producing oxygen for the combustion process.



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CLC involves two-reactors where oxygen is removed from the air in one reactor, the air reactor, using metal or other solid O_2 carriers that will quickly oxidize at high temperature. The oxidized metal is then transported together with fuel to the other reactor, the fuel reactor. Here the oxygen reacts with the fuel, producing energy and a flue gas of mainly CO_2 and water vapour.

- Maturity: 2nd generation; TRL 4 -5 (Pilot scale testing up to 3 MW but still significant challenges).
- Potential for improvements:
 - \circ Energy savings: Efficiency gain 2 4 %-points
- **Key Challenges**: Oxygen carriers able to withstand the long-term chemical cycling, improved fuel conversion, obtain complete combustion, development and optimization of reactor and overall system and process designs
- Some Players: Alstom, Total, Shell, Chalmers, TU Vienna, CSIC, TU Darmstadt, SINTEF, Vito, Ohio State University, University of Utah, Monash University, University of Newcastle, CanmetENERGY, University of Ottawa, University of Calgary, University of British Columbia, Alberta Innovates Tech Futures, University of Kentucky
- **Recommended pathway for technology qualification:** Development of oxygen carriers able to withstand the long-term chemical cycling, improved fuel conversion and combustion, development and optimization of reactor designs, ash separation, and technology scale-up. For coal CLC oxygen carriers based on low value or natural materials (e.g. steel rolling mill residues, ilmenite and limestone) are required. There is an option to develop a low-cost CLC with oxygen decoupling carrier (CLOU, in which the carrier and temperatures are selected to cause molecular oxygen release before reaction with the fuel).

Further work on CLC for coal needs to confirm optimal reactor designs and process configurations, adequate carrier lifetime and good carrier/ash separation. The next stage is for scale-up to about 10 times the current, and, although natural gas-fuelled CLC will probably be first to get there, coal CLC is catching up

Current technology focus is on systems operating at atmospheric pressure, but higher efficiency is possible at high pressure. More development work is required to develop the high-pressure technology variant

- Infrastructure required
 - Steam facility;
 - Air supply;
 - Fuel supply; and
 - Oxygen carrier supply chain.
- Environmental impact: In present state CLC fuel burn-out is not complete. Handling of particles that may contain un-healthy compounds such as metal dust is another issue. Some experience from test facilities using flue gas from FCC cracker may be relevant (In fact, the FCC cracker is a large two-reactor fluidized system with many similarities with CLC)
- Applications: Power generation.

6.2 Pressurized Oxy-Combustion

Pressurization of the oxy-combustion process results in increased cycle efficiency through recovery of the latent heat of water vapour at a sufficiently high pressure to effectively utilize the heat in the power cycle. Capital cost is reduced due to reduction in equipment size and increased heat transfer rates. Flue gas processing is simplified since various impurities such as SO_X, NO_X, O₂ and H₂O are removed much more easily at elevated pressure allowing additional reductions in capital cost.

• Maturity: 2nd to 3rd generation; TRL 2 -4 (Pilot-scale testing up to 5 MW_{th}).

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• Potential for improvements:

• Energy savings: 6+ %-point improvement

- Key Challenges: SOx management to mitigate corrosion issues, very compact heat transfer equipment at high temperature, for very high pressure systems gaseous reactants and flue gases are non-ideal (i.e. near supercritical point) which challenges CFD modelling software used for scale-up, flue gas chemistry at high pressure.
- Some Players: Alstom, GTI, Linde, CanmetENERGY, University of Ottawa, Czestochowa University of Technology, ITEA, Media & Process Technology, Florida International University, SmartBurn, Reaction Engineering International, University of Utah, Praxair, Jupiter Oxygen Corporation, Washington University.
- Recommended pathway for technology qualification: There are a variety of competing pressurized oxy-combustion technologies which are ready for qualification at ~ 1MW_{th}. The different technologies have various advantages and disadvantages which may make them most suitable for a given application and fuel it is still too early to decide which technologies will be commercialized. Some of these technologies should be selected for demonstration at the 50 to 100 MW_{th} scale by about 2020. Many of the technologies will require similar flue gas processing which differs from atmospheric pressure requirements in many respects, so a sustained effort in developing new flue gas processing methods could be complementary to the pressurized oxy-combustion technologies. Many of the technologies use pulverized fuel, so advances in solids pressurization technology, such as are under development for gasification, would be beneficial.
- Infrastructure required
 - Fuel supply
 - Oxygen supply: and
 - Pressurized flue gas processing
- Environmental impact: None expected
- Applications: Power generation and industries using steam, combined heat and power applications.

6.3 Oxygen transport membranes (OTM) power cycle

OTM technology integrates O_2 separation and combustion in one device. The membranes are ceramic tubes. OTM uses the chemical potential instead of pressure as the oxygen separation driving force. In conceptual designs, the OTM is integrated directly with the boiler. The combustion reaction on the fuel side of the membrane creates a very low oxygen partial pressure compared to the air side of the membrane. This difference in chemical potential drives oxygen through the membrane without the need for additional air compression. OTM can be used also as process heater and for syngas production.

- Maturity: 3rd generation; TRL 2 3 (Laboratory-scale, membrane materials and stack tested, rest conceptual stage)
- Potential for improvements:
 - Energy savings: Efficiency gain more than 5 %-points over NGCC w/MEA
- **Key Challenges**: Design, optimize, and test first generation OTM modules; design the unit operation process equipment, including the reactors housing the OTM modules, for both the syngas and oxy-combustion units
- Some Players: Praxair
- **Recommended pathway for technology qualification.** Pilot-scale testing and validation of process
- Infrastructure required
 - Air supply;



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- \circ Fuel supply: and
- Membrane production facilities
- Environmental impact: None expected
- Applications: Power generation.

6.4 Other elements for improving oxy-combustion

Below follow summaries of some technologies that cannot be directly classified as capture technologies but that have potential to reduce costs of CO_2 capture. The descriptions are taken from the references given in the headlines. *Maturity in terms of generation or TRL has not been included*.

Air separation and oxygen production is the major cost of CO_2 capture by oxy-combustion. Most air separation units (ASU) use cryogenic air separation and the traditional technology is considered mature. Improvements can be achieved by at least two advanced technologies: 1) Use of membranes; and 2) novel cryogenic systems.

6.4.1 O₂ separation membranes for oxygen production (IEAGHG,2014; DOE/NETL, 2013)

In the ion transport membrane (ITM) the O_2 separation is based on ionic transport in dense mixed ion and electron conducting membrane. This occurs at high temperatures (> 700 °C) in the presence of an oxygen partial pressure difference across the membrane. The membranes should preferably be very thin and will generally be fabricated as thin layers on porous structures. They are assembled in stacks of wafers. They have a potential for significant energy and cost reductions of air separation.

- Maturity: Laboratory- to pilot-scale, pilot in USA by Air Products
- **Key Challenges**: To obtain high flux vs. long-term stability in operation. Sealing technology and robust and low cost fabrication routes
- Some Players: Saint Gobain, AirProducts, Praxair, AirLiquide; Teknip, CNRS in France, Fraunhofer, IKTS and Eifer in Germany; DTU-Risoe in Denmark, SINTEF, University of Oslo and NTNU in Norway
- **Recommended pathway for technology qualification**: Testing of ITM multi-tube module (long tube -1 m long) with appropriate sealing technology in real conditions is needed. Also further development of stability of membranes in contact with sealing materials and, depending on integration, as well as exposure to various gases and contaminants (e.g. sulfur). Up-scaling of to commercial scales and commercial developing commercial-scale manufacturing methods
- **Infrastructure required**: Excluding elements connected to manufacturing: Module testing in high-pressure gas infrastructures; gas chromatography for analysis; furnace for module testing at high temperature
- Environmental impact: No direct environmental impact is foreseen through the use of OTM
- Applications: Power generation, oxygen production.

6.4.2 Cryogenic air separation (from IEAGHG 2014)

The standard industry method for cryogenic air separation is a double column distillation cycle with a high-pressure column and a low-pressure column. The columns have aluminium structured packing optimised for the purpose. This technology is mature and extensively used for oxygen production.



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An improved version has been proposed, in which a third column is introduced, operating at an intermediate pressure (IEAGHG 2005²²; Higginbotham et al, 2011²³). This is expected to have significant impact on the energy efficiency of oxygen production (see IEAGHG 2014 for more). However, the trade-off is oxygen purity.

6.4.3 Other air separation methods (from DOE/NETL, 2013)

 O_2 separation using a perovskite ceramic oxide adsorbent (composed of lanthanum, strontium, cobalt, and iron) at high temperature (800 to 900°C), the ceramic auto-thermal recovery system (CARS) by Linde represents another approach that has been assessed and pilot-tested at 0.7t/day.

6.4.4 High-pressure oxy-combustion (from SINTEF, 2013)

Cycle analyses of pressurized oxy-combustion in coal-fired boilers have shown efficiency improvements compared to atmospheric operation (which has so far been the usual approach to oxy-coal power production). The main advantages are higher heat recovery due to higher flue gas dew point temperature and reduced CO_2 compression work.

- Maturity: One 5 MW_{th} pilot plant built in Italy by ENEL
- Key Challenges: Pressurization, materials/corrosion
- Some Players: ENEL, Mass. Inst. of Tech.
- Recommended pathway for technology qualification:
 - Fundamental research on oxy-combustion at pressure;
 - System integration and optimization studies;
 - Pilot testing;
 - Demonstration of infrastructure required;
 - Oxygen production facility: and
 - Steam facility.
- Environmental impact: Limited environmental effect is expected for this technology. The exhaust goes into the transport and CCS systems and those stages will set the limit for allowable emission levels
- Applications: Power generation.

6.4.5 Oxy-combustion gas turbine (IEAGHG 2014)

Oxy-combustion gas turbines are mostly associated with the semi-closed oxy-combined-cycle (SCOCC). Component-wise the SCOCC cycle is rather similar to conventional combined cycles, but the gas turbine operates on pure oxygen from an ASU instead of air, and the working fluid is recycled CO_2 from the exhaust.

- **Maturity:** Concept stage plus laboratory-scale combustion development. The variant of Clean Energy Systems (CES) is at a stage of several MW but is more like a steam/oxy cycle. Net Power and partners to test the Allam cycle at 50 MW_{th}
- Key Challenges: Combustor design, turbomachinery heat transfer and corrosion

²² IEAGHG (2005) Oxy Combustion Processes for CO₂ Capture from Power Plant. Report number 2005/9

²³ Higginbotham, P., 2011. Oxygen supply for oxyfuel coal CO₂ capture. 2nd Oxyfuel Combustion Conference, Yeppoon, Australia, September 2011.

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- **Some Players**: Siemens, SINTEF, Lund University, CES, NET Power in collaboration with Toshiba, CB&I and Exelon
- Recommended pathway for technology qualification: An oxy-combustion demonstration plant of the size 10 – 50 MW_e with a single gas turbine for a power generation plant could be an adequate size in the time frame 2014-2016. Demonstrate new oxy-combustion dedicated turbomachinery and retrofitting capability of the technology. Test burner/combustor or turbomachinery. Test host material and cooling programs in relevant environments, necessary for the development of HP turbine
- **Infrastructure required:** For full-scale testing of the technology (i.e. a complete gas turbine with condenser and recirculation of CO₂) a feed of oxygen must be supplied by an ASU of a capacity of ca. 300 kg O₂/hr per MW of thermal power. If components like combustor/burner or turbomachinery are to be tested, a large supply of CO₂ is necessary and other test facilities could supply it from the other capture plants
- Environmental impact: Emission levels of non-climate pollutants such as NO_x and SO_x are the low mostly. The oxygen separation unit is a thermodynamic process and the CO₂ is separated from the exhaust gases by condensation, therefore no chemicals are involved
- Applications: Power generation.

6.4.6 Oxy-combustion boilers (from IEAGHG 2014)

Currently, technologies for oxyfuel combustion for PF (pulverized fuel) or CFB (circular fluidized bed) coal-fired power plants have reached the necessary maturity ready for large scale demonstration (i.e. $100 - 400 \text{ MW}_e$). This is a crucial step to bring this technology forward and achieve the goal of commercialisation by a 2020-2030 horizon. The large-scale demonstration is an important step to sustain the current R&D investment and activities necessary to develop technologies and key components that would lead to cost reduction and improve efficiencies. Some key areas that could be the main focus of future development for oxy-combustion include:

- Materials development contributing to the understanding of the impact on the boiler materials, welding, etc. when operating under oxy-combustion conditions;
- Enabling the use of warm recycled flue gases to increase efficiency (i.e. materials development along the flue gas recycle path); and
- Development of low flue gas recycle rate and high oxygen content in the furnace for CFB only.

6.4.7 CO₂ processing and clean-up (IEAGHG 2014)

The CO_2 processing unit (CPU) is the purification step of the CO_2 -rich flue gas before its delivery to the storage site. The CPU and its development could be sub-divided into three key areas namely:

- Pre-treatment of the CO₂-rich flue gas from the oxyfuel boiler (i.e. removal of SO_x, NO_x, particulates, Hg and water);
- Inert gas removal via a cryogenic process and the use of an auto-refrigeration cycle using impure CO₂ as refrigerant; and
- Development of the process for additional recovery of CO₂ from the CPU vent.

Several major vendors, e.g. Linde, Praxair and Air Liquide, are working to improve all or some of the key areas, see e.g. IEAGHG (2014).



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7. Other new emerging concepts

Several new concepts that are not yet described in detail in open literature have recently received funding. Some Norwegian concepts are briefly described below:

- The CARBOMAG-project by SINTEF and NTNU combines nano-technology with magnetic separation to remove CO₂. Use of magnetism to capture CO₂ has the potential to reduce costs by more than 50% compared to technologies that are in use today. The capture plants can be significantly more compact;
- Combining other promising technologies may lead to step changes. The two technologies chemical looping oxygen production (CLOP) and chemical looping combustion (CLC) each have the potential for high efficiency in power production with CCS. SINTEF is looking at the possibility to produce oxygen by use of metal oxides for gasification and further for combustion of produced syngas;
- Combination of 3rd generation solvents and membrane contactors may lead to savings in energy consumptions for CO₂ capture. The solution by NTNU may also lead to a capture solution with low environmental impact that can be scaled-up in a relatively short time; and
- Liquid crystals that may function both as capture, transport and storage medium have been proposed by NTNU and the University of Bergen. The proposed method may lead to an integrated solution for the CCS chain.

8 Test facilities and their capabilities

This chapter will briefly summarize the capabilities of some test facilities for CO_2 capture technologies. Two distinct kinds of test facilities are considered, as follows:

- Independent test facilities are plants that ideally are independent of technology vendors and developers and of are capable of and willing to test technologies on a neutral basis. Requirement on size is that they are larger than bench-and laboratory-scale. Ideally, they will be connected to a power or industrial plant and be able to test on real flue gases but this is not a strict requirement; and
- Dependent facilities are built to test one specific capture technology and are closely linked to one technology provider. Their size may vary from a few hundred kW up some tens of MW.

The descriptions below are based on web searches and are not comprehensive

8.1 Independent test facilities

8.1.1 The International CCS Test Centre Network (ITCN)

ITCN is a network of five test facilities that have the ability to test some kind or another of capture technologies at scales ranging from a few tens of tonnes CO_2 per year up to more than 50,000 tonnes CO_2 per year. With one exception they are committed to test technologies from more than one vendor. Brief descriptions of the member facilities follow below:

National Carbon Capture Center, USA:

- Operated by Southern Company
- Cost-effective, flexible test bed to demonstrate and develop pre- and post-combustion CO₂ capture technology in an industrial setting with coal-derived gas

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- Post-combustion:
 - Multiple test bays available up to a flue gas capacity equivalent of $4.3 MW_e$ (flue gas stream ~ 17,000kg/hr)
 - \circ CO₂ concentration in flue gases 14%, may be diluted with air to 3%
- Pre-combustion:
 - \circ 6.3MW_e Trig gasifier
 - Air- and O₂-fired syngas
 - Syngas stream 750kg/hr
- Infrastructure: Water and electricity available
- Partners US DOE, EPRI, Duke, AEP, Luminant, Arch Coal and Cloud Peak Coal.

CO₂ Technology Centre Mongstad, Norway:

- Two sites for testing post-combustion technologies: amine and chilled ammonia
- One site available for other technologies
- Two flue gas sources, refinery and combined heat and power (CHP)
- Refinery FCC flue gas: CO₂ concentration 12 14%; flue gas stream 22 50,000Sm³/hr; CO₂ capacity 80,000 tonnes captured per year
- CHP gas turbine flue gas: CO₂ concentration 3.5 9%; flue gas stream 28 56,000 Sm³/hr; CO₂ capacity 20 000 tonnes captured per year
- State-of -the-art on-site laboratory, workshop and central control rooms
- Infrastructure: Water and electricity available
- Owned by the Norwegian state (represented by Gassnova), Statoil, Shell and Sasol.

Shand, Canada:

- Flue gas from 300MW_e coal-fired (lignite) unit at SaskPower's Shand Power Station
- Amine-based post-combustion capture (Mitsubishi Hitachi Power Systems) with capacity for 45,000 tonnes of CO₂ captured per year
- Technical support including on-site and central laboratory and engineering staff with commercial CO₂ capture experience
- Infrastructure: Water and electricity available
- Available for other tests in 2017, also other capturing technologies
- Owned by SaskPower.

Wilhelmshaven, Germany:

- CO₂ capture process based on Fluor Econamine FG plus Technology
- Treating real coal-fired power plant flue gases
 - Capacity of 25,000 tonnes CO₂ captured per year
 - Slip stream 16,000 Nm³/year, CO₂ concentration 13 %
- Integrated into power plant operation control
- Sophisticated on-site laboratory
- Infrastructure: Water and electricity available
- Owned by E.On.

Pilot-scale Advanced Capture Technology (PACT) facilities, UK:

- Treating flue gases from coal-, gas- and biomass-fired dedicated stand-alone units (not connected to power plant)
- Flexible test facilities:
 - $\circ \quad 250 kW_{th} \ air\ /oxy\ combustion \ rig \ for \ coal\ /biomass$
 - \circ Two 330 kW_{th} gas CHP turbines (100kW_e, 170kW_{th})



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- 1tCO₂/day solvent-based capture plant
- Gas mixing facility with trace gas injection capability for synthetic/modulated flue/industrial process gas
- 1MW_{th} air-/oxy-coal combustion plant (via E.ON)
- o 150kW_{th} PF air-/oxy-combustion rig
- 50kW_{th} chemical looping facility
- \circ 750kW_{th} gas turbine burner with deposition probes
- 300kW_{th} circulating fluidized bed combustor/gasifier
- \circ CO₂ transport flow rig
- Mobile carbon capture laboratory for long-term on-site testing of capture media
- Supporting facilities
 - On-line monitoring and analytical facilities for gas and liquid
 - State-of-the-art analytical laboratories
- Infrastructure: water, gas, electricity, gas mixing.

8.1.2 ECCSEL (<u>European Carbon dioxide Capture and Storage Laboratory</u> infrastructure)

The ECCSEL consortium consists of selected 'centres of excellence' on CCS research from 10 countries across Europe. The aim is to establish and operate a new world-class CCS distributed research infrastructure (RI) in Europe. ECCSEL commenced operation in 2015 and is foreseen to contribute significantly to the development of European research and innovation capacities.

ECCSEL laboratories are basically research facilities. Many have already been used to bring identified 2nd and 3rd generation capture technologies to where they are today, and only a limited number have the size, capacity and location to demonstrate technologies at larger scales.

Some ECCSEL CO₂ capture test facilities are:

Tiller, Norway

- Post-combustion capture: Flue gases from propane burner
 - Power equivalent to 140kW gas
 - \circ CO₂ concentration 3 20%
 - Infrastructure: Absorption tower (20cm inner diameter and 19.5m height) stripper column 13.6m, electrically heated re-boiler 60kW
 - Monitoring: Accurate measurement of energy requirements, emission measurements, solvent degradation properties and other process performance parameters
 - The process is automatically operated
- Separate 150kW chemical looping rig
- Owner: SINTEF.

es.CO2, Cubillos del Sil, Spain

- Oxy-combustion
- Pulverized coal: 20MW_{th}; circulating fluidized bed: 30MW_{th}; Biomass: 3MW_{th}
- Infrastructure:
 - Flue gas cleaning system
 - Recycled gas preparation system



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- CO₂ compression and purification unit (CPU)
- CO₂ transport experimental facilities
- Fully equipped laboratory
- Owner: CIUDEN.

University of Stuttgart, Germany

- Post-combustion capture
- Calcium looping rig 200kW.

THAHRA, the Netherlands (TNO's High-Pressure Absorption Hybrid Regeneration Apparatus)

• Owner: TNO.

ETH Zurich, Switzerland

• Post-combustion, direct mineralization.

8.1.3 Other independent test facilities

Australia

- CSIRO Loy Yang Pilot Plant
 - Post-combustion capture
 - Flue gases from coal-fired power plant
 - MEA based solvents
 - Capacity 1,000 tonnes CO₂/year.

Canada

- CanmetEnergy: 0.3 MW_{th} vertical combustor facility, oxy-combustion, slip streams for pre- and post-combustion possible. 1MW_{th} under construction
- Husky Energy Pikes Peak: Post-combustion, flue gases from 14MW_{th} steam generator, capacity 15 tonnes CO₂/day, hope to expand to 150 tonnes CO₂/day. Under construction.

Italy

- CCS Brindisi CO₂ Capture Pilot Plant (not in operation as of September 2015)
- Post-combustion capture with amine
- Slipstream form 2,640MW_e coal-fired power station
- Capture rate 8,000tCO₂/year
- Large range of flue gas compositions
- High flexibility in solvent flow rate; flue gas flow rate, DCS control system, solvent inventory
- Owned by ENEL.

Poland

- Tauron in co-operation with Institute of Chemical Processing of Coal (ICPW)
 - The mobile CO₂ capture solvents and VPSA mobile unit
 - \circ Captures 1.2tCO₂/day from real flue gases
 - Column diameter: 0.3m
 - Absorber height: 14.0m
 - o Desorber height: 15.0m



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• Tested at Lagsza and Jaworzno power plants.

USA

- Environmental and Energy Research Center (EERC), Univ. of North Dakota, USA:
 - Three systems:
 - One oxy-fired that generates 140scfm of flue gases with 85% CO₂
 - Two post-combustion capture systems: solvent absorber and solid sorbent
 - Flue gases from a combustion test facility equivalent of 0.15 0.20 MW_{th} that runs on coal or biomass.

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- University of Kentucky
- University of Utah

Planned independent test facilities:

- <u>UK-China (Guangdong) Carbon Capture, Utilisation and Storage (CCUS) Centre, up to 200</u> tonnes CO₂/day post-combustion capture facility
- <u>University of Wyoming, 1MW_{th}+ post-combustion test facilty for coal-based power</u>
- <u>Carbon Management Canada Research Institutes</u>, with NORAM Engineering and BC Research to develop a new Technology Commercialization and Innovation Centre for development, scale-up and pilot testing for CO₂ capture and conversion technologies, capture facility 1tCO₂/day or <u>0.1MW_{th}</u>.

8.2 Dependent test facilities

Information marked "MIT" is taken from

https://sequestration.mit.edu/tools/projects/index_pilots.html. This web-site includes active as well as terminated projects, although some that are listed have now moved into the terminated category, such as the above mentioned Brindisi (Italy) and La Havre (France).

China

- Huaneng (Dr. Xu Shisen (2014) CCUS Progress in China. Presentation at GHGT-12, Austin, Texas, USA, October 2014)
 - 3,000 tonnes CO₂/year post-combustion capture nn Bejing
 - Verification Plant for post-combustion capture from coal and natural gas 1,000 tonnes CO₂/year (reference as above)
 - $\circ~$ 10,000 tonnes CO_2/year pre-combustion facility palladium membrane H_2/CO_2 separation system.
- Shidongkou CCS Project (MIT)
 - Company/Alliance: Huaneng Power Group
 - Location: Shanghai China
 - Feedstock: Coal
 - Size: Part of 600MW_e reactor: 0.1Mt/yr (approximately 4% of a single unit's output)
 - Capture technology: post-combustion using an amine mix (Huaneng is secretive about its capture technology).

France (MIT)

- Located at EDF coal-fired power plant at Le Havre (not in operation as of September 2015)
- Post-combustion capture on flue gases from pulverized bituminous coal plant



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- Alstom Advanced Amine Process
- CO_2 capacity 7,500 tonnes per year.

Japan

- Kawasaki Heavy Industries, Ltd. (http://injapan.no/energy2015-day2/)
 - Fixed-bed (10 t CO_2/day) and moving-bed (3 t CO_2/day) systems with own adsorbent Mitsubishi Heavy Industries (http://injapan.no/energy2015-day2/).
- Several test-, pilot- and demonstration-scale projects based on own amine technology, including Nanko Pilot Plant (K. Kadono et al., GHGT-11)
 - Location: Osaka, inside Nanko Power Station, (Property of Kansai Electric Power Co.)

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- Post Combustion Capture: Amine-based Chemical Absorption KS-1 (MHI's Solvent System)
- \circ CO2 capacity: 2 ton-CO₂ / day
- Flue Gas Flow: 600 Nm³ / hour (from a gas-fired power plant)
- Tomakomai (MIT)
 - Company/Alliance: Japanese Government and JCCS
 - o Location: Tomakomai, Hokkaido, Japan
 - Feedstock: Hydrogen production unit
 - Size: 0.2 Mt/yr (designed capacity)
 - Capture Technology: Activated amine process
- Toshiba (http://injapan.no/energy2015-day2/)
 - Location: Omuta City, Fukuoka Inside Mikawa Thermal Power Plant (Property of SIGMA POWER Ariake Co.Ltd.)
 - o Post-combustion capture amine-based chemical absorption (Toshiba's Solvent System)
 - \circ CO2 capacity: 10 ton-CO₂ / day
 - Flue gas flow: 2100 Nm3 / hour (from coal-fired power plant).
- IHI (S. Nakamura et al., GHT-12)
 - Location: Aioi, Hyogo
 - Post Combustion Capture: Amine-based Chemical Absorption (IHI's Solvent System)
 - \circ CO2 capacity: 20 ton-CO₂ / day
 - Flue Gas Flow: 4,000 Nm³ / hour (from a coal-fired boiler or a PG boiler)
- CAT1/ CAT30 (S. Tonomura, GHT-11)
 - Company/Alliance: COURSE50
 - Location: Kimitsu, Chiba, inside Kimitsu Steel Works, (Property of Nippon Steel and Sumitomo Metal Corp.)
 - Post Combustion Capture: Amine-based Chemical Absorption
 - $\circ\quad$ CO2 capacity: 1 ton-CO_2 / day / 30 ton- CO_2 / day
 - Flue Gas Flow: blast furnace gas (BFG)
- ASCOA-3 (S. Tonomura, GHT-11)
 - o Company/Alliance: COURSE50
 - Location: Fukuyama, Hiroshima, inside West Japan Works, (Property of JFE Steel and Corp.)
 - Post Combustion Capture: Pressure swing adsorption (PSA)
 - \circ CO2 capacity: 3 ton-CO₂ / day
 - Flue Gas Flow: blast furnace gas (BFG)

South Korea

• Korean Electric Power Company (KEPCO) Research Institute

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- Two post-combustion capture test facilities at power plants on slipstreams from 500MW_e power plants operating on bituminous coal:
 - Boryeong 10MW_e plant based on KEPCO RI Advanced Amine Absorbent; Captured CO₂ : 200tCO₂/day
 - Hadong 10MW_e plant based on KEPCO RI Solid Sorbent; Captured CO₂ : 200tCO₂/day.
- KIER has $2MW_e$ coal-fired power plant which provides spaces for laboratory-scale CO₂ capture units that can be connected with real flue gases from a coal-fired CFB boiler.
- Korea has also completed 1MW (not known if thermal or electric) warm gas clean-up test facility with 0.1MW (ditto) pre-combustion CO₂ capture test-bed slipstreamed from either a 20t coal/day gasifier or, later, the Taean 300MW_e IGCC in September, 2015. These technologies for IGCC use solid sorbents and fluidized-bed processes.

UK

- Doosan Babcock Ltd:
 - o Location: Renfrew, Scotland
 - OxyCoal Clean Combustion Test Facility (CCTF): Single full-scale (40MW_{th}) burner test facility (air- or oxy-combustion mode)
 - \circ Emissions Reduction Test Facility (ERTF): 160kW_{th} combustor (air- or oxy-combustion mode) fitted with FGD and amine-based post-combustion capture (1tCO₂/day).

USA

- Big Bend Station (MIT):
 - o Company/Alliance: Tampa Electric, Siemens
 - Location: Big Bend Power Station, Ruskin, Florida, USA
 - Feedstock: Coal
 - Size: 1MW_e (slipstream from 1,892 MW_e power station)
 - Capture technology: Post-combustion (Siemens POSTCAP technology).
- Plant Barry (MIT):
 - Company/Alliance: Southern Energy, Mitsubishi Heavy Industries (MHI), Southern Company, SECARB (US DOE's Southeast Regional Carbon Sequestration Partnership) and Electric Power Research Institute
 - Location: Plant Barry power station, Mobile, Alabama, US
 - Feedstock: Coal
 - Size: Stage 1: 25MW_e slip stream (0.15MtCO₂/year)
 - Stage 2: 160MW_e: 1MtCO₂/yr (TBD if phase 2 will go ahead)
 - Capture Technology: MHI amine based process called KM-CDR, and utilizes MHIA's KS-1 solvent.
- Polk Station (MIT):
 - o Company/Alliance: Tampa Electric, Siemens
 - o Location: Big Bend Power Station, Ruskin, Florida, USA
 - Feedstock: Coal
 - \circ Size: 30% side stream from 250MW_e
 - Capture technology: IGCC pre-combustion (Siemens POSTCAP technology).
- E.W. Brown (MIT):

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- Company/Alliance: University of Kentucky Center for Applied Energy Research (UKCAER)
- Location: Kentucky Utilities Company's E.W. Brown Generating Station, near Harrodsburg, Kentucky, USA
- Feedstock: Coal
- \circ Size: 2MW_{th}
- \circ Capture technology: Post-combustion, a new system testing an innovative heat integration method that will utilize waste heat from a carbon capture system for heat. The process also implements a concept with the heat integration that increases the solvent's CO₂ capture rate and capacity in the scrubber.

9 Summary and recommendations

9.1 Summary

This report describes efforts to identify emerging technologies $(2^{nd} \text{ and } 3^{rd} \text{ generation})$ of CO₂ capture and identify potential testing facilities that can help bring the technologies out of laboratory- and pilot-scale testing to demonstration-scale testing, i.e. capture rates in the order of 100 tonnes per day and more.

The study is based on a literature and web review of the status of emerging (2^{nd} and 3^{rd} generation) CO₂ capture technologies and existing test facilities. It was performed jointly by the CSLF Policy and Technical Groups. Neither the inventory of emerging technologies nor of test facilities can be regarded as complete.

Around 30 groups of 2^{nd} and 3^{rd} generation (emerging) CO₂ capture technologies have been identified. Most are 3^{rd} generation, i.e. with Technology Readiness Level (TRL) of 1 - 3(4), and must therefore be classified as tested at laboratory- or bench-scale only. A minority is classified as 2^{nd} generation, i.e. TRL 4(5) – 6. The results are summarized in Table 1 below.

Table 6 summarizes identified emerging $(2^{nd} \text{ and } 3^{rd} \text{ generation}) \text{ CO}_2$ capture technologies. Note that the spread in TRL for some groups reflects variations of individual technologies within the group. See Chapter 3.3 for reservations regarding the energy consumption reduction potentials.



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Table 6. Identified emerging $(2^{nd} \text{ and } 3^{rd} \text{ generation}) \text{ CO}_2$ capture technologies. Note that the spread in TRL for some groups reflects variations of individual technologies within the group.

Green=Commercial Yellow=2nd generation Light magenta=3rd generation ?=Uncertain estimates that are not quoted

Capture	Technology	Generation/	Potential for energy	Application (power
approach (Post-	group	Technology Readiness	savings	generation and
, pre- or oxy-		Level (TRL)		industry)
Combustion	A unione the second	Communially, and lable	for an annual and an	(Shall Canada Alar
Post-	Amine-based	Solutions (earlier Aker	Clean Carbon) Eluc	s (Shell Cansolv, Aker
solvents	sorvents	Linde-BASE and Alston	(1)	
solvents	Precipitating	nd rd	$10_{-}20\%$ rel MEA	Power steel cement
	solvents	2 -3 /4-6	(2, 3-3, 6, GI/t, CO)	r ower, steer, cement
	Two phase	nd rd	(2.5, 5.6, 0.6, 1, 0.0, 2)	Down staal comont
	liquid system	2 -3 /4-5	2.0-2.3 GJ/t CO ₂	Power, steer, cement
	Enzymes	3 rd /1-2(3)	30-35% rel. MEA (?)	Power, steel, cement
	Ionic fluids	$2^{nd} - (3^{rd})/1 - 4$	15 -20 % rel. MEA	Power, cement, steel
	Encapsulated solvents	3 rd /1-2	?	Power, cement, steel
	Electrochemical solvents	3 rd /1-2	Uncertain	Power, cement, steel, aluminium
Post-	Calcium looping	$2^{nd}/5-6$	Coal: Efficiency	Power, cement, steel
combustion	system		penalties 5-10%	
sorbents		rd	Gas: no benefits	
	Other looping	3 ¹⁰ /1-2	?	Power, steel, cement
	systems	rd	T T . 1 1 1 1	D
	Vacuum Drassuma Suvina	$2^{nd}-3^{nd}/2-5$	Uncertain, could be	Power, cement, steel
	(VPS)		good	
	Temperature	and a rd	Uncertain, appears	Power, cement, steel
	swing (TS)	2 -3 /1-4	limited	, ,
Post-	Polymeric	$\frac{nd}{2}$ /5.6	Fuel consumption:	Power, cement, steel
combustion	membranes	2 75-0	50% down rel.	
membranes			MEA?	
	Polymeric	$2^{nd}/2-6$	Better than above	Power, cement, steel
	membranes			
	w/cryogenic		2	D
	Other	and ard in a	?	Power, cement, steel
	(alastrophamical	2 - 5 /2 - 4		
	ceramic and			
	composites)			
	Molten		Could result in	Power, cement, steel
	Carbonate Fuel	$2^{nd} - 3^{rd}/3 - 4$	efficiency higher	, , , , , , , , , , , , , , , , , , , ,
	Cells		than base power	
	(electrochemical)		plant	
Post-	Cryogenic (low	$2^{nd} - 3^{rd} / 3 - 5$	Competitive MEA	Power, cement, steel



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combustion,	temp)			
other	Supersonic	3 rd /1-2	?	Power, cement, steel
	Hydrates	3 rd /1-3	?	Power
	Algae	3 rd /1-3	?	Power and most other industries
	CO ₂ -enriched	2 nd /5-6	?	Power
	flue gas			
	Pressurized post-	$2^{nd} - 3^{rd}/2 - 5$?	Power
Pre-combustion	combustion	Applies to commercially	available solvents, e.g	Selevol TM process and
solvents	Solvents for pre-	Rectisol® process used	in steam methane refo	rming in e.g. hydrogen
	combustion	production in the fertiliz	ing and refining industr	ries
Pre-combustion sorbents	Sorption Enhanced Water Gas Shift	2 nd /4-5	Efficiency gain 3-4 %-points	Power, (in combination with IGCC) refinery, H ₂
	(SEWUS)	rd	Appears limited in	production Power refinery H
	Enhanced Steam-Methane reforming (SE- SMR)	3 /1-2	NGCC	production
Pre-combustion membranes	Metal and composite membranes	2 -3 /3-5	Efficiency gain 3 %-points	Power, refinery, H ₂ production
	Ceramic membranes	2 -3 /2-4	As above?	Power, refinery, H ₂ production
Pre- combustion, other	Cryogenic (low temperature)	3 rd /1-3	Efficiency gain 3-4 %-points; 1 GJ/t CO ₂	Power, refinery, H ₂ production
	Concepts with fuel cells	2 nd rd 2'-3'/3-6	Efficiency gain up to 30 %-points rel. IGCC and gas w/MEA	Coal and biomass power, refinery, H_2 production
Oxygen production for oxy-combustion	Cryogenic air separation	Commercially available		
Oxy-	Chemical	$2^{nd}/4-5$	Efficiency gain 2-4	Coal power
combustion	looping		%-points (?)	
	Pressurized oxy-	rd	~35% efficiency	Coal and biomass
	combustion w/	3 /2-4	5570 efficiency	power
	Rankine Cycle	1		
	Pressurized oxy- combustion w/ Brayton Cycle	3 ^{ra} /2-4	~38% efficiency	Coal and biomass power
	Oxygen transporting membranes (OTM) power cvcle	3 rd /2-3	Efficiency gain 5 %-points over NCCC w/MEA(?)	Power



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In Table 6, the potential for energy consumption reductions vary from "very small" to "significant". However, it is important to note that the numbers are based on a literature survey and may not have been derived in a consistent manner. Furthermore, the technologies are at different levels of maturity, which will influence the uncertainties of the estimates. Factors that contribute to the uncertainties in energy consumption estimates include:

- Comparison to different baselines (old, new, unfavourable, etc. in addition to different; assumptions and battery limits);
- \circ Discrepancies in reporting efficiency changes (% relative some baseline) or energy requirements (GJ/tonne CO₂);
- The relative value of electricity vs. thermal energy;
- Discrepancies in converting the thermal energy required for CO₂ capture to useful work; and
- Limited information and testing of emerging technologies.

Cost reduction potential is not included in Table 6. In addition to the uncertainties in energy consumption estimates (energy consumption is an important operational cost) factors that will contribute additional uncertainties to cost estimates include:

- Cost unit (e.g. cost of electricity (COE), levelized cost of electricity (LCOE), cost per tonne of CO₂ captured or abated;
- Whether a technology is assessed as a first-of a kind (FOAK) processor nth of a kind (NOAK), e.g. how and to what extent capital cost reductions are included; and
- Unfamiliar production methods and materials.

It is important to be conscious of these uncertainties when choosing technologies for further development and testing.

The study has identified 11 test facilities for CO_2 capture technologies that are or will be independent of technology providers and that may be used to speed up the development of emerging capture technologies. Only two of these are sufficiently large to allow the next step in the technology development to be full-scale. The others must be classified as small-scale testing capabilities, i.e. < 10,000 tonnes CO_2 /year or the equivalent of $2MW_e$ coal-fired power. These are often run on simulated flue gases. Testing at these smaller facilities will require at least one intermediate step before going to full-scale. The majority of the identified test facilities are designed for postcombustion capture of CO_2 .

There also several test or demonstration facilities for CO_2 capture technologies that are owned by technology providers to test specific proprietary technologies. In general, these are not available for testing of other technologies. Some of these facilities are briefly described in the report.

The study revealed that the literature uses a range of definitions for technology maturity and test scales and sometimes inconsistent use of terms. For example, although it is difficult to avoid a sliding scale between the terms "pilot-scale" and "demonstration-scale" facilities, a difference in terms of the captured CO_2 has been found to vary with almost three orders of magnitude and at least one order in terms of power rating.



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9.2 Recommendations for follow-up by CSLF

Many technologies are developed by universities or small R&D companies that do not have the facilities, financial resources, and competence, to develop technologies beyond the lab or small bench scale without external support by others and access to larger test facilities. To progress the 2^{nd} and 3^{rd} generation CO₂ capture technologies further in a cost efficient manner CSLF should consider the following:

- Implement mechanisms that allow developers of emerging technologies and operators of test facilities to co-operate in mutually beneficial and cost-effective ways, e.g. help to establish biand/or multi-lateral agreements and funding mechanisms that allow emerging technologies to be tested at another nation's facilities. The International Test Centre Network (ITCN) and the European ECCSEL network initiatives are examples of how governments co-operate to increase testing capacities;
- Promote co-operation between facilities with different capabilities, both below and above $2MW_{th}$ or $(10^4 \text{ tonnes } CO_2/\text{year}, \sim 30 \text{ tonnes } CO_2/\text{day})$. This would increase the range of test opportunities and facilitate and accelerate knowledge sharing and exchange of experiences among CSLF member countries and between two or more test facilities;
- Based on the successful model of the ITCN and ECCSEL, the CSLF should encourage and facilitate enhancing the networks to cover additional regions, sectors, and levels of scale. This would help to lay the ground work to accelerate the development and testing of technologies in additional environments and facility configurations / conditions. As well, with increased membership, costs can be spread across a larger number of participants.;
- Enhance opportunities for researchers and developers to participate in extended visits and staff exchanges to other demonstration projects and test centres (six months or more) as well as training opportunities, much along the lines of the European initiative ECCSEL. This item should be co-ordinated with the re-established CSLF Academic Community Task Force;
- \circ Contribute to the derivation of a consistent terminology for new CO₂ capture technologies, maturity (2nd and 3rd generation vs. emerging or transformational; consistent use of TRLs) and for different testing scales (bench-, laboratory-, pilot- and demonstration-scale); and
- Contribute to the derivation of consistent performance indicators, e.g. common methododology for cost and energy consumption as well as test conditions that need to be represented during pilot testing that will simulate steady state, process upsets, and dynamic load following.

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The IEAGHG gave CSLF access to an interim version of their report 'IEAGHG, ''Assessment of emerging CO₂ capture technologies and their potential to reduce costs'', 2014/TR4, December 2014.'

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Abbreviations and acronyms

APGTF	Advanced Power Generation Technology Forum (UK)
ASU	air separation unit
BFG	blast furnace gas
CCS	carbon capture and storage
COE	cost of electricity
COURSE50	CO ₂ Ultimate Reduction in Steelmaking Process by Innovative Technology
	for Cool Earth 50
CPU	CO ₂ purification unit
CSLF	Carbon Sequestration Leadership Forum
DOE	Department of Energy (USA)
DRI	direct reduction iron
EC	European Commission
ECCSEL	European Carbon Dioxide Capture and Storage Laboratory Infrastructure
EU	European Union
FOAK	first-of-a-kind
GCCSI	Global CCS Institute
HSE	health, safety and environmental
IEA	International Energy Agency
IEAGHG	IEA Greenhouse Gas R&D Programme
IFE	Institute for Energy Research, Norway
IGCC	integrated gasification combined cycle
LCOE	levelized cost of electricity
NEDO	New Energy and Industrial Technology Development Organization (Japan)
NETL	National Energy Technology Laboratory (USA)
NOAK	n th -of-a-kind
R&D	research and development
TG	Technical Group (of the CSLF)
WGS	water gas shift
UK	United Kingdom
ULCOS	Ultra-low CO ₂ Steelmaking consortium
USA	United States of America
ZEG	Zero Emissions Gas Power Project, an IFE project
ZEP	European Technology Platform for Zero Emission Fossil Fuel Power Plants



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APPENDIX A - CO₂ capture from industrial sources

Cement

 CO_2 emissions from cement production stem from calcination of the raw material, the limestone, and from (fossil) fuel combustion to provide process heat. The former is responsible for more than 50% of the CO_2 emissions from a cement plant. Great efforts have been made by the cement industry to reduce the CO_2 emissions through efficiency improvements and the use of substitute clinker and fuels, including biomass and waste (for more information, see IEAGHG, 2013a).

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Post-combustion capture technologies are well suited to capturing CO_2 from cement production. They may be retrofitted to existing plants without fundamental changes in the clinker-burning process. Commercially available solvent-based technologies can be applied, as can emerging processes described above based on improved solvents, on sorbents or on membranes. The composition of the cement plant's flue gases and its impurities is an issue that needs consideration and will require tests at pilot scale. As surplus heat is usually heavily exploited in cement plants, heat for re-generation of solvent/sorbent may require a separate heat supply.

Application of calcium looping in a cement plant would create some synergies because the purge stream of de-activated calcium sorbent could be reused as raw material in the cement clinker production process.

Post-combustion capture technologies for cement production are being tested at a few locations:

- Norcem, Brevik, Norway: Several small-scale or pilot-scale trials of post-combustion capture using cement plant flue gases (2013- 2017). Companies involved in this project include Aker Solutions (amine scrubbing), RTI (dry adsorption with specialized polymers), KEMA, Yodfat and NTNU (membranes) and Alstom (calcium looping);
- ITRI/Taiwan Cement Corp.: Pilot plant capturing 1tCO₂/h from a cement plant and a power plant using a calcium looping process, commissioned June 2013; and
- Skyonic Corp. has developed the SkyMine® process. In this process, salt and water are electrolyzed to produce hydrogen and chlorine gases and sodium hydroxide solution, which is reacted with CO₂ in the flue gases to produce sodium bicarbonate, which can be sold on the market. Other combinations of chemicals can also be produced. The first SkyMine® facility opened October 2014 in San Antonio, Texas at Capitol Aggregates cement plant. To date, the plant equipped with SkyMine® technology has reduced its carbon-emissions by 15 percent 83,000 tons of CO₂ annually.

Oxy-combustion can also be used to remove CO_2 from cement production. In this process, the fuel combustion and calcination both take place in a high-purity oxygen atmosphere and the captured CO_2 is condensed out of the combustion gas. Oxy-combustion requires modification of the cement clinker process and energy to separate O_2 from air. R&D and laboratory testing is still required. A pilot plant trial of oxy-combustion in a cement plant calciner with a capacity of 2-3t/h of feedstock has been undertaken by FLSmidth, Air Liquide and Lafarge at Dania, Denmark.

Pre-combustion technologies can be used to capture CO_2 from combustion of fuel, but CO_2 generated by the calcination of calcium carbonate is released to the atmosphere without being captured. This technology is therefore at a disadvantage for cement production.



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Iron and steel

Steel mills need power plant and air separation units to support the iron and steel production processes and these are generally included as parts of an integrated steel mill. Surplus off-gases from the steel mill are typically used by the power or cogeneration plant as fuel to produce electricity or steam. The main purpose of the air separation unit is to deliver large amount of oxygen needed by both the iron making and steelmaking processes. Other industrial gases, such as nitrogen and argon, are also used as utility gases for these processes. Thus, CO_2 emissions in an integrated steel mill come from multiple point sources. However, the distribution of the direct CO_2 emissions among the different units within the integrated mill is very site specific and dependent on the manner in which the offgases are used.

For a blast furnace – basic oxygen furnace (BOF) steel mill in a coastal location in Western Europe producing 4 million tonnes of hot roll coil without CO_2 capture, the top five sources of CO_2 emissions are from the flue gases of the hot stoves, power plant, sinter plant, coke ovens' under-fired heaters and lime kilns. These sources account for ~90% of the total direct CO_2 emissions of the steel mill (IEAGHG, 2013b).

The iron and steel industry has incorporated several best practices in their operations which should improve the energy intensity and CO_2 emissions per tonne of crude steel produced. Such best practices include:

- Use of better grade raw materials input to the blast furnaces;
- Higher level of scrap recycling in the BOF steelmaking process;
- Increased utilization of the different off-gases available on-site; and
- Various energy efficiency improvements and upgrades to the different iron and steelmaking processes, including the finishing mill.

However, to achieve reductions of CO_2 emissions by more than 50%, CO_2 capture will be necessary. Recognizing the challenges associated with decarbonising the industry, the steel community has initiated several programmes to study the possibilities of CCS:

- In Japan, the COURSE50 Programme, funded by NEDO and a consortium of Japanese steel and allied industries, evaluates removal of CO₂ from the blast furnace gas (BFG) by chemical absorption with a solvent and physical adsorption using solid sorbent;
- In South Korea, the Ministry of Knowledge supports the programme POSCO/RIST, with some contributions from the private sector. The programme develops capture technology to remove CO₂ from the BFG using aqueous ammonia solution;
- In Europe, ULCOS, a consortium consisting of all major EU steel companies, of energy and engineering partners, research institutes and universities and is supported by the European Commission, has the aim to reduce the CO₂ emissions of today's best routes by at least 50%. ULCOS has pursued four options, of which three will require CCS and the fourth is based on carbon-free electricity. The three options requiring CCS are:
 - ULCOS BF or oxygen-blown blast furnace with top gas recycle, in which CO₂ removal from the BF top gas has been considering using either pressure swing adsortion (PSA), vacuum PSA (VPSA), PSA or VPSA in combination with cryogenic separation, or chemical absorption;
 - The Hisarna process, developed by ULCOS, which involves a series of gas cleaning, incinerator and heat recovery steps that eventually leads to a CO_2 -rich (90-95%) gas, from which the CO_2 is removed via cryogenic separation; and



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 ULCORED, a direct reduction iron (DRI) production method in which a H₂-rich syngas is used as reduction agent. In the gas-based version of ULCORED, a partial oxidation reactor and a shift reactor produce H₂ and CO₂. The latter is removed using PSA or VPSA. In coal-based ULCORED, gasification will have to proceed a water gas shift reactor. CO₂ can be removed using PSA, VPSA or physical absorption.

Air Products and Danieli Corus have developed a decarbonization scheme in which the CO_2 is removed from the top gas from the BF by a pre-combustion like process, using a water gas shift reactor to produce a gas rich in H₂ and CO₂, and then separating the two using a physical solvent. The CO_2 is compressed and stored and the H₂ is used in a turbine to produce power (http://www.ieaghg.org/docs/General_Docs/Iron%20and%20Steel%20Presentations/08%20Lanyi%20BF%20Plus%20for%20CCS%20Workshop.pdf).

Post-combustion like processes can be used in the DRI methods ENERGIRO and MIDREX. The former can use PSA, VPSA or amine or potassium carbonate separation technologies to remove CO_2 from the shift reactor, the latter can use PSA or amine-based separation to remove CO_2 from the top gas.

In summary, CO_2 capture technologies based on post- and pre-combustion principles are applicable to the iron and steelmaking industry.

Refineries

 CO_2 emissions from refineries come from a range of sources and are very site specific. The sources can broadly be divided into three categories:

- 1. Hydrogen production;
- 2. Fluid catalytic cracking; and
- 3. Process heaters and boilers and utilities (e.g. combined heat and power, power plant, etc.).

Hydrogen production is usually based on steam methane reforming or partial oxidation and petcoke gasification, i.e. well established technologies. CO_2 removal and storage from hydrogen production is a 'low-hanging fruit' and is presently taking place at the Port Arthur refinery, USA and planned to take place at Tomakomai, Japan and Quest in Canada (oil sand upgrader).

The largest single CO_2 emitter in a refinery is often the fluid catalytic cracker (FCC). The emissions are associated with regeneration of the catalyst and thus process- rather than combustion-related. The CO_2 concentration is usually in the range 10 - 20%. The off-gas from the FCC can be removed by post-combustioncapture technologies, as demonstrated at the CO_2 Technology Centre Mongstad (TCM), where both amine and chilled ammonia have been shown to work well. Oxy-firing has also been considered.

The third category above has much in common with general power production and has the same opportunities for CO_2 removal.

High purity sources

Several industrial processes result in high-purity and high-concentration CO_2 streams, which can be readily prepared for compression, transport and storage.

<u>Ammonia</u> is primarily used for production of fertilizers. The building blocks of ammonia are hydrogen and nitrogen. The former is normally produced from natural gas that is steam reformed and



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CO-shifted. CO_2 is removed from the process by various methods including membranes, chemical absorption using amines, PSA and physical sorbents. As in refineries, CO_2 capture from ammonia production is a 'low-hanging fruit'.

<u>Natural gas processing</u> is performed on a large scale globally to remove unwanted quantities of CO_2 from sales gas or liquified natural gas (LNG). However, the removed CO_2 is transported and stored underground in a limited number of cases. Chemical absorption is the most commonly used method to remove CO_2 , but other post-combustion capture methods may also be applied.

<u>Ethylene oxide</u> has a range of uses in the chemical industry. It is produced by the oxidation of ethylene using metallic silver as a catalyst. By-products of the process are H_2O and CO_2 . After removal of the ethylene oxide, CO_2 can easily be separated out.

Biomass conversion

The global demand for biofuels is expected to increase significantly over the next 20 - 30 years. Both of the main routes for conversion of raw biomass feedstock to biofuels, i.e. gasification and biological processing (fermentation), result in CO₂ emissions. If these emissions are captured, a net negative removal of CO₂ from the atmosphere may be achieved, given that the biomass production is sustainable and regarded as CO₂-neutral.

The gasification process creates a gas rich in H_2 and CO_2 , after the synthesis gas has been subjected to a water gas shift reaction. This process is similar to the pre-combustion decarbonization process for power plants.

The fermentation process is used to produce bio-ethanol, commonly from sugar and starches. A byproduct is a relatively pure stream of CO_2 .

The paper and pulp industry emits CO_2 from biomass combustion, with 13 - 14% CO_2 concentration. This can be removed by post-combustion capture technologies, although this is expensive using 1^{st} generation technology.

'Black liquor' is a toxic by-product of pulp and paper production. It is primarily a liquid mixture of pulping residues (like lignin and hemicellulose) and inorganic chemicals from the process (sodium hydroxide and sodium sulfide, for example). Rather than discharging the black liquor, it can be gasified to produce synthesis gas, to which pre-combustion capture technologies can be applied to remove the CO_2 .