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3 **Emerging CO₂ capture systems**

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18 **Abstract**

20 In 2005, the IPCC SRCCS recognized the large potential for developing and scaling up a wide range of
21 emerging CO₂ capture technologies that promised to deliver lower energy penalties and cost. These
22 included new energy conversion technologies such as chemical looping and novel capture systems
23 based on the use of solid sorbents or membrane-based separation systems. In the last 10 years, a
24 substantial body of scientific and technical literature on these topics has been produced from a large
25 number of R&D projects worldwide, trying to demonstrate these concepts at increasing pilot scales,
26 test and model the performance of key components at bench scale, investigate and develop
27 improved functional materials, optimize the full process schemes with a view to a wide range of
28 industrial applications, and to carry out more rigorous cost studies etc. This paper presents a general
29 and critical review of the state of the art of these emerging CO₂ capture technologies paying special
30 attention to specific process routes that have undergone a substantial increase in Technical
31 Readiness Level towards the large scales required by any CO₂ capture system.

33 **1. Introduction**

35 One important message from the IPCC SR on CCS (2005) was that a range of CO₂ capture
36 technologies were already mature and ready for large scale demonstration, because gas separation
37 processes were already operating in a mature industrial market, at scales close to those required by
38 CCS. However, there was still scope for large reductions in capture costs by optimizing these mature
39 gas separation technologies and other enabling components in the full CO₂ capture systems. Several
40 reviews in this Special Issue are devoted to analysing the recent advances of the classic “post-
41 combustion”, “precombustion” or “oxyfuel combustion” CO₂ capture systems. The IPCC SR also
42 noted that there was also potential for emerging CO₂ capture systems to compete with their more
43 mature counterparts by offering lower capture cost and efficiency penalties. This review is only
44 concerned with this second category of emerging CO₂ capture processes.

Table 1. CO₂ Capture technology toolbox, with reference to the progress of TRL from the IPCC SR (2005)

2005)

Separation process	Application	TRL*		Comments
		2005	2015	
Absorption				
Physical	Industry	9	9	Commercial technology for the separation of H ₂ /CO ₂ mixtures from syngas (<3 Mt CO ₂ /y).
	Pre-combustion	8	8	Most components are TRL 9, but hydrogen-based power generation is less mature.
Chemical	Industry	9	9	Commercial technology in refineries and for the natural gas sweetening.
	Post-combustion	7	8	Demonstrated at a capture rate of 1 Mt CO ₂ /y in the Boundary Dam CCS project.
Cryogenics				
Air separation	Industry	9	9	Commercial technology for oxygen production (<4000t O ₂ /d).
	Oxy-combustion	5	7	Combustion island has been demonstrated up to 30 MW _{th} .
CO ₂ anti-sublimation	Post-combustion	3	3	
High temperature solid looping				
Chemical looping	Oxy-combustion	3	6	Demonstrated at 1 MW _{th} pilot plant using hard coal and ilmenite as oxygen carrier
	Pre-combustion	2	3	
Calcium looping	Post-combustion	2	6	Demonstrated at a scale of > 1 MW _{th} using oxyfuel combustion-calcination
	Pre-combustion	2	2	Challenging sorbent regeneration at high pressure and temperature
Solid sorbents				
Adsorption	Industry	9	9	Commercial technology for natural gas sweetening and H ₂ production (i.e. Port Arthur CCS project)
	Pre-combustion	8	8	Most components are TRL 9, but hydrogen based power generation is less mature.
	Post-combustion	2	5	CO ₂ capture from flue gases by VPSA <2 t CO ₂ /d.
	Oxy-combustion	6	6	VPSA is commercial for oxygen production, but at low capacity (<500t O ₂ /d)
Low T G/S reactions	Post-combustion	4	6	Initial results from a 10 MW _e fluidized bed pilot
	Pre-combustion	3	5	Sorption enhanced water gas shift (SWEGS)
Membranes				
Polymeric membranes	Industrial	9	9	Commercial technology for natural gas sweetening (i.e. Sleipner CCS project)
	Post-combustion	3	5	Demonstrated at a capture rate of 1t CO ₂ /d using polymeric membranes.
Other membranes	Pre-combustion	3	3	
	Oxy-combustion	4	5	Oxygen production using ion transport membranes (5 t O ₂ /d)

*Technology readiness level (TRL): 1) basic principles observed, 2) technology concept formulated (basic process design), 3) experimental proof of concept (pilot testing of key components at small bench scale), 4) technology validated in lab (continuous operated pilots at lab scale < 50 kW_{th}), 5) technology validated in relevant environment (pilots operated at industrially relevant conditions at 0.05-1 MW_{th}), 6) technology demonstrated in relevant environment (steady states at industrially relevant environments: pilots in the MW_{th} range), 7) system prototype demonstration in operational environment (industrial pilots operating at over 10 MW_{th}), 8) system complete and

qualified (system demonstration at industrial scale), 9) actual system proven in operational environment (competitive manufacturing of full system).

Table 1 is an update of the “capture toolbox” included in the IPCC SR (IPCC, 2005), which attempts to classify capture technologies by the gas separation principle and by the classic Post-, Pre-, Oxy combustion process schemes, depending on where and how the key gas separation is carried out (CO₂ from flue gas combustion gases, H₂ or CO₂ from fuel gases, O₂ from air). The industrial applications for the current uses of these separation processes at large scale can be treated separately. The first difficulty when attempting to review the status of emerging CO₂ capture technologies is that such CO₂ capture process options are sometimes difficult to classify under just one of the previous categories. As shown in Table 1, we have adopted a classification method that serves to justify the different sections discussed in this work. Existing and novel CO₂ capture processes that rely on chemical or physical gas-liquid absorption are considered to be outside the scope of this review, as they are addressed in other review papers in this Special Issue in connection with post-combustion and precombustion systems. Oxyfuel combustion systems are the main user of cryogenic O₂, that will be reviewed separately in a different review paper this Special Issue.

The scope of this review is therefore restricted to the emerging CO₂ capture processes briefly introduced below:

- High temperature solid looping systems. These processes rely on fast gas-solid reactions at very high temperatures involving the reversible reaction of the bulk of a solid particle with O₂ (chemical looping combustion or reforming) or CO₂ (calcium looping). The fact that the gas separation takes place at very high temperature allows for efficient integration with existing steam cycle concepts for power generation. Apart from a special Network by the IEAGHG dedicated to these systems (ieaghg.org/networks/high-temperature), several hundred papers have been published in these fields in the last 10 years and substantial progress in TRL has been made.
- Solid sorbents. The main technologies under this category rely on the ability of gases to be adsorbed on a solid surface (the adsorbent). This gas separation technology is mature in a number of large-scale industrial applications, for different target gases and concentrations. However, the main focus of this review will be on its application to post-combustion CO₂ capture from power plants, where a very intense R&D effort has been made to develop suitable materials, gas-solid contactors and appropriate operation strategies. This section will also include a review of the status of other low-temperature solid sorbent systems, where a reaction between the bulk of the solid with a gas takes place.
- Membranes. These processes rely on the selective permeation of a target gas from one side to the other of a solid membrane material. This separation technology is mature in some industrial applications, but its application to the power sector for large scale CCS is still the subject of much R&D work. Polymeric membranes which target the separation of CO₂ from flue gases have experienced the greatest advance in the last 10 years but some notable advances have also been achieved with some inorganic membranes for oxygen transport membranes and the pre-combustion separation of CO₂ from H₂.

The number of specific CO₂ capture process schemes to be considered under the previous categories is very large. Different processes emerge from combinations of the few gas separation principles mentioned above, adapted to different fuels, different target separation gases (CO₂, O₂ or H₂), and different industrial settings. Furthermore, substantial changes in the process may be needed for different functional material properties or when different lay outs for mass and thermal integration are implemented. It is therefore unavoidable in a review on emerging CO₂ capture processes to be very selective. We have tried to use as a guide of selection the Technical Readiness Level scale as indicated in Table 1. This shows substantial differences in the progress in TRLs of emerging technologies in the last 10 years. How to apply this scale is of course open to debate. As active

scientists developing a range of these emerging capture systems we may have different views on the prospects of some of these technologies and we may share the scepticism of many in the CCS community regarding their final ability to deliver a breakthrough in CO₂ capture cost. Therefore, the objective of the general review conducted in this manuscript is not to pick winners but to discuss in a brief and transparent way the fundamental design issues behind these emerging technologies. We will also report on their progress in the last 10 years and provide evidence to support the idea that some of these processes could actually be major players in the future if CCS ever achieves widespread deployment.

An added value of the current document with respect to other specialized reviews available on the emerging process routes derives from our deliberate focus on a wide system perspective when reviewing individual technologies. Following the wording of the IPCC SR in 2005, we intend to provide in this document a “clear scientific view on the current state of knowledge” of some emerging CO₂ capture technologies that could become relevant technologies for climate change mitigation. The first consequence of this “full system approach” is that any emerging concept needs to be conceived from the beginning to operate at very large scale (of the order of several MtCO₂/y per plant).

Figure 1. Simplified mass and energy balance in a CO₂ capture system.

Mass and energy conservation laws (Figure 1) dictate some necessary conditions for any novel CO₂ capture system, or key piece of equipment, or functional material within such system. Since the carbon flow entering the capture system (F_c) is large (1 MtCO₂/y translates into a minimum of $F_c=720$ molC/s in continuous operation) it should be possible to approximate the scale of the capture system (“volume” or “surface” required for the key reactor(s) or gas separation device(s) within the capture system) by assuming there is some knowledge of the “characteristic reaction time”, t^* , or “contact time”, or “residence time” of material flows stoichiometrically linked to F_c . The meaning of t^* varies depending on the process: for a system involving gas-solid reactions it is linked to the time required to achieve a certain molar conversion. For systems involving membranes this time is related to the inverse of the product of permeability and selectivity for a certain gas. Only capture processes with very short t^* are viable in practice for large scale CO₂ capture, while those needing high values of t^* are likely to require very large (and most likely very costly) devices to achieve the desired conversion and/or separation efficiency in the capture system. An example of a process scheme that received a lot of attention during the IPCC SR and has progressed little because of the limitation imposed by the unavoidable character of the mass balance in Figure 1 is the *exsitu* mineral carbonation process (Mazzotti et al., 2005). Since the reactions times required to achieve reasonable carbonation conversions of the most common natural minerals are of the order of one hour, extremely large reactor volumes would be needed to achieve the desired mineral conversions. Alternatives to accelerate these reaction rates come with their own energy and environmental challenges. As a consequence, and to the best of our knowledge, only niche applications involving

the fast carbonation of very active industrial residues have provided credible opportunities for overcoming this fundamental difficulty with *exsitu* mineral carbonation processes.

For the emerging CO₂ capture systems reviewed in this work, experts in the different fields of emerging CO₂ capture processes can usually apply well established design rules, derived from similar chemical engineering applications, to rule out the viability of some CO₂ capture options that involve too slow, too inefficient or too energy-consuming reactions or associated unit operations. The same expertise can be used to demonstrate that some novel concepts are much closer than anticipated to large scale demonstration, because they rely on mature enabling technologies and expertise already available in the chemical and/or power sectors. The following sections present a brief review of the state of the art of key emerging CO₂ capture technologies that fall into this second category.

2. Chemical looping

Chemical-looping combustion (CLC) is a new combustion process with inherent separation of the CO₂ greenhouse gas. The concept uses a metal oxide in the transfer of oxygen from combustion air to the fuel and hence, a direct contact between air and fuel is avoided. Two inter-connected fluidized beds, a fuel reactor and an air reactor are commonly used in the process. The outlet gas from the fuel reactor ideally consists of CO₂ and H₂O, the latter easily removed by condensation. Over the last years considerable research has been conducted on CLC with respect to reactor design, oxygen carrier development and prototype testing. Presently, more than a thousand materials have been tested in the laboratory, and the process has been successfully demonstrated in actual operation in chemical-looping combustors in the 300 W – 1 MW size range, using oxygen carriers based on oxides of the Fe, Mn, Cu, Ni, Co metals. The total time of operational experience exceeds 7000 h. From this testing, it can be established that >99% conversion of the fuel can be obtained and that 100% CO₂ capture is possible using gaseous fuels. Similar high performance is not reached for solid fuels, but the use of solid fuels in CLC nevertheless appears attractive considering the low energy penalties and costs (see 2.5).

The fundamental advantage of chemical-looping combustion is that CO₂ is inherently separated from the other flue gas components, that is N₂ and unused O₂; thus, no energy is expended for the gas separation nor is any gas separation equipment needed. The CLC system is composed of two reactors, an air and a fuel reactor, as seen in Figure 2. The fuel is introduced to the fuel reactor, which contains a metal oxide, Me_xO_y. The fuel and the metal oxide react according to:

The gas stream leaving the fuel reactor contains CO₂ and H₂O, and when H₂O is condensed a stream of CO₂ is obtained. The reduced metal oxide, Me_xO_{y-1}, is transferred to the air reactor where it is regenerated per reaction (2):

The air which regenerates the metal oxide produces a flue gas containing only N₂ and some unused O₂. Depending on the fuel and metal oxide used, reaction (1) is normally endothermic, whereas reaction (2) is always exothermic. The total amount of heat emanating from reactions (1) and (2) is identical to that of normal combustion. The advantage of chemical-looping combustion over normal combustion is that CO₂ is not diluted with N₂ but obtained in a separate stream without the need for any active gas separation.

The lower temperature level and absence of flames means that no thermal NO_x is formed. If the fuel contains nitrogen, fuel- NO_x will form in the fuel reactor, which if removed from the CO_2 stream means that NO_x emissions may be avoided. Similarly, the gas stream from the fuel reactor will also contain SO_2 from the fuel sulphur. With respect to control of emissions it should be a significant advantage to have the NO_x and SO_2 highly concentrated in the small CO_2 stream.

The metal oxides used for the transfer of oxygen are called oxygen carriers. The reactor system is made up of two interconnected fluidized beds, which consist of the oxygen-carrier particles that are circulated between the two beds, Figure 3. There are many possible solutions for connecting the two beds in CLC, although most designs use a high velocity riser to transfer the particles to the other reactor via a cyclone. The air reactor is normally used as the riser as in Figure 3, where particles are transferred from the riser and cyclone to the fuel reactor via a loop seal. The fuel reactor in Figure 3 is a bubbling fluidized bed, although a circulating fluidized bed would likely be used at larger scale. The return to the air reactor in Figure is via an overflow exit, but there are several other options. Important to the function of the system are the two fluidized loop-seals preventing gases in the air reactor and the fuel reactor from mixing.

Figure 2. Chemical-looping combustion. $\text{Me}_x\text{O}_y/\text{Me}_x\text{O}_{y-1}$ denotes recirculating oxygen carrier material.

Figure 3. CLC process, exemplified by two interconnected fluidized reactors. 1) air reactor and riser, 2) cyclone, 3) fuel reactor, 4) loop seals.

CLC was first introduced by Lewis et al. as way to produce pure CO_2 from fossil fuels (Lewis et al., 1951). Much later Ishida et al. proposed the use of chemical-looping combustion as a means to mitigate global warming, started to investigate oxygen-carrier materials (Ishida et al., 1994) and introduced the name of the process, Chemical-Looping Combustion (Ishida et al., 1987). A design based on the circulating fluidized bed principle was presented in 2001, Figure 3; the study investigated the critical design parameters of such a system, including the solids inventory and the recirculation rate of oxygen carriers between the reactors, and identified the relationship between these parameters and the oxygen carrier properties (Lyngfelt et al., 2001).

A number of reviews related to chemical-looping combustion have been published in the past few years. Hossain and Lasa (Hossain, 2008) focus on oxygen-carrier materials, whereas Fang et al. (Fang, 2009) gives a broader overview of the technology. Lyngfelt et al. (Lyngfelt et al., 2008) reviewed studies of more than 600 oxygen-carrier materials and an update of this work adds 300 materials (Lyngfelt et al., 2011). The design of existing chemical-looping combustors and the results from operation of these using various oxygen-carrier materials are presented by Lyngfelt (Lyngfelt, 2011).

Moreover, a book on chemical-looping systems has been published by a team at Ohio State University (Fan, 2010). A comprehensive review, covering most aspects of CLC, comes from ICB-CSIC in Zaragoza, Spain (Adánez et al., 2012), and yet another general review is provided by Lyngfelt (Lyngfelt, 2013). Furthermore, an additional book on “looping” technologies with seven chapters dedicated to chemical-looping will soon appear (Fennell et al., 2015). There are also reviews of oxygen carrier materials for CLOU (Imtiaz et al., 2013), chemical-looping combustion of solid fuels (Lyngfelt, 2014a) in addition to chemical-looping-based process concepts (Moghtaderi, 2012). Excellent overviews of various aspects of chemical-looping are also provided in a number of PhD theses.

Chemical-looping processes have also been proposed, in which the principle of oxygen transfer is used for purposes other than full combustion, e.g. chemical-looping reforming and chemical-looping gasification processes. The desired properties of the chemical-looping materials are dependent on both the fuel and the application, and an overview of important applications is provided below.

2.1 Main process routes under development

2.1.1 Combustion of gaseous fuels

Gaseous fuels can be used directly as the fluidizing medium of the fuel reactor. Important gaseous fuels, such as natural gas and refinery gas, contain large fractions of methane. Thus, early oxygen carrier development focused on oxygen carriers having high reactivity towards methane. Although the chemical-looping process itself has no direct energy penalties, the application to gaseous fuels will not necessarily yield a highly efficient power plant, because power plants burning natural gas normally utilize the combined gas-turbine/steam-turbine process with utmost efficiency. To reach similarly high efficiencies using chemical-looping combustion, it would be necessary to develop chemical-looping combustion for pressurized conditions. Although pressurized fluidized bed combustion is an existing technology, pressurized CLC would nevertheless require significant development efforts and while adding complexity and costs to the process. Similar comment would apply to novel proposals making use of complex arrays of packed bed reactors. Moreover, it is unclear whether it is possible to reach the high gas turbine inlet temperatures, typically 1200°C, required to attain the highest energy efficiencies. Normally, oxygen carriers are tested at temperatures below 1000-1050°C. However, there are applications for using gaseous fuels other than power production, such as steam generation and hydrogen production.

2.1.2 Combustion of liquid fuels

Liquid fuels comprise a range of liquids with varying compositions and physical properties. The fuels of greatest interest for chemical-looping combustion are the less costly heavy fuel oils. Steam and/or recycled CO₂ could serve as a fluidizing gas, and systems for injecting and distributing the liquid fuels across the bottom cross-section of the fluidized bed are needed. A possible solution might be to use a volatiles distributor, originally proposed for solid fuels (Lyngfelt, 2014b). The minor operational experience presently available using liquid fuels includes operation of kerosene in a 300 W unit, and fuel oil in a 10 kW unit (Moldenhauer et al., 2014).

2.1.3 Combustion of solid fuels

CLC research initially used gaseous fuels, but the pilots taken into operation in the last few years have all been using solid fuels, thereby clearly indicating a shift in focus. First to study solid fuels for CLC was Lewis et al (Lewis et al., 1951) using copper and iron oxides; almost fifty years later research was restarted and presently there are a number of publications covering both laboratory work actual operation in smaller pilots, Section 2.3.

CLC with solid fuels would use the circulating fluidized bed concept shown in Figure 3, but the fuel reactor system needs to be adapted for the use of solid fuels. Testing in smaller pilots shows that the use of solid fuels is feasible. When using solid fuels, the fuel particles release combustible gases called volatiles when heated. The volatiles can react directly with the oxygen carrier in contrast to the char remaining after devolatilization which has to go through an intermediate gasification step, Figure 4. This step is determinant for the fuel reactor design, and the following three indicators are useful to evaluate fuel reactor performance: solid fuel conversion, gas conversion and CO₂ capture.

Figure 4. Reactions in CLC fuel reactor when oxidizing solid fuel.

CLC using solid fuels requires an adequate design of the fuel reactor, as well as oxygen carriers with suitable properties:

- The ash, normally part of solid fuels, will most likely shorten the lifetime of the oxygen carrier as the ash needs to be removed from the reactor system, thereby causing losses of the oxygen carrier. Moreover, ash might directly affect the oxygen carrier (Azis et al., 2010). Therefore, low cost materials like ilmenite, iron and manganese ores have been studied.
- Solid fuels, after having released volatiles that may directly react with the oxygen carrier, forms a char residue unable to react directly with the oxygen carrier. This char residue is gasified, e.g. by steam, producing syngas, Figure 4. The gasification of char is a slow process, with the consequence that the fuel reactor requires a design to provide sufficient residence time in order to avoid char particles reaching the air reactor. In addition, it is necessary to use smaller fuel particles than in normal fluidized-bed combustion. Often the solids flow going from the fuel reactor to the air reactor passes through a so-called carbon stripper. The carbon stripper provides additional residence for conversion and also separates char from the solids flow. Char loss to the air reactor should be avoided, as it will burn and produce CO₂ that will not be captured.
- In order to achieve a high level of conversion of the volatiles, the fuel inlets need to be designed in a way that allows for good contact between the volatiles released from the fuel and the bed material.

An advantage when using solid fuels in CLC is that low-cost materials available, such as ores of iron, manganese and ilmenite, are quite reactive towards the syngas released through gasification. However, the syngas produced by the char particles is released inside the bed in contrast to gaseous fuels which are introduced from below. Thus, some syngas released, particularly in the upper regions, will have insufficient contact with the bed material. For this reason, a complete conversion of the gas in the fuel reactor would be difficult to obtain. There are several options for reaching complete gas conversion, although the possibility normally considered is oxygen polishing. Oxygen polishing involves the introduction of pure oxygen downstream of the fuel reactor in order to oxidize remaining unconverted gases like H₂, CO and CH₄. Another option is to use a so-called CLOU material, i.e. oxygen-carrier particles able to release oxygen in the fuel reactor – oxygen which can subsequently convert the remaining gases.

2.1.4 Chemical-looping with oxygen un-coupling (CLOU)

Chemical-Looping with Oxygen Uncoupling (CLOU) is closely related to chemical-looping combustion and is applicable to the combustion of all fuels mentioned above. It differs from CLC through the spontaneous release of oxygen inside the fuel reactor. Thus, instead of the fuel gas reacting directly with the oxide, the oxidation of the fuel involves two distinct steps: i) the release of gaseous oxygen and ii) the combustion of the fuel by the oxygen released, Figure 5.

Figure 5. Chemical-Looping with Oxygen Uncoupling (CLOU) using CuO/Cu₂O.

The process demands an oxygen carrier capable of reacting with the oxygen in the air reactor but which decomposes to a reduced metal oxide and gas-phase oxygen in the fuel reactor. The driving force for this transfer is the difference in oxygen concentration between air and fuel reactors, and the needed property of the oxide system is to have an equilibrium partial pressure in-between that of the air reactor and the fuel reactor. Three monometallic oxide systems with suitable thermodynamic properties have been identified, Mn₂O₃/Mn₃O₄, CuO/Cu₂O and Co₃O₄/CoO (Mattisson et al., 2009). Co₃O₄/CoO has the disadvantage of an overall endothermic reaction in the fuel reactor, as well as high costs and health and safety risks. The equilibrium oxygen concentration is 5% for Mn₂O₃/Mn₃O₄ at a temperature of around 800°C. For CuO/Cu₂O this concentration is 5% at a temperature of around 950°C. In a combustion process, most oxygen in the combustion air needs to be consumed in order to avoid large gas flows and thermal losses associated with exiting flue gas. This means that the O₂ concentration of the gas leaving the air reactor should preferably be kept at 5% or below.. Consequently, Mn-system needs to operate at a temperature below 800°C in the air reactor. However, the reaction rates at these temperatures are likely too slow, and no successful outcome using Mn₂O₃/Mn₃O₄ as CLOU material is presently known. However, CLOU using CuO has been proven effective, first in laboratory batch fluidized-bed tests with solid fuels, and later in small pilot operation with solid fuels. Another interesting group of materials are the combined manganese oxides, that have lower equilibrium oxygen partial pressures than the pure manganese system and therefore are possible to oxidize at higher temperatures. Materials studied include manganese oxides combined with Fe, Si, Ca, Mg (Rydén et al., 2014). Many of these materials are only capable of releasing limited amounts of oxygen in this way; however, this release could still be quite beneficial for the conversion of both solid and gaseous fuels.

Although the CLOU mechanism is clearly useful for any fuel, the advantages when using solid fuels are very obvious. In normal chemical-looping combustion of solid fuels, there is a need for an intermediate gasification step of the char using steam or carbon dioxide to form reactive gaseous compounds which in their turn react with oxygen carrier particles. The gasification of char with H₂O and CO₂ is inherently slow, resulting in slow overall rates of reaction. Since no intermediate gasification step is needed and char reacts directly with gas-phase oxygen, this slow gasification step is avoided by using CLOU.

When using gaseous fuels, the CLOU process should also yield significant improvement as the direct contact between reacting gas and oxygen carrier becomes unnecessary. Therefore, CLOU could make it easier to reaching full conversion, by compensating for inadequate contact between gas (bubble phase) and particles (dense phase) in a fluidized bed. When using gaseous fuels, the oxygen carrier may also react directly with the gas in parallel to the oxygen release, making it difficult to clearly distinguish between the two mechanisms of CLOU and CLC.

2.1.5 Hydrogen production with CO₂ capture

Hydrogen from gaseous fuels

The chemical-looping concept can also be used for the production of hydrogen with simultaneous CO₂ capture. Chemical-looping processes for the hydrogen production from gaseous fuels include *i*) autothermal chemical-looping reforming, *ii*) chemical-looping combustion with steam reforming and *iii*) chemical-looping with water-splitting.

Autothermal chemical-looping reforming, ACLR, uses chemical-looping for partial oxidation to form a syngas that after water-gas shifting can be separated into CO₂ and H₂,

Figure 6. The principle was patented a long time ago (Anon., 1950). Using nickel-based oxygen carriers, a syngas free from methane can be produced at atmospheric pressure (Rydén et al., 2004), whereas non-nickel oxygen carriers have poor selectivity to CO and H₂ and generally produce a gas with mainly CH₄ and CO₂ in partial oxidation (Zafar et al., 2005).

Figure 6. Principle of autothermal chemical-looping reforming, ACLR.

Chemical-looping combustion with steam reforming, CLC-SR, is a marriage between conventional steam reforming and CLC (Rydén et al., 2006), Figure 7. As in commercial steam reforming, the reactions take place inside tubes at elevated pressure using suitable catalysts. The steam reforming tubes may be placed in a separate fluidized-bed heat exchanger. Hence, the reformer tubes are not heated by direct firing but rather by the oxygen carrier used as bed material, thus extracting the heat generated by the CLC process. The fuel used in the fuel reactor is the tail gas from the steam reforming remaining after hydrogen separation, containing a mixture of CH₄, CO₂, CO and H₂. The CLC-SR process offers several important advantages:

- only one gaseous component, H₂, needs to be separated, because the remaining gas stream is used as fuel in the process and needs to contain combustible gases like H₂, CO and CH₄. This is in great contrast to ACLR, where the gas stream needs to be separated into two essentially pure streams, CO₂ and H₂.
- the chemical-looping takes place at atmospheric pressure, while the reforming is performed at high pressure
- in contrast to ACLR, where NiO is likely needed, CLC-SR may use oxygen carriers with low costs and low health and safety risks

- the temperature around the tubes is considerably lower and more uniform than in the gas boilers used in conventional steam reforming. This means that risks of local overheating, so-called hotspots, are avoided. The lower temperature means that a greater fraction of the combustion heat is used for steam reforming, with the consequence that reforming efficiency is increased. CLR-SR may well be the only CO₂ capture technology which results in increased energy efficiency, i.e. if the efficiency loss of the subsequent CO₂ compression is excluded.

Figure 7. a) Conventional steam reforming and b) steam reforming with chemical-looping combustion.

Chemical-looping with water-splitting, or One-Step Decarbonisation, uses three reactors, (Mizia et al., 2009). The process requires an oxygen carrier which is reduced stepwise via different oxidation states, e.g. $\text{Fe}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{FeO}$. In the fuel reactor the fuel and oxygen carrier needs to move in countercurrent flow, in the upper part of the reactor Fe_2O_3 is reduced to Fe_3O_4 while accomplishing complete combustion of the fuel and in the lower part, Fe_3O_4 is further reduced to FeO , Figure 8. Then, in the water splitting reactor, the FeO is oxidized to Fe_3O_4 by steam to give hydrogen. Finally, the material is led to the air reactor where it is regenerated to form Fe_2O_3 . Note the two needed changes in oxidation state: Fe_2O_3 to Fe_3O_4 is needed to fully oxidize the fuel, while FeO to Fe_3O_4 is needed for water splitting. The process elegantly avoids any gas separation in the hydrogen production, albeit at the price of an added complexity of the reactor system.

Figure 8. Principal scheme of One-Step Decarbonisation.

The three concepts above were evaluated in the EU Cachet project for the purpose of producing decarbonized hydrogen to use in power production (Beavis, 2009).

Hydrogen from solid fuels

Hydrogen production from solid fuels using chemical-looping is similar to the chemical-looping reforming and water-splitting processes proposed for gaseous fuels. The idea to use a chemical-looping process for the production of syngas using solid fuels and two interconnected fluidized beds is old, (Anon., 1950). Recent processes add the use of lime to enhance fuel conversion to H_2 by *in situ* CO_2 removal, e.g. the Alstom Hybrid Combustion-Gasification Process and the GE Fuel-Flexible Process (Fan, 2010). With respect to water-splitting, it should be mentioned that the main process for hydrogen production 80-90 years ago was the so-called steam-iron process. In this process, iron oxide was reduced by coal to iron, which then reacted with steam to form hydrogen, (Fan, 2010). A related process studied today and using Fe/FeO in the production of hydrogen through water-splitting is the Syngas Chemical-Looping Process (SCL), (Fan, 2010).

2.2 Oxygen carrier materials

The oxygen carrier is the cornerstone of CLC processes and needs to provide adequate performance at reasonable cost. Important criteria for a satisfactory oxygen carrier are the following:

- High reactivity with fuel and oxygen and the ability to convert the fuel fully to CO_2 and H_2O
- Sufficient oxygen transfer capacity
- Low production cost and low risks for health, safety and the environment.
- Low fragmentation and attrition, as well as low tendency for agglomeration

The different oxide systems have advantages and disadvantages and the choice of oxygen carrier will depend on its application. Generally, low cost oxygen carriers are preferred when using solid fuels, whereas oxygen carriers that are more expensive and more reactive towards methane might be suitable for gaseous fuels. Although laboratory experiments with oxygen carriers provide valuable information, they are insufficient to prove that the oxygen-carrier particles work in the actual process. Consequently, it is crucial to investigate these materials under realistic conditions and adequate time periods in chemical-looping combustors. An overview of operational experiences is provided in section 2.4.

2.2.1 Monometallic oxides

Early work in oxygen carrier development mainly concentrated on the four monometallic oxides Fe, Mn, Cu and Ni. Normally, the active metal oxides studied were combined with an inert material, such as Al_2O_3 . The inert material is believed to increase the porosity and promote the reactivity of the particles, help maintain the structure and possibly also increase the ionic conductivity of the particles. Even though the mass ratio of oxygen available for the oxygen transfer in a particle decreases when inert material is added, the reactivity with fuel and oxygen may nevertheless be higher.

The ability of metal oxides to convert combustible gases to CO_2 and H_2O has been investigated thermodynamically and the metal oxide systems of Fe_2O_3/Fe_3O_4 , Mn_3O_4/MnO , Cu_2O/Cu , NiO/Ni and CoO/Co are potential candidates as oxygen carriers. The maximum conversion of CO to CO_2 is given in Table 2 and the maximum conversion of H_2 is fairly similar. At equilibrium the conversion of methane is always complete with these oxide systems, albeit not necessarily to CO_2 and H_2O as CO and H_2 may form. The thermodynamics are not as favourable for CoO/Co , with maximum 93% conversion at $1000^\circ C$; moreover, this oxygen carrier is expensive and carries health and safety risks.

Table 2. Maximum CO conversion to CO_2 at equilibrium

	Fe_2O_3/Fe_3O_4		Mn_3O_4/MnO		CuO/Cu		NiO/Ni		CoO/Co	
Temperature, $^\circ C$	800	1000	800	1000	800	1000	800	1000	800	1000

CO conversion	1.0000	1.0000	1.0000	0.9999	1.0000	1.0000	0.9949	0.9883	0.9691	0.9299
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A comparison of the monometallic oxide systems is given in Table 3. In general, the most reactive materials are unfortunately the most expensive. There are also health, safety and environmental aspects to be considered when using nickel oxide. Moreover, nickel oxide has a thermodynamic limitation: it cannot fully convert fuels to CO₂ and H₂O. Depending on temperature, the maximum conversion is 99-99.5%. The reaction is more or less exothermic for all oxides in both the air and the fuel reactor, with H₂ or CO as fuels, but with methane the reaction is endothermic in the fuel reactor for all oxides except CuO. The exothermic reaction is clearly advantageous when using CuO since it removes one condition for the particle circulation; for oxides with endothermal reaction in the fuel reactor the circulation needs to be sufficient to maintain an adequate temperature in the fuel reactor. On the other hand, Cu has the disadvantage of a low melting temperature. As discussed in the following section on CLOU materials, the CuO/Cu₂O system can be used in the CLOU process as it is able to release gaseous oxygen. Both CuO and Cu₂O have considerably higher melting temperatures than does Cu.

An oxygen carrier needs to react at a sufficient rate. The inventory of oxygen carrier necessary for the reactors is related to its reactivity. Consequently, a lower rate would necessitate a larger solids inventory or worse, result in incomplete fuel conversion. The circulation of oxygen-carrier materials must also be able to transfer a sufficient amount of oxygen to the fuel reactor. The oxygen transfer capacity, R₀, i.e. the maximum mass fraction of oxygen that can be transferred, is shown in Table 3. The R₀ data in Table 3 pertain to pure systems and R₀ will therefore be reduced if diluted with support materials. In the case when the reaction in the fuel reactor is endothermic, the necessary circulation is normally not set by the oxygen transfer capacity but by the heat balance in order to reach a sufficiently high fuel reactor temperature (Lyngfelt et al., 2001, Jerndal et al., 2006).

Table 3. Qualitative estimation of pros and cons for the active oxides

	Fe ₂ O ₃ /Fe ₃ O ₄	Mn ₃ O ₄ /MnO	CuO/Cu	NiO/Ni	comments
R ₀	0.03	0.07	0.20	0.21	Oxygen ratio
Reactivity towards methane	☹	← decreasing	increasing →	☺	
Cost	☺	← decreasing	increasing →	☹	
Health, safety & environm. risks	☺	☺	← decreasing risk	☹	
Thermodynamics				☹	<99.5% conv. for NiO
Reaction enthalpy w. CH ₄			☺		CuO exothermic w. CH ₄
Melting point			☹		1085°C for Cu
CLOU			☺		CuO/Cu ₂ O

Comprehensive studies of oxygen carriers (Adanez et al., 2004, Johansson, 2007) normally indicate a major difference in reactivity between the various oxides, Table 3. However, most reactivity comparisons are focused on CH₄. In general, the reactivity is significantly higher using H₂ and CO than when using CH₄ and may be rather high for cheaper materials showing low reactivity with CH₄.

Reactivity may significantly increase with reaction temperature, especially in the case of low reactivity materials and CH₄. On the other hand, the reactivity of iron and manganese materials with CO and H₂ may be high even at lower temperatures and the same applies to nickel materials with CH₄. Although the highly reactive Ni materials have been operated at much lower temperatures, CLC

operation with oxygen carriers has normally used fuel reactor temperatures in the range of 800-1000°C. The upper and lower limits of operational temperature are highly dependent on oxygen carrier properties and fuel used. Thus, low reactivity at low temperature and the risk of agglomeration at high temperature may impose important limits. In order to compensate for the endothermic heat of reaction in the fuel reactor, the oxides of Fe, Ni and Mn, are expected to operate at a temperature in the fuel reactor which is typically 50°C lower than that of the air reactor.

2.2.2 Combined metal oxides

Combined metal oxides are compounds where two or more oxides are combined chemically, constituting new oxides, e.g. $\text{Cu}_{0.95}\text{Fe}_{1.05}\text{AlO}_4$ and NiFeAlO_4 . Some materials have perovskite structure, e.g. $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$, and $\text{Sr}(\text{Mn}_{1-x}\text{Ni}_x)\text{O}_3$. An interesting group of materials with CLOU properties, i.e. capable of releasing oxygen, are Mn oxides combined with oxides of Ca, Mg, Ni or Fe. Many of the Mn-combined materials are promising, but few of them have been successfully tested in actual operation. An exception is calcium manganate materials with the general formula $\text{CaMn}_{(1-x)}\text{Me}_x\text{O}_3$, in which Me is a metal, e.g. Fe, Ti, Mg, and x is in the order of 0.1. A naturally occurring combined oxide, commonly used with solid fuels, is ilmenite, FeTiO_3 , which is also a low-cost material.

2.2.3 Low cost materials

Low-cost materials mainly investigated for use with solid fuels, include iron ore, manganese ore, ilmenite and industrial waste materials. Most studies have used ilmenite that is available as a natural ore, has a reasonably high reactivity towards syngas and shows good fluidization behaviour.

2.3 Progress in reactor testing and pilot demonstration

Basic design relations are provided in the first tentative design of a chemical-looping reactor system (Lyngfelt et al., 2001). The necessary circulation is normally determined by the heat balance, to compensate for the endothermic reaction in the fuel reactor. This heat balance is obviously dependent on both the fuel and oxygen carrier, but the reactions of coal or natural gas with nickel oxide, iron oxide and oxidized ilmenite give comparable heat balances. For coal with iron or ilmenite, the solids circulation typically needs to be in the order of 5 (kg/s)/MW_{th}, assuming a temperature difference between the fuel reactor and the air reactor of 50°C. This circulation is higher than that normally used in circulating fluidized bed boilers but is fully realistic. Required solids inventories in the fuel reactor are determined by the reactivity of the oxygen carrier in combination with the gas-solids contact, but is typically estimated at 100-1000 kg/MW_{th}, corresponding to a residence time of the order of a minute. The solids inventory of the air reactor is normally expected to be lower and less critical for two reasons: i) most oxygen carriers show high reactivity in oxidation and ii) in contrast to the fuel reactor, there is no need whatsoever to achieve complete conversion of the incoming reactant, i.e. oxygen.

Cold-flow models are useful to identify stable and suitable operating conditions for various designs of CLC reactor systems. A 100 kW solid fuel system, Figure 9, was studied with the cold-flow model and a film showing the model in operation is available [in](#) the internet (Markström et al., 2011).

There are several options for organizing two interconnected fluidized beds and the circulation between them; one possibility is shown in Figure 3. The smaller CLC pilots used show different approaches involving various loop designs, internally circulating fuel reactors, bubbling air reactors, and different options for controlling circulation, including separate risers and controllable valves (Lyngfelt, 2011). These smaller units may use designs adequate for small scale research. Large-scale systems will likely avoid bubbling bed reactors. Thus, a circulating fluidized-bed air reactor controlling the global circulation and a fuel reactor with an internal circulating loop would be

probable basis for design. Systems for solid fuels would include designs aimed at achieving both a long residence time and a narrow residence time distribution of the solids in the fuel reactor to minimize loss of carbon to the air reactor.

Figure 9. Chalmers' 100 kW solid fuel chemical-looping

Figure 10. Layout of the ALSTOM 3 MW_{th} chemical-combustor pilot (Iqbal et al., 2012)

A quick glance at layouts of chemical-looping pilots for solid fuels, Figure 9 and Figure 10, may give the impression that the technology would differ significantly from the power plants using circulating fluidized-bed (CFB) technology. However, a proposed design of a 1000 MW_{th} CLC power plant rather underlines the similarities Figure 11. A CLC and a CFB boiler would have similar cross-sectional areas, because the same gas flow would pass through the beds at similar velocities. The most important difference is the part that makes up the fuel reactor because it needs to be adiabatic and is therefore fitted with well insulated walls. Other important differences include:

- ducts leading circulating solids from the air reactor cyclones to the fuel reactor.
- ducts connecting the bottom parts of the reactors, leading circulating solids from the fuel reactor to the air reactor.

- a shorter air reactor. The absence of homogeneous gas-phase reactions between combustibles and air, as well as the absence of char particles, implies that reactor height can be lowered.
- a post-oxidation chamber to reach full conversion of the fuel reactor gas by oxygen polishing (not shown in the figure). Assuming the duct leading from the fuel reactor cyclone to the convection pass can be used for this purpose, this chamber is not necessarily added equipment.
- a significant reduction in the heat transfer area inside the air reactor, attributable to the higher temperature compared to CFB.

Figure 11. Top, side and front view of reference CFB (top) and CLC-CFB (bottom).

2.4 Operational experience

A number of reviews that include accounts of operational experiences are available (Lyngfelt, 2011, Adánez et al., 2012, Lyngfelt, 2013, Lyngfelt et al., 2014b, Fan, 2010). Twenty-four CLC units in the size range of 0.3-3 MW with a total operational time of more than 7300 h are presented in Table 4. More detailed descriptions of the units have been provided in the reviews above. Recent units, all operating with solid fuels, are a 1 MW unit in Darmstadt, Germany (Ströhle et al., 2014b), a 5 kW unit in Huazhong, China (Ma et al., 2014) and a 50 kW unit in Zaragoza, Spain (Pérez-Vega et al., 2014). With respect to manufactured oxygen carriers, the operational experience includes 2800 h with nickel-based materials in 12 units, 627 h with copper-based materials in six units, 1077 h with iron-based materials in eight units, 180 h with cobalt-based materials in two units and 545 h with combined oxide materials in six units. With respect to low-cost materials, such as waste materials or

1 ores, 404 h of operation have been reported for iron-based materials in four units, 810 h with
 2 ilmenite in eight units and 148 h with manganese ores in three pilots.

3 Table 4. Testing in chemical-looping combustors, SF: solid fuels, LF: liquid fuels

Location	Unit	Oxides tested	Time	Fuel	Year
Chalmers	10 kW	NiO, Fe ₂ O ₃ , ilmenite, CaMnO ₃	1618	nat. gas, fuel oil	2004
KIER	50 kW	NiO, CoO	31	nat. gas	2004
CSIC	10 kW	CuO, NiO	120	nat. gas	2006
Chalmers	0.3 kW	NiO, Mn ₃ O ₄ , Fe ₂ O ₃ , ilmenite, CaMnO ₃ , Mn-Si, Mn-Si-Ti, Mn-Fe-Si, Mn ore,	1040	nat. gas, syngas	2006
Chalmers	10 kW-SF	ilmenite, manganese ore, CaMnO ₃	253	coal, petcoke	2008
CSIC	0.5 kW	CuO, NiO, Fe ₂ O ₃ , , CaMnO ₃	949	nat. gas	2009
KAIST	1 kW	NiO + Fe ₂ O ₃	?	CH ₄	2009
Vienna UT	140 kW	ilmenite, NiO, Fe ₂ O ₃ , CuO, CaMnO ₃	519	nat. gas, CO, H ₂	2009
Alstom	15 kW	NiO	100	nat. gas	2009
Nanjing	10 kW –SF	NiO, Fe ₂ O ₃	260	coal, biom.	2009
KIER	50 kW	NiO, CoO	450	nat.gas, syngas	2010
Nanjing	1 kW – SF	NiO, iron ore	260	coal, biomass	2010
IFP-Lyon	10 kW	NiO, Mn ore	90	CH ₄	2010
Stuttgart	10 kW	ilmenite	?	syngas	2010
Xi'an Jiaotong	10 kW- Pr	CuO/Fe ₂ O ₃	15	coke oven gas	2010
CSIC	0.5 kW-SF	ilmenite, CuO, Fe ₂ O ₃ , iron ore	441	coal, biomass	2011
Chalmers	0.3 kW LF	NiO, Mn ₃ O ₄ , CuO	199		2011
Chalmers	100 kW – SF	ilmenite, Mn ore, iron ore	116	coal, biochar	2012
Hamburg	25 kW –SF	ilmenite	60	coal	2012
Ohio	2.5 kW –SF	Fe ₂ O ₃	300	coal	2012?
Ohio	25 kW –SF	Fe ₂ O ₃	530	coal, CH ₄ , syngas	2012
Darmstadt	1 MW-SF	ilmenite	?	coal	2012
Alstom, Windsor	3 MW-SF	CaSO ₄ /CaS	75	coal	2012 ?
Huazhong	5 kW-SF	iron ore	6	coal	2014
Zaragoza	50 kW-SF	ilmenite	?	coal	2014

4 Operation with gaseous fuels shows excellent performance, 100% CO₂ capture and up to 100% fuel
 5 conversion to CO₂ and H₂O. For solid fuel operation, a full conversion of fuel reactor gas is not
 6 attained except when using expensive oxygen-releasing copper-based oxygen carriers. With low-cost
 7 materials, the gas conversion typically varies between 80% and 95%, depending on e.g. solids
 8 inventory, oxygen carrier, fuel and reactor design. Moreover, there is also a loss of char to the air
 9 reactor, even though CO₂ capture rates up to 98% have been reported. A significant loss of char with
 10 the gas stream leaving the fuel reactor has also been reported. This loss is expected to become much
 11 smaller with the use of full-scale reactors and more efficient cyclones.

12 2.5 Cost structure

13 The major advantage of chemical-looping combustion is the avoidance of large energy penalties and
 14 costs for gas separation. Common to all CLC applications is the cost of the oxygen carrier. The added
 15
 16

costs of CLC related to solid and gaseous fuels are quite different and need to be addressed separately.

2.5.1 Oxygen carrier cost

Because of uncertainties in the life of the oxygen carriers in actual operation, the selection and cost of oxygen carrier are paramount. In the case of solid fuels, where life is particularly uncertain, low-cost natural minerals or waste materials are likely the main option. An analysis of the effect of the cost of materials is made below. While the price of ores, metals and oxides may vary from year to year, current prices are in the range of 200-250 €/tonne for manganese ore, around 150-200 €/tonne for ilmenite and even lower for iron ore. The cost of oxygen carrier adds to the CO₂ capture cost. This added cost for the oxygen carrier can be expressed as the cost per tonne of CO₂ captured and is denoted by

$$CCC_{OC} = \frac{C_{OC} \cdot SI}{SE \cdot \tau} \quad (3)$$

where CCC_{OC} is the Cost of CO₂ Capture caused by the Oxygen Carrier in €/tonne CO₂ captured, C_{OC} is an estimated cost of the oxygen carrier in €/tonne, SI is the solids inventory in tonne/MW_{th}, SE is the specific emission in tonne CO₂/MWh_{th} and τ is the average lifetime of the oxygen carrier. A pilot operation using ilmenite suggested a lifespan of 600-700 h (Linderholm et al., 2014) based on the production of fines. This lifespan estimation does not consider any interaction with ash, and a more realistic lifespan would probably be 100-300 h. Assuming a lifespan of 200 h with ilmenite, the cost would be 2 €/tonne CO₂, Table 5. Consequently, a lifespan of 100-300 h yields a cost range of 1.3-4 €/tonne CO₂. For manganese ore, a shorter lifespan based on the present limited experience is assumed, leading to a higher estimated cost for manganese ore of around 5 €/tonne CO₂.

Table 5. Examples of CO₂ capture costs related to oxygen carrier materials

	ilmenite	manganese ore
SE, tonne/MWh _{th}	0.334	0.334
SI, tonne/MW _{th}	0.75	0.75
τ, h	200	100
C _{OC} , €/tonne oxygen carrier	175	225
CCC _{OC} , €/tonne CO ₂	2.0	5

Results from pilot operation using gaseous fuels indicate that a long lifespan of the oxygen carrier is possible. Long-term operational testing, >1000 h, with a nickel oxygen carrier indicated that the loss of fines fell during the first 100 h to stabilize at a very low level, below 0.003%/h, corresponding to a lifespan well above 10 000 h. Similarly, operational results with calcium manganate materials suggested a lifespan of around 10 000 h. Assuming such long lifespans can be reached when using gaseous fuels, has the consequence that the cost of the materials could be increased between one or two orders of magnitude without increasing the costs per tonne of CO₂ captured in comparison to the data in Table 5. However, the added costs and efforts of verifying the longer lifespans also have to be considered for more expensive materials.

2.5.2 Costs of CLC using solid fuels

Fluidized-combustion of coal is presently used in power plant sizes of up to 600 MW_e. A cost comparison is facilitated by the large similarities between chemical-looping combustion and circulating fluidized bed (CFB) combustion. A detailed analysis of the differences between a commercial CFB plant and a CLC power plant, including an estimation of the costs related to these differences, has been made (Lyngfelt et al., 2014a). The largest cost, 10 €/tonne CO₂, is the compression and purification of CO₂ common to all CO₂ capture technologies. Other costs include oxygen production for “oxy-polishing” of the incompletely oxidized gas from the fuel reactor, oxygen

carrier, boiler design differences, steam to fluidize the fuel reactor and coal milling. The costs add up to 20 €/tonne of CO₂ and are summarized in Table 6. Another, less recent, cost estimation in the EU ENCAP project based on a 455 MW_e CLC solid fuel power plant indicated a low efficiency penalty as well as a low capture cost, 10 €/tonne of CO₂ (Ekström et al., 2009). A study by EDF in France indicated a net plant efficiency of 41.6% including CO₂ capture and compression (Authier et al., 2013).

Table 6. Estimated added costs for CFB-CLC

Type of cost	estimation, €/tonne CO ₂	range, €/tonne CO ₂	Efficiency penalty, %
CO ₂ compression	10	10	3
Oxy-polishing	6.5	4-9	0.5
Boiler (fuel reactor and post-oxidation chamber)	1	0.1-2.3	-
Oxygen carrier	2	1.3-4	-
Steam and hot CO ₂ fluidization	0.8	0.8	0.8
Coal grinding	0.2	0.2	0.1
Lower air ratio	-0.5	-0.5	-0.5
Total	20	15.9-25.8	3.9

An optimization of the costs of a CLC system using solid fuels would likely focus on the costs of oxygen production versus the costs of oxygen carrier and fuel reactor design. Thus, as indicated in Table 6, there are several € per tonne of CO₂ to gain if the gas conversion could be improved by a more reactive oxygen carrier or improved reactor design.

2.5.3 Costs of CLC using gaseous fuels

For gaseous fuels, the added costs of a chemical-looping process would be highly dependent on application and size. In the case of power production, an atmospheric CLC process with steam cycle would need to compete with the much higher efficiency of a combined gas-turbine steam-turbine cycle. In the case of steam production alone, there would be an added cost related to the fact that a gas-fired boiler is less costly and complex than a dual fluidized-bed reactor system. In the case of CLC-SR, chemical-looping combustion with steam methane reforming, there is on the other hand an expected improved efficiency. In the first two cases, no detailed cost studies have been made, whereas the CLC-SR process was investigated in the Cachet EU-project. This project focused on the power production using hydrogen produced from natural gas with CO₂ capture. From the results, it is possible to deduce that the CLC-SR process would produce CO₂-free hydrogen with an energy efficiency of around 80%, and at a cost of 38 €/MWh using natural gas at the price of 19 €/tonne. Note that this pure and useful CO₂-free fuel, is nevertheless less costly than crude oil, i.e. as long as oil is priced at above \$80 per barrel.

2.6 CLC Outlook

Although more development work is required, it is clear that the CLC technology provides unique advantages of avoiding the large costs and energy penalties inherent in gas separation. In the case of gaseous fuels:

- The technology has been successfully demonstrated in a number of smaller pilots and should be ready to scale up to a size of 1 to 10 MW.
- Present technology, i.e. atmospheric conditions and an operational temperature of 800-950°C, would have significantly lower efficiency in power production than in natural gas

combined cycle (NGCC) plants. CLC for higher pressures and temperatures would require significant development efforts.

- There are a number of applications for which gaseous fuel CLC could be used for steam and/or hydrogen production.

In the case of solid fuels:

- The technology is similar to the established combustion of coal in circulating fluidized bed.
- CLC operation with low-cost mineral ilmenite works well, but the conversion can be further improved by using more reactive materials, e.g. manganese ores.
- The following options to fully convert the gas leaving the fuel reactor to $\text{CO}_2/\text{H}_2\text{O}$ are available: i) oxygen polishing, ii) separation/recycling of unconverted gas iii) using two fuel reactors in a series and iv) CLOU oxygen carriers. At present, the primary focus is on oxygen polishing.
- The optimization of the fuel reactor system would primarily need to consider three costs, i.e. costs of the oxygen carrier, costs of the fuel reactor system, and costs downstream of the fuel reactor to make up for incomplete conversion, e.g. oxygen polishing. Consequently, a good understanding of these costs is needed to find the optimal design and operation.
- There is a unique potential for a dramatic reduction in the cost and energy penalty of CO_2 capture, with an estimated penalty of below 4% and a cost of 20 €/tonne of CO_2 .

3. Calcium Looping

The concept of “Calcium looping”, or “Carbonate looping”, CaL, embraces a wide variety of CO_2 capture process routes with different levels of maturity, technical complexity and economic viability (see Table 7). All these process options share the use of Calcium Oxide as a regenerable sorbent of CO_2 . CaO can react at high temperature with CO_2 to form CaCO_3 . A subsequent calcination reaction of CaCO_3 in a rich atmosphere of CO_2 (and maybe steam) closes the “calcium loop”. The high temperatures required for sorbent regeneration by CaCO_3 calcination and the high temperature of CO_2 absorption by the carbonation reaction make Calcium Looping systems very different from other post-combustion CO_2 capture systems: heat recovery can be highly efficient using state of the art steam cycles, thereby reducing the overall energy penalty of the system.

The equilibrium curve of CO_2 on CaO sets up the temperature ranges that are relevant for CO_2 capture applications. This equilibrium indicates that it is possible to reduce the concentration of CO_2 in a flue gas at atmospheric pressure below 1.2 %vol at 650 °C, while temperatures over 900°C are required to deliver a pure stream of CO_2 when calcining CaCO_3 . The need for high temperatures in a CO_2 rich calciner is the main challenge when it comes to define the method for supplying the necessary heat for CaO regeneration. The calcination enthalpy of CaCO_3 is very high (168 kJ/mol at 900°C) and it is intrinsically difficult to supply a large heat flow to a high temperature reactor. The next sections review the status of the different process schemes, giving more prominence to CaL systems with the highest TRL.

Table 7. Summary of the main process routes involving CaO as a regenerable sorbent of CO_2 .

Type	Process	TRL	Main process operation conditions	Comments	Ref
Post-combustion	Calcium looping with oxy-fuel combustion for calcination	6	<ul style="list-style-type: none"> Standard CaL configuration: Interconnected CFBs Carbonation: Circulating fluidized bed, 600-700 °C, 1 bar Calcination: Oxy-CFB, 900-930 °C, 1 bar Internal circulation reactors: 5-10 kg/m²s Inventory of solids in the reactors <1000 kg/m² Gas velocity in the reactors: 5 m/s 	<ul style="list-style-type: none"> Largest demonstration at 1.7 MW_{th} pilot plant integrated with power plant High CO₂ capture efficiency can be achieved (close to the maximum limit given by the equilibrium) ASU required for oxy-combustion in the calciner Possibility of rapid scale up due to similarities with existing CFB combustion technology 1000s of hours experience in large pilots 	(Shimizu et al., 1999, Arias et al., 2013, Dieter et al., 2013, Kremer et al., 2013)
		4	<ul style="list-style-type: none"> Carbonation: Bubbling fluidized bed, 600-700 °C, 1 bar Calcination: kiln reactor, temperature profile from 1300 to 600 °C, 1 bar Pneumatic transport of solid from calciner to carbonator 	<ul style="list-style-type: none"> Demonstration at bench scale and 1.9 MW_{th} pilot plant integrated with cement plant under commissioning ASU required for oxy-combustion in the calciner Large scale issues related with bubbling carbonator and T profile in calciner 	(Chang, 2014)
	Calcium looping for in-situ CO ₂ capture from biomass combustion	4	<ul style="list-style-type: none"> Standard CaL configuration: Interconnected CFBs Carbonation-Combustion: CFB reactor, 700 °C, 1 bar Calcination: Oxy-CFB reactor, 900-930 °C, 1 bar Fuel used in the carbonator and calciner: biomass 	<ul style="list-style-type: none"> Tested in a 300 kW_{th} pilot plant Negative CO₂ emissions technology (BECSS) Narrow operation window in the carbonator-calciner Limited CO₂ capture efficiency at 80% Oxycalcination with biomass not tested 	(Alonso et al., 2014)
	Calcium looping with oxy-fuel combustion for calcination using pure oxygen	3	<ul style="list-style-type: none"> Standard CaL configuration: Interconnected CFBs Oxy-calcination under very high oxygen concentration Reduction or elimination of the CO₂ recycle 	<ul style="list-style-type: none"> Lower heat demand in the calciner compared with standard configuration Oxy-CFB combustion already tested with 50%O₂ at small pilot scale Currently being tested at MWt (CaO₂ project) 	(Jia et al., 2007)
	Calcium looping with oxy-fuel combustion for calcination and preheating of carbonated solids	2	<ul style="list-style-type: none"> Standard CaL configuration: Interconnected CFB Preheating of carbonated solids entering the calciner using: <ul style="list-style-type: none"> Indirect heating by means of heat pipes or heat exchangers Direct heating by using a high temperature flue gas 	<ul style="list-style-type: none"> Reduction of heat demand in the calciner Preheating temperature limited by the equilibrium 	(Epple, 2009, Abanades, 2013)
	Calcium looping with oxy-fuel combustion for calcination and sorbent reactivation	2	<ul style="list-style-type: none"> Standard CaL configuration: Interconnected CFB Sorbent reactivation in an additional reactor located between the carbonator and the calciner Reactivation agents: H₂O_(v) or CO₂ 	<ul style="list-style-type: none"> Use of steam enhances sorbent attrition and increases the energy penalty due to low hydration temperature and the steam extraction from the turbine No energy penalty associate with the use of CO₂ Use of steam only tested at lab scale Use of CO₂ currently being tested at pilot scale (ReCaL project) 	(Ramkumar et al., 2010), (Diego et al., 2014)
	Calcium looping with calcination by indirect heating	2	<ul style="list-style-type: none"> Calcination: indirect heating, <900 °C, 1 bar Through metallic wall between the calciner and a combustor Using heat pipes to transfer heat from an external combustor 	<ul style="list-style-type: none"> Low energy penalty. ASU no needed Large heat surfaces needed to transfer heat to the calciner Special alloys needed for heat pipes High combustion temperatures needed in the external combustor (>1000 °C) 	(Abanades et al., 2005, Junk et al., 2013)

	Calcium looping with entrained carbonator	2	<ul style="list-style-type: none"> • Direct heating of CaO recycle using a high T flue gas • Carbonation: Entrained bed reactor, 600-700°C, 1 bar, gas velocity>10 m/s • Calcination: Entrained bed oxy-fired reactor, 900-930 °C, 1 bar 	<ul style="list-style-type: none"> • More suitable for CO₂ capture in cement plants • Fine particle size needed • Short reaction times, highly active sorbent 	(Romano et al., 2014)
	Endex process	2	<ul style="list-style-type: none"> • Carbonation: 760-850 °C, p_{CO2}>15 bar • Calcination: 650-760 °C; p_{CO2}<0.03 bar 	<ul style="list-style-type: none"> • Challenging heat transfer to the calciner • Circulation of solids between reactors at different pressures • Compression of flue gas needed/ Low CO₂ pressure produced 	(Ball et al., 2010)
Pre-combustion No capture	Acceptor Gasification Process	7	<ul style="list-style-type: none"> • Coal Gasification conditions: 800-850 °C, 10 bar • Sorbent regeneration conditions: >1000 °C, 10 bar • Fuel: lignite • Sorbent: limestone/dolomite 	<ul style="list-style-type: none"> • Tested in a pilot plant of 40 t/d of coal • Designed to produce synthetic gas • Regeneration by air-combustion of lignite char • Problems related with materials handling and corrosion 	(Curran, 1967)
	Absorption Enhanced Reforming	7	<ul style="list-style-type: none"> • Biomass Gasification intended to produce H₂ rich fuel gas • CFB gasifier reactor: 600-700°C, 1 bar • Calcination: air fired CFB combustor, 800-900 °C, 1 bar 	<ul style="list-style-type: none"> • Tested in a 8 MW_{th} pilot plant (Guessing) • Medium calorific gas obtained (H₂ conc. ~50%v) 	(Hofbauer, 2003)
	LEGS	4	<ul style="list-style-type: none"> • Fuel: Biomass • Gasification: FB reactor, 650-800 °C, 1 atm • Calcination: FB reactor, 850-900°C, 1 bar 	<ul style="list-style-type: none"> • Tested in a 20 kW_{th} pilot plant • H₂ concentration >75%v 	(Weimer et al., 2008)
Pre-combustion	Ohio State Univ CLP Process	3	<ul style="list-style-type: none"> • Carbonation: Reactor, 550 -700°C, 1 -33bar • Calcination: Reactor, 900-950 °C, 1 bar • Hydration: Reactor, 493 °C, 2 bar 	<ul style="list-style-type: none"> • Three reactor system • Partially tested at bench scale for coal gasification and NG reforming 	(Ramkumar et al., 2011)
	SER at high pressure with oxy-fuel regeneration	2	<ul style="list-style-type: none"> • SER: CFB reactor, 600-700°C, 17-25 bar • Sorbent regeneration: Oxy-CFB combustor, 1000-1200 °C, 17-25 bar 	<ul style="list-style-type: none"> • Sorbent problems associated to high regeneration T • Operation issues related to the interconnected FB operating at high P 	(Romano et al., 2011)
	SER at low pressure with oxy-fuel regeneration	2	<ul style="list-style-type: none"> • SER: CFB reactor, 600-700°C, 1 bar • Sorbent regeneration: Oxy-CFB combustor, <900 °C, 1 bar 	<ul style="list-style-type: none"> • Low P hydrogen produced. Compression step needed • Increasing pressure (up to 3 bar) may decrease CAPEX 	(Martínez et al., 2013)
	ZEG process	2	<ul style="list-style-type: none"> • SER: FB reactor, 600 °C • Hydrogen used in a solid oxide fuel cell (SOFC) • Sorbent regeneration: FB reactor indirectly heated by SOFC waste heat, 880 °C, 1 bar 	<ul style="list-style-type: none"> • No NOx emissions • Challenge heat transfer to regenerator reactor 	(Meyer et al., 2011)
	Ca-Cu process	2	<ul style="list-style-type: none"> • SER: Fixed bed reactor, 650 °C, 35 bar • Oxidation: Fixed bed reactor, 830°C, 35 bar • Calcination/Reduction: 870 °C, 1 bar 	<ul style="list-style-type: none"> • Coupling of chemical and Calcium looping • Feasible material, cheap reactor design 	(Fernández et al., 2012)

3.1 Post-combustion Calcium looping processes with oxy-combustion in the calciner.

A full, viable process scheme for a post-combustion CO₂ capture system using Calcium looping is outlined in Figure 12. This concept was published in a seminal work by Japanese workers (Shimizu et al., 1999) and has been scaled up in recent years to TRL6 (see Table 7). This Calcium looping process is also called “carbonate looping” or “regenerative carbonation cycle” by some developers. The full Calcium looping system includes several elements commercially available (the existing power plant, the Air Separation Unit (ASU), the CO₂ Compression and Purification Unit (CPU) and the additional Steam Cycle to recover waste heat from the carbonator and calciner reactors). The oxy-fired Circulating Fluidized Bed Combustor used under calcination conditions (oxy-CFBC) is also a highly developed technology (TRL7-8). However, the core of the system is the interconnected carbonator-calciner reactor system, with a continuous circulation, of solids only recently tested at TRL5 (Rodríguez et al., 2011, Abanades et al., 2009, Charitos et al., 2010, Charitos et al., 2011), and TRL6 (Arias et al., 2013, Ströhle et al., 2014a).

Figure 12. Scheme of a Calcium looping for post-combustion CO₂ capture in a power plant (adapted from (Dieter et al., 2014)).

In the most developed configuration, the carbonator is a circulating fluidized bed reactor that can accommodate the very large flow rate of flue gas coming from the existing power plant by operating at velocities between 3-5 m/s. This is a standard velocity range in commercial Circulating Fluidized Bed Combustors, CFBCs, which translates (assuming 12-15%_{vol} of CO₂ in the flue gas) into molar flow rates of 8-10 mol CO₂/m²s. The capture of a large fraction of this CO₂ requires a matching flow of “active CaO” (able to react sufficiently fast and/or to a sufficient extent during the short residence time of the particles (typically less than 100 s) in the carbonator reactor). The fraction of active CaO or CO₂ carrying capacity of the CaO particles, is known to be modest due to the decay of CaO activity with the number of carbonation-calcination cycles (Barker, 1973). As a result, maximum carrying capacities of below 0.2 are usually expected in a CaL system despite substantial make-up flows of

limestone (Abanades, 2002). This means that the total CaO molar circulation flow arriving at the carbonator must be one order of magnitude higher than the CO₂ molar flow. However, it should be noted that this large solids flow required to circulate between reactors (around 3-10 kg/m²s, depending on the CaSO₄ and ash content of the circulating solids) is perfectly normal in existing large scale CFB combustors, that operate with a very similar type of solids (Johansson et al., 2007).

Because of the close similarity with other CFBC systems, several reactor models have been published to estimate CFB carbonator performance as a function of operating conditions and design parameters (Lasheras et al., 2011, Romano, 2012, Pathi et al., 2014, Alonso et al., 2009, Hawthorne et al., 2008, Ylatalo et al., 2012). They all confirm that 80-90% capture efficiencies are possible in the carbonator despite the modest carbonation conversion of the circulating solids and reasonable low bed inventories in the reactor.

The calciner reactor in Figure 12 is usually assumed to be an oxyfired circulating fluidized bed combustor. In general, oxyfuel combustion seems naturally suited for CFBC as the large solid circulation has a vast heat transfer capability towards external heat exchangers and the rapid mixing of solids minimizes temperature profiles during oxyfuel combustion ((Kuivalainen et al., 2010)). It can be argued that these temperature profiles are likely to be further moderated by the presence in the calciner of decomposing particles of CaCO₃, due to its strong endothermic character. A recent EU project ("CaO₂" project, see Table 8) is trying to exploit this principle, in order to reduce the recycling of CO₂ needed in the oxyfired calciner (not shown in Fig 12) and minimize the calciner footprint and the heat requirements. In any case, the calciner reactor of Figure 12 can be assumed to be a high conversion reactor, because the kinetics of calcination are known to be extremely fast over 900°C as long as the reactor diverges only a few degrees from the equilibrium. Furthermore, recent measurements of calcination rates of highly cycled particles have revealed much faster calcination rates for typical carbonated particles in the calcium loop, as they have large open pore structures and low carbonate conversions (Martínez et al., 2012).

Several papers have been published in which the complete integration of the two interconnected reactors is described, including the steam cycle designed to recover waste heat streams from the calcium loop. As seen in Figure 12, the main heat sources in Calcium looping are the carbonation heat released in the carbonator reactor, a fraction of the heat from the hot solids leaving the calciner and the hot flue gases leaving the carbonator and calciner. Some schemes also integrate the waste heat from the purge of solids and the heat released during the compression of CO₂ into the steam cycle. A recent paper by Romano et al. (Romano et al., 2013a) has reviewed the work published so far on the process integration of CaL post-combustion systems. Energy penalties for the full system of Figure 12 are reported to vary between 6 and 9 net percentage points. The largest penalties correspond to conservative assumptions for calcination temperatures (several studies assume 950°C) and a low O₂ content in the gas to the calciner (high recycles of CO₂ largely increase energy consumption in the calciner). In general, all studies agree that the main unavoidable penalty is associated with the purification and compression of CO₂ (3-4 net efficiency points) with the remaining penalties being mainly associated with the consumption of pure O₂ for the combustion of the fuel fed to the calciner. The penalty linked to the calcination of the fresh sorbent can be avoided if the sorbent purge is used as a feedstock for cement manufacture. The impact of SO₂ on sorbent activity and the fraction of ashes of the coal used in the calciner are important issues to determine the system performance. Based on the typical assumptions for these parameters, the energy requirements in the oxy-fired calciner in the CaL system of Figure 12 are large (of the same order as the thermal power input to the reference plant without capture). This means that the steam generator, G2, in Figure 12 is of comparable scale to the steam generator in the reference plant, G1. Indeed, it can be argued that a CaL system is in fact a new oxyfired CFBC power plant that, thanks to the intermediate role of the carbonator reactor, is capturing not only the carbon contained in the

1 coal fed to the oxyfired CFBC calciner but also the carbon captured as CaCO_3 from the air-fired
2 reference plant.

3
4 The CaL system may be viable and competitive as represented in Figure 12, but there is substantial
5 potential for energy and equipment cost savings by minimizing the energy requirements in the
6 calciner and/or by reducing the O_2 consumption in the calciner. This is one of the main targets of
7 current R&D on CaL systems. Strategies proposed for this purpose are one, or a combination, of the
8 following:

- 9
- 10 - Minimize the temperature of calcination and/or increase the temperature of carbonation.
11 Current experience acquired from large scale pilots (Arias et al., 2013, Ströhle et al., 2014a,
12 Dieter et al., 2013) indicates that it is possible to calcine over 90% of the circulating solids at
13 temperatures close to 900°C with a CO_2 concentration of around 80%v (water vapour is the
14 main remaining gas at the exit of the calciner).
 - 15 - Increase the activity of the circulating material. This allows the solid circulation to be
16 minimized, thereby reducing the heat requirements for heating up the circulating solid
17 stream from the temperature of the carbonator to that of the calciner. Different strategies
18 have been being proposed to obtain a more stable sorbent (i.e. sorbent hydration, sorbent
19 doping, recarbonation) some of which have been reviewed in some recent papers (Blamey
20 et al., 2010, Kierzkowska et al., 2013).
 - 21 - Maximize the O_2 content in the gas mix fed to the calciner. This will reduce the CO_2 recycle
22 and avoid the consumption of energy used to heat up the gas recycle.
 - 23 - Preheat the solid stream coming from carbonator before it enters the calciner. This was
24 proposed by (Epple, 2009) by arranging heat exchangers or heat pipes between the
25 circulating solids streams and with high temperature heat sources in the system. The direct
26 heating of the carbonated solids by placing them in contact with hot CO_2 rich gases has also
27 been proposed (Romano et al., 2011) with the same objective.
 - 28 - Indirect heat transfer through a wall from the combustion chamber generating the flue gas
29 fed to the carbonator. This has only been developed at a conceptual level (Abanades et al.,
30 2005), underlying the difficulty of exploiting the very large heat transfer areas between two
31 high temperature fluidized beds. Other novel concepts involving heat pipes and high
32 temperature alloys are still in the practical development stage (Reitz, 2014) (Figure 13 right).
 - 33 - Direct heat transfer using high-temperature circulating solids from the combustion chamber.
34 This is possible only when the reference plant generating the flue gases is a circulating
35 fluidized bed operating at temperatures of around 1000°C . The hot solid stream abandoning
36 the combustor enters the calciner and transports the heat necessary for calcination
37 (Martínez et al., 2011). Other novel options involving gas-solid heat transfer in suspension
38 preheaters similar those used in cement plants are also under consideration (see Figure 13
39 left) (Abanades, 2013, Romano et al., 2013b).
- 40
41
42

Figure 13. Examples of advanced CaL process schemes that avoid the need for an air separation unit by supplying heat for calcination from the combustion chamber. Left side) Direct heat transfer using suspension preheaters (adapted from (Abanades, 2013)). Right side) Indirect heat transfer using heat pipes (adapted from (Junk et al., 2013)).

An important parameter in the design of calcium looping systems is the limestone consumption or make-up flow. Limestone is a very cheap CO₂ sorbent precursor and costs only around 10-30 €/tonne in many locations. Therefore, make-up flows ratios (mol of fresh sorbent entering the system / mol of CO₂ captured) as high as 0.1 may translate into an operating cost comparable to solvent-based post-combustion systems, since these can reach a unit cost that is several orders of magnitude larger than the cost of crushed limestone. Furthermore, it is increasingly being better understood the potential synergy between a CaL system and a cement plant (Dean et al., 2011, Romano et al., 2013b, Ozcan et al., 2013, Rodríguez et al., 2012, Romeo et al., 2011). The purge material, with a high CaO content, can be used as feedstock for clinker production, thereby reducing the operating costs of the looping cycle and de-carbonising both the power plant and cement industry. The purge material could be also used for desulphurising the flue-gas, since the deactivated material for CO₂ capture has very good SO₂ absorption properties, at least in CFBC environments. The process concepts of calcium looping for use in other large scale industries (like Blast Furnace gases or Direct Reduction Schemes) can also be envisaged in the future.

Finally, an important issue for all CO₂ capture technologies is their ability to adapt to scenarios where large load changes and flexibility is required. The flexibility of Calcium looping system could increase to a large extent by taking advantage of the solids circulating between reactors at high temperature for storing thermal energy and chemical energy (calcining during low demand periods and carbonating during high power demand periods)(Arias et al., 2014). Although these are still concepts that are in an early stage of R&D (TRL 1-2), they offer good potential for moving up in scale given the maturity of technologies for storing, handling and circulating large flows of CaO and derived materials.

In addition to coal-based power generation CaL systems, process schemes for Natural Gas Combined Cycles have also been considered recently (Berstad et al., 2012). Experimental proof of the concept

of Calcium looping adapted to biomass combustion (negative emissions concepts) has also been analysed and tested at TRL4 and TRL5 (Alonso et al., 2014, Alonso et al., 2011) by transforming the carbonator into a full combustion boiler by firing biomass in air at sufficiently low temperature (700°C) to allow the simultaneous capture of CO₂ with CaO.

3.2 Pre-combustion Calcium looping

The original process concepts that make use of the CaO/CaCO₃ reversible equilibrium for CO₂ separation in coal gasifiers date back to the XIX century (see (Anthony, 2011)). The Acceptor Gasification Process (Curran, 1967), was developed in USA to obtain a fuel gas of high heating value by shifting coal gasification reactions towards H₂ (at temperatures of 815 °C and a pressure of 20 bar), as the particles of CaO fed to the gasifier deplete the gasification atmosphere of CO₂. The regeneration of CaCO₃ was achieved by burning coal in an air-fired fluidized bed combustor at an identical high pressure as that in the gasifier, requiring temperatures over 1060°C to ensure fast calcination under the high partial pressure of CO₂ (about 4 atm) in this combustor. This concept was experimentally demonstrated at a pilot plant of 40 t/d of coal (TRL7 with no CO₂ capture), though many problems arose related with the handling of the materials in the interconnected bubbling fluidized bed twin reactor system at high pressure. More recently, the Absorption Enhanced Reforming (AER) process was developed in Europe (Pfeifer, 2013) to obtain a gas with a high heating value from the gasification of biomass at atmospheric pressure. The AER system comprises two interconnected fast fluidized beds (a biomass gasifier and an air-fired combustor-calciner) and has been successfully demonstrated at TRL7 in the 8 MW_{th} pilot plant at Güssing (Hofbauer, 2003). Other far less developed and more challenging variants that use coal as fuel include the HyPr-RING process (Lin et al., 2011), the Lime Enhanced Gasification, LEGS, (Weimer et al., 2008) and the Calcium Looping Process, CLP, (Ramkumar et al., 2011).

In the Sorption Enhanced Reforming, SER, of natural gas with steam, a bed composed of a reforming catalyst and CaO can yield almost pure H₂ with very high fuel conversions and minimal CO and CO₂ formation. This process has been already studied and partially tested at laboratory scale conditions (see review from (Harrison, 2008)). A fundamental barrier for these processes when they are designed as CO₂ capture systems is the challenge problem of CaCO₃ decomposition at the high pressure (10-20 atm) of the reformer required to obtain high energy efficiency. There are also alternative fixed-bed configurations that involve pressure swing strategies similar to novel packed bed CLC systems (Hamers et al., 2014) but incorporating the use of a second gas-solid exothermic reaction to supply the heat required for the calcination of the CaCO₃. However, these systems are at a very early stage of development (Fernández et al., 2012).

Pre-combustion Calcium Looping systems for CO₂ capture are still today less mature and more challenging than their post-combustion counterparts. Although they offer the promise of a higher energy efficiency, inherent to H₂ production and the downstream conversion routes (i.e. fuel cells or advanced combined cycles fired for H₂), they are still in need for further development (apart from new pelletized materials with the ability to sustain chemical and mechanical properties for many cycles) and experimental testing at a small scale (TRL 3-4) to obtain relevant design parameters for large scale systems. Accordingly, the following sections will only refer to the combustion-based Calcium Looping systems introduced in 3.1.

3.3 Pilot demonstration of CO₂ capture by Calcium Looping in combustion systems

The CaL concept to capture CO₂ from a combustion flue gas at atmospheric pressure was experimentally tested in a Circulating Fluidized Bed Combustion test facility (Anthony, 1988) adapted to allow multicycle carbonation-calcination test to be carried out with a batch of lime (Abanades et

al., 2004). This installation was also used for early sorbent attrition and oxy-calcination studies under a high concentration of O₂ (Jia et al., 2007). These tests showed that it was possible to achieve a high CO₂ capture efficiency (>90%) using reasonable bed inventories of active material and gas-solid contact times characteristic of high velocity fluidized beds. Higher capture efficiencies have been reported in experiments conducted in other batch rigs, using bubbling fluidized beds (see for example (Fang et al., 2009)) operating at lower gas velocities. However, it is clear from the discussion in the Introduction of this paper that large scale carbonator reactors must be able to accommodate high superficial gas velocities (>3 m/s) in order to have reasonable cross-sections. Therefore, circulating fluidized bed or entrained bed carbonators seem to be the most suitable reactors for the CO₂ carbonation step.

Two continuous lab scale pilots designed and built at CSIC in Spain and Stuttgart University's IFK in Germany (Charitos et al., 2010, Rodríguez et al., 2011) reported extensive experimental work in circulating fluidized bed carbonators operating in full continuous mode. The INCAR-CSIC pilot is a 30 kW_{th} test-rig with two CFB interconnected fluidized bed reactors (100 mm id and 6.5 m height). The IFK pilot operates with a much taller circulating fluidized bed carbonator (12.4 m) interconnected to a bubbling fluidized bed calciner. The CO₂ capture efficiencies measured in these pilots were consistently around 90% under conditions close to those that can be expected in large systems. In particular, the higher riser and higher gas velocities in the IFK pilot led to capture rates close to those targeted in commercial CaL systems (up to 10 mol CO₂/m²s). The IFK researchers observed negligible attrition with their limestone, while intense attrition was observed in the CSIC pilot with two different limestones (Charitos et al., 2011, González et al., 2010). More than 800 operation hours have been accumulated in these rigs, including experiments with simultaneous combustion of biomass in the carbonator that allowsr "in situ" CO₂ capture during the combustion of biomass (Alonso et al., 2011).

Table 8. Main characteristics of large Calcium looping pilot plants (>100 kW_{th}).

	La Pereda (Spain)	Darmstad (Germany)	IFK (Germany)	La Robla (Spain)	ITRI (Taiwan)
Thermal input	1.7 MW _{th} referred to carbonator	1 MW _{th} referred to calciner	50-230 kW _{th} referred to carbonator	300 kW _{th} referred to the biomass fed to carbonator	1.9 MW _{th} (1 t _{CO}
Configuration	Calciner: CFB Carbonator: CFB	Calciner: CFB Carbonator: CFB	Calciner: CFB Carbonator: FFB* and TFB*	Calciner: CFB Carbonator: CFB	Calciner: rotary Carbonator: FB
Height	Calciner: 15 m Carbonator: 15 m	Calciner: 11.4 m Carbonator: 8.6 m	Calciner: 10 m Carbonator: 10 m (FFB*), 6 m (TFB*)	Calciner: 12 m Carbonator: 12 m	Calciner: 5m (le Carbonator: 2.5
Diameter	Calciner: 0.75 m Carbonator: 0.65 m	Calciner: 0.4 m Carbonator: 0.59 m	Calciner: 0.21 m Carbonator: 0.21 m (FFB+), 0.33 m (TFB+)	Calciner: 0.4 m Carbonator: 0.4 m	Calciner: 0.9 m Carbonator: 3.3
Control of solid flow	Cone valves	Screw conveyors	Cone valves	On:Off loop seal	Kiln rotation sp
Flue gas source	Integrated with power plant	Flue gas from coal burner	Synthetic flue gas	Flue gas generated in carbonator	Integrated with cement plant
Calciner operation	Oxy-fired with coal	Oxy-fired with coal/propane	Oxy-fired with coal and flue gas recycle	Air-fired with biomass	Oxy-fired with
Project name or website	http://recal-project.eu/ ; http://cao2.eu	http://www.project-scarlet.eu/	http://cal-mod.eu-projects.de/	MenosCO2	HECLOT

* FFB: fast fluidized bed, TFB: turbulent fluidized bed.

On the basis of experience acquired at TRL4, the design and commissioning of the 1.7 MW_{th} CaL pilot at “la Pereda” was undertaken (Sánchez-Biezma et al., 2011). This pilot treats about 1/100 of the flue gas of a CFBC power plant located in Spain. Hawthorne et al. (Hawthorne et al., 2011) reported the design, construction and commissioning a 200 kW_{th} pilot at IFK in Stuttgart in Germany. These large pilots have published updated results (examples of Figure 14, extracted from (Arias et al., 2013, Dieter et al., 2013)) and are still active in EU projects. Another project in Germany has published the first positive results from a 1 MW_{th} test facility, located at Darmstadt University (Galloy, 2011) which is being refurbished to operate over much longer periods in steady state (<http://www.project-scarlet.eu/>). In Taiwan, ITRI (Chang et al., 2013) has built a 1.9 MW_{th} pilot plant specially adapted for the cement application by using a rotary kiln calciner. Moreover, a 300 kW_{th} CaL pilot designed to test CaL with “in situ” biomass combustion in a combustor-carbonator reactor has also reported positive results after several hundred hours of operation (Alonso et al., 2014).

The experimental results from CaL pilots can be interpreted using a methodology developed under the FP7 EU “CaOling” project (Charitos et al., 2011). This is based on a CO₂ mass balance closure during steady state, in which the flow of CO₂ reacting with the CaO in the carbonator bed is matched with the flow of CaCO₃ measured in the circulating stream of solids and the CO₂ flow removed from the gas phase. These terms can be estimated independently in these facilities by periodically sampling solids from the twin reactors. As an example, the carbon mass balance shown in Figure 14b compares the flow of CO₂ disappearing from the gas phase with the flow of CaCO₃ generated in the solid phase, indicating a reasonable closure. Basic reactor models (assuming a perfect and instant mixing of solids in both reactors and plug flow in the gas phase) have been used to interpret the results obtained from these pilots by using an average reaction rate (s⁻¹) for the solids extracted from the carbonator (Rodríguez et al., 2011, Alonso et al., 2011). These basic models proved to be useful tools for scaling up to larger pilots. However, more advanced 3D models are being developed to predict the behaviour of larger units (Ylätaalo et al., 2014), where deviations from instant solid mixing and ideal distribution of gas reactants require a greater spatial and time resolution in the reactor model.

The co-capture of SO₂ and CO₂ is extremely efficient in CaL systems because of the very high Ca/S molar ratio inherent to the active CaO required for CO₂ capture. During the experimental campaigns carried out in the 1.7MW_{th} pilot plant of La Pereda, SO₂ capture efficiencies higher than 95 % from flue gas fed to the carbonator (with an inlet concentration of 200-300 ppmv during this period) have been consistently observed (Arias et al 2013). This is at the expense of an increase in limestone consumption to compensate for the irreversible deactivation (forming CaSO₄) of part of the active CaO capturing CO₂.

Figure 14. Example of experimental results from large CaL pilots. a) typical run results from the IFK 200kW_{th} pilot (Dieter et al., 2014). b) closure of the carbon balance in the 1.7 MW_{th} pilot of la Pereda (Arias et al., 2013).

From the experimental results and modeling work linked to existing CaL pilots, several key parameters have been revealed as playing a major role in reactor performance. It is first necessary to ensure a sufficient flow of active CaO to match the flow of CO₂ to be captured from the flue gas. As mentioned above, this is relatively easy to achieve even when materials of low activity (measured as maximum molar conversion of CaO to CaCO₃ at the end of the fast carbonation period) are circulating between the reactors, due to the large solid circulating capacity of CFB reactors. Another important operating variable that affects the CO₂ capture efficiency in the carbonator is the inventory of solids in the reactor (kg of solids per unit of cross-section of the reactor). Both variables (inventory and activity) are interrelated, so that the use of a low activity sorbent may be compensated for by using large inventories in the carbonator and vice versa. Since the fluid-dynamics of high velocity CFBs with CaO particles is very similar to CFBCs, (Diego et al., 2012) have estimated that the internal circulation in the carbonator and calciner reactors in a CaL system is higher than that needed between reactors to capture CO₂ in a wide range of operation conditions. Therefore, only a fraction of the solids leaving the carbonator and calciner reactors will need to be transferred to the other reactor.

When the carbonator and calciner are circulating fluidized bed reactors, many of the key elements in the twin reactor system (the risers, the cyclones, the return legs and loop seals, the heat transfer equipment to recover heat towards an efficient steam cycle, the structural components and materials, etc.) can be confidently scaled up using the existing know-how and experience acquired from commercial CFBC power technology. Figure 15 shows an example of such an exercise (Ylätaalo et al., 2014) for a system treating a flue gas flow of 116 kg/s produced in a 250 MW_{th} power plant. The carbonator and calciner have cross-section areas of 44 and 60 m², respectively, so that they can achieve a flue gas velocity of 6 m/s. In order to accommodate the cyclones, standpipes and loop seals, the total height of the reactors is 35 m. The structural connection shown in Figure 15 allows the recirculation of a fraction of the solids leaving the reactors (approximately a 40%) in order to allow the circulation of solids between the reactors to be adjusted. This solution can also be modularized to enable it to be applied in larger units as is currently in the case in CFB based power plants.

Figure 15. Preliminary lay-out of a large scale Calcium Looping system for capturing the CO₂ produced in a power plant (Power plant: 250 MW_{th}, Calciner: 277 MW_{th}, CO₂ capture efficiency: 85 %). From (Ylätalo et al., 2014)

The experience acquired in larger pilot plants confirms that post-combustion Calcium looping using CFB reactors is a promising technology for CO₂ capture as it bears a very close similarity to existing CFBC combustion and oxy-combustion technologies. This is what facilitates a simple analysis of the cost structure of large scale CaL systems.

3.4 Cost structure of a post-combustion CaL system

The cost of CO₂ capture using emerging technologies is highly uncertain because of the inherent gaps of knowledge about the design and operational aspects of the system when applied at large scale. Furthermore, it is well known that developers tend to be over-optimistic in their cost estimates for emerging energy technologies (IPCC, 2005). Therefore, it has been recommended (Rubin et al., 2013) to estimate the capital cost of emerging CO₂ capture concepts with a process contingency factor that increases the capital cost by 30-70%. The choice of a high contingency factor can have very negative consequences for the economics of Calcium Looping (Mantripragada, 2014) when this is also applied to the standard power generation equipment required to produce electricity from the additional energy input to the CaL system. Accordingly, the following paragraphs will refer only to the cost structure of a mature CaL system, focusing on a n-th plant of its kind, assumed to be able to exploit highly mature subsystems in the power sector. A brief discussion of the contingency cost and other non-technical factors is introduced at the end of the section through a sensitivity analysis.

As mentioned above, the full CaL system of Figure 12 includes within its boundaries an existing air-fired power plant as well as a second power plant linked to the carbonator and calciner CFB reactors (through the steam cycle G2). The cost of this second power plant can be assumed to be proportional to the cost of an oxy-fired CFBC system with the same coal input. Therefore, the largest cost component of the system will include (see Figure 12) that of the coal and ash handling equipment linked to the calciner, the ASU, the CFB carbonator reactor (assumed to be the boiler in the steam cycle G2), the heat recovery equipment, the steam turbine, the flue gas cleaning equipment, the auxiliaries and a certain share of the CPU unit. The remaining share of the CPU corresponds to the part of the CPU that treats the CO₂ captured from the existing power plant. For the sake of simplicity, and to avoid unnecessary details on mass and heat balances that have been extensively reported in the literature since the early work of (Shimizu et al., 1999), we will assume from this point that 55% of the coal fed to the full system is air-fired to the existing power plant and

45% is fired to the oxy-fired CFB calciner. We will also assume that all energy penalties and cost of the common equipment (like the CPU) are also shared in accordance with the 55/45 rule. On the basis of these assumptions, the cost of most of the elements in the Calcium Loop can be approximated from recent existing cost studies on oxy-fuel combustion plants (DOE/NETL, 2010, ZEP, 2011). Only the refractory combustion chamber used as calciner requires a separate cost estimation (the heat transfer surfaces linked to Q3, or the coal and oxidant feeding equipment linked to the calciner have already been accounted for in the “boiler cost” of the oxy-fuel combustion plant referred to above). The calciner is a piece of equipment that can be claimed to be similar to industrial scale CFBC mineral roasters. Therefore, we can assume it to be similar to large scale refractory CaCO_3 precalciners in cement plants, for which some cost information exists (IEA, 2008).

Table 9 summarizes the main parameters adopted for the cost calculations carried out in this work. The reference plant is assumed to be a newly built air-fired pulverized coal power plant with a specific cost of 1900 $\$/\text{kW}_e$ (assuming a net efficiency of 45%) and specific emissions without capture of 750 $\text{kg CO}_2/\text{MWh}_e$. The equipment costs of the remaining key parts of the full system are justified below:

- The equipment cost of the oxyfired-CFB power plant subsystem is assumed to be 3500 $\$/\text{kW}_e$ -net (2722 $\$/\text{kW}_e$ -gross assuming a gross efficiency of 45% before including penalties associated with the CPU and ASU), which is consistent with the estimation by (DOE/NETL, 2010, ZEP, 2011).
- The equipment cost of the CPU is assumed to be 180 $\$/\text{kW}_e$ -gross, which is only applies to the fraction of the CO_2 captured in the existing air-fired power plant as the rest is already included in the equipment cost of the oxyfired CFB power plant.
- The equipment cost of the refractory calciner is assumed to be 280 $\$/\text{kW}_e$ -gross. This is calculated from the cost of the precalciners used in a cement plant (including a five stage preheater) (IEA, 2008).

Table 9. Summary of main assumptions used for the economic analysis and cost results.

	Units	Reference	CaL (full Fig. 1)	Oxy-CFB
Specific costs, TCR	$\$/\text{kW}_e$ -net ($\$/\text{kW}_e$ -gross)	1900 (1900)	2890 (2495*)	3500 (2722)
Capacity factor		0.85	0.85	0.85
Fixed charge factor, FCF		0.1	0.1	0.1
Fixed fraction costs, FOM		0.04	0.04	0.04
Variable costs, VOM	$\$/\text{kWh}_e$	0.005	0.007**	0.007
Fuel cost, FC	$\$/\text{GJ}$	2.0	2.0	2.0
Net efficiency	$\text{kW}_e/\text{kW}_{th}$	0.45	0.388	0.350
CO_2 emission factor	$\text{kg}_{\text{CO}_2}/\text{MWh}_e$	750	67***	48***
Cost of electricity (COE)	$\$/\text{kW}_e$	0.047	0.066	0.077
Avoided costs (AC)	$\$/\text{t}_{\text{CO}_2}$	---	27	41

*Calculated for gross output as $\text{TCR}_{\text{CaL}} = (\text{TCR}_{\text{reference}} + \text{TCR}_{\text{CPU}}) * 0.55 + (\text{TCR}_{\text{Oxy-CFB}} + \text{TCR}_{\text{CC}}) * 0.45$

**This includes the cost of limestone, calculated assuming 10 $\$/\text{t}$ limestone and a make up flow consumption of 0.5 kg limestone/ kg coal fed to the calciner.

***Assuming a CO_2 capture efficiency of 0.92 for the CaL and 0.95 for the Oxy-CFB.

As indicated in Table 9, all the specific cost figures increase when they refer to net power outputs estimated with an overall efficiency on the full system of 6.2 net points (from 45% LHV to 38.8 %, assuming a net penalty linked to the CPU of 3 net points and a net penalty linked to the ASU of 7 net points that becomes 3.2 net when it refers to the full system, where only 45% of the fuel is oxy-fired). This overall penalty is consistent with recent process integration studies reviewed above, for CO_2 capture rates of around 90-95% for the overall system. Efficiency penalties associated with the

calcination of the make up flow of limestone required to maintain a given activity in the capture loop are considered zero, as it is assumed that an equivalent energy credit would be obtained from a cement plant or desulfurization plant using deactivated CaO from the CaL system. Under these conditions, the specific CO₂ emissions decrease to 67 kg_{CO2}/MWh_e. With a further assumption of 10 \$/tonne of CO₂ to account for transport and storage a final set of reference cost figures of COE= 0.074 \$/kWe and AC= 38 \$/tCO₂ can be estimated (they would be 0.086 \$/kWe and 54.3 \$/tCO₂ for the Oxy-CFB case).

	Units	-1	0	+1
Calciner cost	\$/kWe	200	280	360
Cost of Oxy-CFB	\$/kWe	2000	2720	3400
Cost of reference plant	\$/kWe	1400	1900	2200
Calciner power fraction		0.35	0.45	0.45
Limestone Cost	\$/t	0	10	20
Limestone make-up	kg/kg _{coal}	0	0.5	1

Figure 16. Sensitivity analysis on the cost of the electricity (a) and avoided costs (b) of a standard CaL system.

Figure 16 shows the effect of some parameters on the cost of the electricity and the avoided costs. Post-combustion CaL typically yields cost figures that are somewhere between the extremes for the reference plant and a reference oxy-fired system (included in Table 9 and Figure 16 as a reference, using equivalent assumptions for equipment cost and energy penalties). One of the most important parameters in the economics of CaL is the contribution of the cost of the oxyfired CFB. Since oxyfired CFBC is an enabling technology for the CaL system, any benefit directed at reducing cost of oxy-fired CFB technology will also benefit CaL. Another important parameter which can improve the economics of CaL is the cost associated with the existing power plant. This can be reduced by a greater integration of the power plant (by feeding warm flue gases to the carbonator, by integrating elements of the two separate steam cycles). The integration of the power plant and the carbonator of the Calcium looping can also avoid the need for an FGD unit (at the expense of an increase in limestone consumption) due to the ability of this reactor to capture SO₂ from flue gases. However, it is evident that the best prospects for cost reductions in CaL systems come from measures intended to minimize the equipment cost linked to the fraction of coal burned in the oxyfired-CFB as indicated

1 in section 3.1. However, the cost of more advanced high efficiency CaL concepts (such as those in
2 Figure 13) are uncertain at present.

3
4 Finally, as mentioned above, the increase in capital cost shown in Table 9 when the contingency
5 factor is included has drastic effects on the economics of Calcium looping. For example, an increase
6 of 30% in the TCR due to a contingency factor, would put CaL in a non-competitive position with
7 respect to an oxyfuel combustion system delivering the same power output. In this scenario, a CaL
8 system could still be competitive with respect to stand-alone oxy-fired systems because CaL could be
9 retrofitted to existing power plants (where they would be repowered with the additional electricity
10 produced from the coal fed to the calciner) but it would not be competitive with other post-
11 combustion systems that have a capture cost comparable to oxyfuel systems. It is therefore essential
12 to demonstrate in practice that CaL systems can be designed confidently (with low contingency
13 factors) due to the current maturity of all its components and that advanced concepts of calcium
14 looping that are still under development can really reduce capital and operating cost with respect to
15 the standard CaL system of Figure 12.

16 17 3.5. Outlook for Calcium looping 18 19 20 21

22 **4. Solid sorbents** 23

24 This section deals with large scale gas separation processes involving low temperature solid sorbents
25 interacting with a substantial fraction of a gas (i.e. CO₂ in post- or pre-combustion capture).
26 Therefore, purification processes targeting the removal of a trace component in a gas mixture are
27 considered outside the scope of this review (even if these processes can be important in a range of
28 industries, including future CCS systems). As mentioned in the introduction (Figure 1), the need to
29 target the separation of a very large flow of gas imposes particular characteristics to these systems
30 and the materials operating in them. Most of the text below refers to adsorption-based processes,
31 because they are the most developed and receive wider R&D attention for CO₂ capture. A small
32 section reviews the status of other low temperature post-combustion systems involving bulk gas-
33 solid reactions. These type of materials and interactions are also present in some emerging pre-
34 combustion systems (i.e. sorption enhanced water gas shift SEWGS process, as noted in Table 1) .
35

36 **4.1 Adsorption** 37

38 Adsorbents can be used to separate gases in a range of possible process configurations, which
39 depend primarily on the type of interaction between the material and the target molecule and the
40 method used to regenerate the adsorbent which is typically achieved either reducing the pressure
41 (Pressure Swing Adsorption, PSA) or increasing the temperature (Temperature Swing Adsorption,
42 TSA) (Ruthven, 1984, Yang, 1987). The difference between the adsorption conditions and the
43 regeneration conditions will determine the actual working capacity of the material as qualitatively
44 described in Figure 17. To predict how to achieve the optimal process performance is not
45 straightforward, since this depends on a range of physical properties of the adsorbent material; the
46 way in which the adsorbent material is packaged; and the sophistication of the process configuration.
47

Figure 17. Adsorption isotherms at different temperatures and working capacity.

The gas separation can be based on physisorption or chemisorption which differ primarily by the heat needed for regeneration. The principles by which a physical adsorbent shows selectivity for a molecule over another can be understood relatively easily considering the fundamental properties of carbon dioxide and those of the main components of interest in the gas mixtures present in carbon capture applications. As can be seen from Table 10, CO₂ is a non-polar molecule with a large quadrupole.

Table 10: Physical properties of selected gases relevant to carbon capture applications.

Molecule	Polarizability (Å ³) ¹	Quadrupole moment (10 ⁴⁰ cm ²) ¹	Dipole moment (Debye) ¹	Kinetic diameter (Å) ²
CO ₂	2.507	14.3	–	3.3
N ₂	1.710	4.7	–	3.64
CO	1.953	9.5	0.112	3.76

¹ (NIST); ² (Breck, 1984).

Qualitatively the dispersion forces typical of interactions between an adsorbate and an adsorbent increase in proportion to the polarizability of the molecule and depend on the relative size of the molecule and the micropores of the solid. Therefore any non-polar adsorbent such as a non-modified carbon or silicalite will show selectivity towards CO₂ over oxygen, nitrogen, hydrogen, carbon monoxide and water (Ruthven, 1984). While a process can be in principle designed once a selectivity is present, the actual absolute amounts adsorbed in non-polar materials are low for post-combustion carbon capture (less than 0.5 mol/kg at 0.1 bar and 40 °C, ie less than 3% in weight) resulting in unrealistic sizes of process units and limited ranges of achievable product purity and recovery. The introduction of surface modifications or localised charges (cations in zeolites or open metal sites in metal-organic-frameworks) effectively tunes the electrical field within the adsorbent in order to act on the quadrupole of CO₂ through the gradient of the electrical field. The selectivity can be increased considerably and absolute amounts adsorbed arrive at values above 2 mol/kg (at 0.1 bar and 40 °C, ie approximately 10% in weight or more). The drawback of using a polar adsorbent is that now the material is also very hydrophilic and water will displace CO₂ reducing the actual capacity of the solid. This does not preclude the use of these materials since adsorption separations are dynamic processes and if countercurrent regeneration is used the penetration of the water front in the adsorbent bed can be controlled (Zhang et al., 2007). From Table 10 it can be seen that it is

also possible to increase further the selectivity of the materials towards CO₂ if the micropore sizes are close to 3.6 Å, where a molecular sieving effect takes place. This approach has been used in Chabazite, which has a nominal maximum diameter for a diffusing molecule of 3.72 Å (Baerlocher et al., 2007) which can be tuned by changing the cations in the structure (Zhang et al., 2008). The properties of zeolite Rho (4.06 Å nominal maximum diameter for a diffusing molecule) can also be modified to the point where molecular sieving is achieved even with cations that should be too large for CO₂ to pass, confirming the mechanism of cation gating or molecular trapdoor, where the fluctuations in the positions of the cations are used to control the access to the cages (Lozinska et al., 2012, Lozinska et al., 2014, Shang et al., 2013). The challenge for these materials is that in order to be used in practical applications the crystal dimension has to be very small so that the diffusional time constant of CO₂ is not too slow, but the selectivity to N₂ in post-combustion applications is effectively infinite. It is worth noting that micropore diffusion control is to be expected only in zeolites with pore sizes close to 4 Å (Ruthven, 1984) and in general unless a molecular sieving effect is achieved it is always preferable to avoid this kinetic limitation. Assuming erroneously micropore diffusion as the controlling mechanism for larger micropores will lead to the incorrect conclusion that the particle size of the adsorbent beads should be as large as possible to reduce pressure drops (Hu et al., 2014).

Table 11. Adsorption properties of selected physisorption adsorbents

Adsorbent	Pore volume ¹ (cm ³ /g)	CO ₂ capacity ² (mol/kg)	ΔH _{ads} (kJ/mol)	Saturation capacity (mol/kg)	Ref.
K-CHA	0.434	3.8 mol/kg (303 K)	24.6	4.8	(Zhang et al., 2008)
Na-CHA	0.434	4.2 mol/kg (273 K)	39.4	5.2	(Zhang et al., 2008)
Li-CHA	0.434	4.7 mol/kg (273 K)	38	5.1	(Zhang et al., 2008)
Ca-CHA	0.434	3.9 mol/kg (273 K)	41.7	4.5	(Zhang et al., 2008)
Ca-X		2 (323 K)	53.3	3.6	(Brandani et al., 2003)
Ca-A		2.5 (323 K)	43.9	3.3	(Brandani et al., 2003)
Na,Cs-Rho	0.439	2.25 (298 K)			(Lozinska et al., 2012)
Na-Rho	0.439	3.07 (298 K)			(Lozinska et al., 2012)
K-Rho	0.439	1.50 (298 K)			(Lozinska et al., 2012)
Na-ZK-5		4.05(298 K)			(Lozinska et al., 2012)
Li-ZK-5		4.67 (298 K)			(Lozinska et al., 2012)
LiX		2.5 (308 K, 8.97 kPa)	70		(Park et al., 2014a)
13X	0.506	2.6 (295 K)	42.5		(Harlick et al., 2004)
NaY		2 (295 K)	36.1		(Harlick et al., 2004)
13X		3.03 (308 K)			(Mangano et al., 2013)
Silicalite	0.242	0.343 (303 K)	29.3		(Dunne et al., 1996)
HKUST-1	0.801	0.62 (295 K)	25.1		(Yazaydin et al., 2009)
Pd(2-pymo) ₂	0.385	0.86 (293 K)	48.6		(Yazaydin et al., 2009)
MOF-177	1.890	0.08 (298 K)	15.7		(Yazaydin et al., 2009)
Ni-CPO-27	0.530	4.07 (298 K)	26.0		(Liu et al., 2012a, Yazaydin et al., 2009)
Co-CPO-27	0.543	2.81 (298 K)	25.4		(Yazaydin et al., 2009)
Mg-CPO-27	0.702	5.95 (298 K)	26.7		(Liu et al., 2012a, Yazaydin et al., 2009)
UMCM-150	1.186	0.26 (298 K)	20.6		(Yazaydin et al., 2009)
Mg-CPO-27		4.66 (308 K)			(Mangano et al., 2013)
PAC (grass cutting)	0.379	0.9 (298 K)	34		(Hao et al., 2013)
AC		0.389 (308 K , 8.77	35		(Park et al., 2014a)

		kPa)			
BPL		0.13 (298 K)	25	10.35	(Himeno et al., 2005)
JX101		0.18 (298 K)	24.7	11.87	(Wu et al., 2007)
BPL		0.35 (308 K)			(Mangano et al., 2013)

¹ (First et al., 2011); ² At 10 kPa unless specified in the table.

In pre-combustion applications, given the increased partial pressure of CO₂, the capacity of the adsorbent depends on the available micropore volume which is related to the saturation capacity of the material. Materials with high heats of adsorption tend to saturate at relatively low pressures and are therefore less suitable for pre-combustion capture, this can be mitigated in part by operating the separation at a higher temperature.

Table 11 shows typical adsorption properties for selected materials of different classes of adsorbents. From the data it is clear that for post-combustion applications working capacities of good novel materials (mainly zeolites and MOFs) are in the range of 2-3 mol/kg and heats of adsorption are in the range 30-45 kJ/mol. Carbon based or mesoporous materials without active surface groups have higher saturation capacities and are therefore more suitable for pre-combustion applications if a good selectivity is achieved. Chemisorption can be achieved by introducing amine groups or other chemically active surface modifications that form a chemical bond with CO₂. In this case the highly porous materials provide a structure that maximises the density of the specific adsorption sites. The adsorption isotherms in these materials are almost rectangular, ie very sharp, making them suitable primarily for temperature swing processes, and working capacities are typically around 1 mol/kg (Chen et al., 2014). Increasing the process temperature to 80 °C has been shown to lead to conditions suitable for VSA using these types of materials (Ebner et al., 2011).

Table 12 shows the adsorption properties of a range of amine-supported materials. These systems are clearly highly selective, but require an increased amount of heat to regenerate the material and the heat of adsorption is comparable to the heat of reaction of the corresponding aqueous solution. The key advantage over traditional liquid phase absorption systems based on amine or sodium hydroxide solutions is the fact that the heat capacity of the solid adsorbent is lower than that of the solution and evaporation of water is avoided (Webley, 2014). This leads to an overall reduction in the energy penalty of the carbon capture process since less energy is needed to heat the system to the regeneration temperature. These materials are still selective to CO₂ in the presence of water and in fact show improved separation performance with water present, so that countercurrent regeneration or feed gas pre-drying is not needed.

Table 12. Adsorption properties of selected amine based chemisorption adsorbents

Adsorbent	Amine group	T (K)	Partial pressure of CO ₂	CO ₂ capacity (mol/kg)	ΔH _{ads} (kJ/mol)	Ref.
PE- MCM-41	DEA	298	0.05 atm	2.85 (dry) 2.85 (wet)		(Franchi et al., 2005)
PE- MCM-41	TRI (anhydrous grafting)	298	0.05 atm	1.55 (dry) 1.66 (wet)		(Harlick et al., 2006)
PE MCM-41	TRI (H ₂ O aided grafting)	298	0.05 atm	2.65 (dry) 2.94 (wet)		(Harlick et al., 2006)
H5a-DT	TRI	298	0.9 atm	1.2 (dry) 0.96 (wet)	60	(Knowles et al., 2006)
H5a-DT	TRI	348	0.9 atm	0.455 (dry)	92	(Knowles et al., 2006)
H5c-p24	AP	298	0.9 atm	1.59 (dry)	60	(Knowles et al., 2005)
MCM-41	TEPA	298	0.1 atm	2.7 (dry)		(Liu et al., 2013)
MCM-41	PEI600	298	0.1 atm	1.6 (dry)		(Liu et al., 2013)

CARiACT G10	PEI	373 313	0.012 atm	0.25(dry) 1.9 (dry)	50	(Ebner et al., 2011)
CARiACT G10	PEI	353	1 atm	2.8 (dry)	50	(Ebner et al., 2011)
Carbon	TEPAN	348	1 atm	1.4 (dry)		(Arenillas et al., 2005)
Silica	PEI	343	0.15	2.18 (dry) 2.5 (wet)	90	(Zhang et al., 2014)

To understand why a standard adsorption process is not immediately applicable to carbon capture from large power plants, each type of process configuration has to be considered separately. The one thing that applies to all configurations is the challenge inherent in the scale of the process. Consider a 1 GW coal fired power plant which emits 800 tonnes of CO₂ per hour. If the cycle time of the process is 1 hour and the working capacity of the adsorbent is 10% in weight, at least 16,000 tonnes of adsorbent material (half the material is adsorbing while the other half is being regenerated) is needed. Assuming a bulk density of 700 kg/m³, the volume of the adsorption units would be approximately 22,900 m³. If the process can be intensified to run in just 1 s, this volume would shrink to 6.35 m³ (4.44 tonnes of material). This is an idealised and simplified calculation, but it should clarify why cycle times much shorter than those of typical adsorption processes need to be achieved because a significant reduction in cycle times increases the productivity of the process and in principle a point can be reached where the use of very expensive materials with improved working capacities would not affect the overall cost of the separation, but would reduce the energy penalty. Clearly material and process development have to progress at a similar pace in order to achieve overall cost reductions in the carbon capture process.

In PSA or vacuum swing adsorption (VSA) the feed gas is equilibrated with the solid at a high pressure and regenerates the solid by reducing the pressure of the column. This has one very important advantage: the regeneration can be achieved in a very short time, leading to typical cycle times of a few minutes or seconds. Since the size of the adsorption columns needed in the process is inversely proportional to the working capacity of the material and directly proportional to the cycle time, a high working capacity in a fast pressure swing adsorption system is desirable, but as fast cycles are approached, mass and heat transfer limitations become important. Also critical is the rate at which gas can be fed through the system and the corresponding pressure drops associated with the adsorbent column and gas lines (Webley, 2014). For post-combustion carbon capture energy requirements dictate the use of vacuum pressures, because the energy to compress the entire flue gas well above atmospheric pressure would be too high. As we will see there is no single accepted optimal configuration for post-combustion carbon capture applications, a fact that can be understood because in pressure swing adsorption it is intrinsically simple to obtain the weakest adsorbed component with high purity and the process optimization is normally aimed at reducing the energy consumption, by going to multicolumn/multistep configurations which improve the purity and recovery minimizing the energy consumption (Ruthven et al., 1994). Figure 18 shows an example of a six-column multi-step PSA cycle with corresponding table describing the process schedule (Luberti et al., 2014).

Figure 18. Step configurations of a six-column PSA cycle with two-stage pressure equalisation (AD: Adsorption; DPE: Depressurising Pressure Equalisation; ID: Idle; PP: Providing Purge; BD: Blowdown; PU: Purge; PPE: Pressurising Pressure Equalisation; PR: Pressurisation; $t_{AD} = t_{cycle}/3$; $t_{PP} = t_{PU} = t_{PR} = t_{cycle}/9$; $t_{BD} = t_{DPE} = t_{PPE} = t_{cycle}/18$).

From the qualitative discussion on physisorption and chemisorption it is clear that CO_2 is never the most weakly adsorbed component and as a result it is one of the *heavy* products for which non-standard process steps are needed in order to arrive at the prescribed recovery and purity. The other very important point is that the purity and recovery for the heavy components are closely related to the vacuum pressure selected. This process constraint imposes a practical limit on the value of the low pressure Henry law constant (effectively the steepness of the isotherm at low pressure), so materials with high absolute capacities may have relatively low working capacities. This particular issue can be compensated by increasing the temperature of the separation process, since gas adsorption is an exothermic process, and a trade-off between absolute and working capacity can be found (Ruthven, 1984). From this brief discussion it should be clear that the process conditions cannot be set without the knowledge of the properties of the materials and that the performance of different materials should not be compared at the same process conditions.

If the analogy between gas separations and gas compression is used, it is also clear that one option is to achieve the post-combustion separation with more than one stage. A first VSA unit will do most of the separation with a high recovery and a second smaller polishing step will achieve the required purity, with each stage being potentially a complex multicolumn multistep system. In pre-combustion capture, since the process stream is typically above 20 bar, PSA is the most likely option and in fact it is the process of choice in hydrogen purification (Ebner et al., 2009). The key challenge here is to achieve an efficient concentration step for the CO_2 product and the adsorbent materials that will be required in this case should have a high microporosity and in general weaker adsorption interactions than the low pressure post-combustion capture systems.

In TSA both the light and heavy component can in principle be obtained at high purity (Ruthven, 1984). While this may appear to be a more attractive proposition for carbon capture applications,

the key challenge then becomes the cycle time, since standard TSA processes run over several hours (Webley, 2014). Heating and cooling an adsorbent in a few minutes is a real challenge, to do this in seconds is virtually impossible, especially for cooling. Rapid heating can be achieved for example using electrical swing adsorption (ESA) (Grande et al., 2008), where the thermal input is achieved through ohmic heating of either the material itself or of a conductive solid added to the structure. The drawback is that electricity is converted back to thermal energy. Therefore, it is difficult to see how a significant use of thermal energy obtained from electricity cannot result in a large energy penalty for the integrated process. TSA can be applied to both physisorption and chemisorption adsorbents, with the main advantage in favour of the chemisorption systems being the fact that these are often compatible with water and direct heating using steam is a viable option. The water in the product stream then needs to be condensed to arrive at high purity CO₂. Here the limitations come from the thermal stability of the amine-supported materials and the need to provide a large amount of heat at the regeneration temperature. Because of stability issues it is not possible to use large temperature differences to generate the large heat fluxes required. It is also not possible to use condensing steam or hot water in direct contact with the solid. This would result in capillary condensation in the macropores of the solid and the need for an intermediate drying step, which will add to the overall cycle time and reduce productivity. If fixed beds are used, then extended heat transfer surfaces are needed increasing the complexity and cost of the units. One alternative is to use circulating fluidized beds to increase the heat transfer performance of the system. In this case careful attention is needed to ensure that the stringent purity and recovery requirements are met and the adsorption and regeneration sections have to be operated with careful pressure balancing of the units, i.e. the regeneration has to be carried out in a diluting easily condensable vapour that is weakly adsorbed or in nearly pure CO₂ at pressures close to those of the flue gas. This limits for example the use of vacuum in the regeneration step unless a non-continuous CFB system is used, which can have sections sealed-off from the flow for brief periods of time. TSA becomes the most likely option as the concentration of the CO₂ in the flue gas is decreased, i.e. carbon capture from gas fired power plants, while it is an unlikely choice in pre-combustion applications.

The way in which the material is structured or packaged in an optimal configuration can now be understood. In rapid VSA very low pressure drops are needed to achieve fast pressurisation, pressure equilibration and evacuation steps. If the adsorption selectivity is equilibrium driven, then the material will have a small characteristic thickness (or size in the case of beads) to limit macropore mass transfer resistances, but this in turn will increase pressure drops. This leads to an optimal size of the adsorbent particles which will be the result of the best compromise between the two opposing effects. If the technology is pushed to the limit, i.e. cycle times of seconds or fractions of seconds, then the only way to achieve an efficient system is to shift towards structured adsorbents such as adsorbent sheets or monoliths (Ruthven et al., 1996). The reduced pressure drop in monoliths leads to higher superficial velocities compared to traditional packed beds, which allow reduced footprints even in comparison with circulating fluidized beds. Examples of the use of monoliths for carbon capture include carbon based materials (Brandani et al., 2004) and extruded 13X (Rezaei et al., 2010). An important issue when attempting to predict the separation performance of monoliths is to use an accurate model to take into account the shape, wall thickness and channel size distributions of the actual structure as demonstrated by Ahn and Brandani (Ahn et al., 2005a, Ahn et al., 2005b).

Clearly these structures are beneficial also in TSA and alternative promising structures have been proposed where the adsorbent material is embedded in polymeric hollow fibres which are sufficiently hydrophobic to avoid capillary condensation and significant water fluxes (Lively et al., 2009). The hollow fibres can then be used as intermittent heat exchangers with either cold or hot water (or steam) flowing in the inner core and achieve rapid TSA process conditions.

4.2. Process configurations and cost estimates

Table 13 includes the details of several studies that have investigated post-combustion carbon capture using adsorption processes and includes a few systems that have been tested at small pilot plant scale. The first publication with a detailed simulation of a carbon capture PSA is that of Kikinnides et al. (Kikinnides et al., 1993), but is not included since the specific energy was not reported. The majority of cases are based on variants of either single stage or two-stage VSAs. The first demonstration of an adsorption system for carbon capture was developed in Japan in the early 1990s (Ishibashi et al., 1996). The specifications for the system were very stringent: 99% purity and 90+% recovery. This was achieved through a two stage VSA system where the first step included also a thermal swing component. The operating conditions were modified over a number of years in order to improve the performance and the system was able to achieve the targets using 2.02 MJ/kgCO₂ captured. The important point discussed by Ishibashi et al. (Ishibashi et al., 1996) is that due to the limited budget for the project the quality of the vacuum systems was rather low and if the data obtained is extrapolated to systems with vacuum pump efficiencies normal at larger scales the specific energy should be halved, thus arriving at approximately 1 MJ/kgCO₂. Considering that the purity/recovery for this system was over-specified and that part of the energy input was thermal, it can be seen that this early attempt achieved an equivalent specific thermal energy below 3 MJ/kgCO₂ (having assumed a Carnot efficiency of 33%), which is slightly better than the equivalent MEA absorption power requirement of approximately 3.5 MJ/kgCO₂ (see for example Ahn et al. (Ahn et al., 2013)). The need to introduce also a thermal swing effect (long cycle times) was due to the 99% purity target and results in a process that is not competitive.

From the table it is clear that most process simulations arrive at VSA configurations that require approximately 0.5-0.75 MJ/kg CO₂, and these values are consistent with the less stringent purity requirements compared to Ishibashi et al. (Ishibashi et al., 1996) and assume efficient vacuum systems. The pilot plant results tend to show again the use of lower quality vacuum systems, while confirming the purity/recovery that can be achieved. An important point that emerges from the comparison of different configurations is that 2-stage systems tend to achieve similar performance to single stage processes, but can operate at a higher regeneration pressure. Since achieving high vacuum conditions on large systems is not simple (Webley, 2014), this may be the key reason for which dual stage VSA systems will become the preferred option in post-combustion carbon capture using adsorption.

Not included in Table 13 are commercial projects for which limited data is available. For example, Air Products is introducing VSA units in Port Arthur, USA, to capture 1 million tonnes of CO₂ per year from the tail gas of hydrogen purification PSA units from steam methane reformers (Baade et al., 2012). Figure 19 shows the flow diagram of the plant.

Figure 19. Flow diagram of carbon capture based on VSA units at Port Arthur, USA. Courtesy of Air Products.

Air Liquide (Perrin et al., 2013) has operated at pilot scale a PVSA unit on a blast furnace gas (steel manufacture) in Lulea, Sweden, as part of the ULCOS project and has completed the FEED study for a full scale plant of approximately 1 million tonnes of CO₂ per year. This indicates that individual components and standard VPSA adsorption processes are available at TRL 7-9. More advanced solutions based on structured monoliths are now at the stage where they are being demonstrated at commercial scale (Ebner et al., 2009) and include H₂ PSA using structured monoliths with rotary valves or beds from Questair (TRL 6-8) that can reach process intensification scales of 50:1 compared to conventional systems. Rotary thermal swing systems for carbon capture applications are being developed by Inventys (Inventys, 2011) where the carbon capture system is being demonstrated at small scale (TRL 4-5) with extruded monoliths, while the scaled up system would be based on rotary wheel regenerators from Howden, which are at higher TRLs. It is also worth mentioning the ADA-ES (ADA-ES, 2014) 1 MWe pilot plant being tested as part of a DOE funded project. This system is a TSA process based on a circulating fluidized bed with amine based adsorbents, but limited information is available particularly on the purity achieved by the real unit.

1 Table 13. Summary of process configurations for post-combustion carbon capture

Process	Adsorbent	$y_{\text{CO}_2, \text{feed}}$ (%)	$P_{\text{High}}/P_{\text{Low}}$ (P in kPa) or desorption condition	Purity (%)	Recovery (%)	Energy ¹ (MJ/kg _{CO2})	Reference	Result type
2-stage PVSA	13X _{APG}	15.0	150/10	96.5	93.4	0.53	(Wang et al., 2012)	Sim.
2-stage PVSA	13X _{APG}	15.0	150/6	96.6	97.9	0.59	(Wang et al., 2012)	Sim.
2-stage PVSA	AC beads	15.0	350/10	95.4	73.6	0.72	(Shen et al., 2012)	Sim.
2-stage PVSA	AC beads	15.0	350/5	96.4	80.4	0.83	(Shen et al., 2012)	Sim.
2-stage VSA	st 1 : 13X _{APG} _{nd} 2 : ACBs	16.0	st 1 : 123/7.5 _{nd} 2 : 123/20	95.2	91.3	0.76	(Wang et al., 2013)	Sim.
2-stage PVSA	13X	10.5	st 1 : na/6.7 _{nd} 2 : na/13	99.7	78.8	0.51	(Cho et al., 2004)	Sim.
2-stage PVSA	5A	15.0	150/10	96.1	91.1	0.65	(Liu et al., 2011)	Sim.
PVSA	13X	15.0	652/10-70	88.9	96.9	1.50	(Ko et al., 2005)	Sim.
VSA	13X	10.0	115/6.7	50-70	30-90	0.90-1.10	(Park et al., 2002)	Sim.
VSA	5A	15.0	120/10	69.2	98.9	0.45	(Liu et al., 2011)	Sim.
VSA	13X	12.0	100/3	95.0	>70.0	0.54	(Xiao et al., 2008)	Sim.
VSA	13X	13.0	100/2	93.8	91.5	0.43	(Delgado et al., 2011)	Sim.
VSA	13X	15.0	100/3	95.0	90.0	0.55	(Haghpanah et al., 2013)	Sim.
PVSA	13X	15.0	150/2.2	97.0	93.3	0.69	(Krishnamurthy et al., 2014)	Sim.
TSA	5A	10.0	433 K	95.0	81.0	3.23 th	(Clausse et al., 2011)	Sim.
2-stage PVSA	st 1 : 13X _{APG} _{nd} 2 : ACBs	16.0	st 1 : 125/7.5 _{nd} 2 : 125/20	95.6	90.2	2.44	(Wang et al., 2013)	Pilot
2-stage PVSA	13X	10.5	st 1 : na/6.7 _{nd} 2 : na/13	99.0	80.0	2.30-2.80	(Cho et al., 2004)	Pilot
2-stage PTSA	CaX	11.5	na/5-15	99.0	90.0	2.02 mix	(Ishibashi et al., 1996)	Pilot
PVSA	13X	12.6	120/5-6	90-95	60-70	0.52-0.86	(Zhang et al., 2007)	Lab
VSA	5A	15.0	101.3/5.5	71-81	79-91	2.64-3.12	(Liu et al., 2012b)	Pilot
PVSA	13X	15.0	150/1.1	95.9	86.4	1.70	(Krishnamurthy et al., 2014)	Pilot
PVSA	13X	15.0	150/2.2	94.8	89.7	1.71	(Krishnamurthy et al., 2014)	Pilot
TSA	5A	10.0	423 K	>94	75-85	6.12-6.46 th	(Merel et al., 2007)	Lab

2 ¹ Energy consumption as reported in the references cited: electrical unless otherwise specified (th =
3 thermal; mix = combination of electrical and thermal).
4

Table 14 presents a summary of the rather limited data on cost estimates for adsorption based carbon capture processes available in the literature. The information shown reflects the fact that there is not a simple accepted process configuration and that the full optimization of an adsorption process requires the solution of complex dynamic models which are not readily available in standard simulation packages. This limits the number of research groups that attempt to arrive at reliable conclusions on predicted costs of this evolving technology.

Table 14. Summary of cost estimates for adsorption based carbon capture processes

	(Ho et al., 2008c)			(Glier et al., 2013)	(SRI-International, 2011)	(Krutcka et al., 2011)
Plant type	Supercritical bituminous coal	Supercritical bituminous coal	Supercritical bituminous coal	Supercritical bituminous coal	Supercritical bituminous coal	Supercritical bituminous coal
Capture system	PVSA Skarstrom 13X	PVSA 7-step 13X	PVSA 7-step new adsorb.	CFB TSA MOF	CFB TSA ACS-1	CFB TSA Supported-amines
Net power output (MW _e)	500	500	500	498	550	343
Net plant efficiency (%)	30	-	-	32	36	-
CO ₂ Recovery (%)	85	85	90	90	90	90
CO ₂ Purity (%)	48	70	95	95	95	95
Plant operating life (years)	25	25	25	30	30	30
Capacity factor (%)	85	85	85	85	85	85
Capital cost for capture (\$/kW)	890	800	650	-	-	1,042
CO ₂ Avoided cost (\$/ton _{CO2} avoided)	46	41	30	-	-	-
LCOE (\$/MWh)	-	-	-	99	96	106

Nevertheless, as Glier and Rubin (Glier et al., 2013) point out at this stage adsorption based processes show significant promise in comparison with amine based carbon capture systems. Considering the improvements that can be obtained from a combination of reduced cycle times, novel materials and optimised process configurations it is possible to push adsorption based technologies even further but the actual final performance will depend on the regeneration conditions and the stability of the adsorbent materials to impurities present in process streams. The most likely development of demonstration units based on adsorption processes will probably come in applications that require smaller scales than large power plants (Webley, 2014), such as those being developed by Air Products and Air Liquide, which will help to build confidence in the operators.

4.3 Other Low Temperature Gas Solid systems

CO₂ can be removed from a combustion flue gas by absorption using reactive solids at low temperature. In contrast to the surface-dominated adsorption mechanism described in previous sections, the separation process using these sorbents is based on the reversible reaction of CO₂ with the bulk of solids containing alkali metals. Sodium and potassium carbonates have been proposed as the most suitable sorbents for this kind of processes. The carbonate reacts with CO₂ at temperatures below 100 °C in the presence of steam to form the bicarbonate. The decomposition of the bicarbonate is carried out in a range of temperatures between 120 and 200 °C to regenerate the sorbent and to release concentrated CO₂. Typically, this process is carried out by circulating the

sorbent between two independent reactors operating at carbonation and regeneration conditions. To avoid the attrition of the sorbent, the carbonates are supported on a substrate (i.e. alumina) in order to improve the mechanical stability and facilitate fast reactions thanks to an adequate pore structure. Mixtures of K_2CO_3 and Na_2CO_3 with different supports are being developed in order to maximize the maximum carbonation conversion, the reaction rates and the attrition resistance (Zhao et al., 2013).

Novel concepts are being explored by using these sorbent materials in high velocity fluidized beds, integrating one or more sorbent systems operating at different temperatures (Kim et al., 2014). A few pilot plant configurations have been built and operated to test this process continuously. RTI has constructed and designed a lab facility able to treat a synthetic flue gas flow of $10 \text{ m}^3\text{N/h}$ (Nelson et al., 2009). The pilot consists of a co-current down flow gas-solid carbonator and a regenerator composed of two mechanical screw conveyors/heat exchangers which use steam to supply the heat for regeneration. Southeast University in Nanjing, China, uses two bubbling bed carbonators and a bubbling fluidized bed regenerator (Xiaoping, 2011). The most important pilot demonstration of these kind of projects was commissioned by KIER and KEPRI in Korea, able to treat a flue gas flow of $2000 \text{ Nm}^3/\text{h}$ (0.5 MW). The facility is comprised of a fast fluidized-bed absorber and a bubbling fluidized-bed regenerator and CO_2 capture efficiencies around 80% have been reported (Yi et al., 2007). This process configuration has been already scale-up and tests have been initiated in a 10 MWe pilot plant (Park et al., 2014b).

4.4. Outlook for Adsorption Based Systems

Major improvements in the process performance of adsorption based systems can be achieved through combined developments of both materials and processes. The key strategy has to be that of reducing cycle times, which can also lead to the use of more expensive novel adsorbents due to the reduction in the size of the units. A priority should be the development of structured packings or monoliths for novel families of adsorbent materials that are appearing in the literature on a regular basis. The use of monoliths or low pressure packings will allow to increase productivity and reduce the footprint of the capture processes.

For physisorption based processes for post-combustion capture an important aspect will be managing the water contained in the flue gas and whether in some conditions producing clean water from the capture process may be beneficial. If this is not the case, then the added cost of the pre-processing units would need careful assessment. Since the kinetics of physisorption are typically fast, physisorbents are the candidate materials for pushing the technology to cycle times of a few seconds using pressure or vacuum swing adsorption. The ability to engineer the properties of physisorbents makes these materials important candidates for pre-combustion carbon capture processes and for capture from industrial sources, where the gases to be treated are typically in a wide range of relatively high CO_2 concentrations.

For amine supported chemisorption based materials, improving the stability of the materials with temperature and understanding the mechanisms of degradation should be a key priority. Since adsorption kinetics will be slower than in physisorption systems there may be an intrinsic limit to the cycle times that can be achieved, but it is difficult to ascertain this at this time given the limited data available on adsorption/desorption kinetics for these materials. Given the high selectivity of these materials they are the candidate materials for capturing CO_2 from streams at low concentrations, i.e. flue gases from gas fired power plants.

Adsorption based processes are complex and to select the optimal material and configuration is not a simple task. Simplified indicators should be considered for what they are: very rough initial approximations which can lead to preliminary decisions on which materials to investigate further. There is the need to arrive at reference configurations for which detailed process simulations can provide a clearer assessment of the advantages of the novel materials.

For dry chemisorption at intermediate temperatures the main advances can come through an improved integration of the capture process with the energy production cycle in order to improve further the energy efficiency.

5. CO₂ capture using membranes

This section presents an overview of the research and development fronts for gas separation membranes likely to deliver the greatest benefits for CCS. The benefit can be achieved by separating and concentrating the CO₂ directly (i.e. CO₂ capture) or by removing other components from the gas mixture thereby concentrating CO₂ (e.g. transporting H₂ out of syngas) or by excluding N₂ from a combustion mixture producing a stream with higher CO₂ concentration (e.g. through the use of an oxygen or ion transport membrane). The advantages of using membranes include relatively small footprint, no phase change, simple mechanical system, (usually) steady-state operating conditions, easy scale up and flexibility (Bernardo et al., 2009, Bredesen et al., 2004).

A membrane is a thin barrier that allows selective passage of different species. Membranes are usually fabricated into modules which are then piped together in parallel and/or series to form a membrane system or network that is designed to meet the separation requirements in terms of purity and production rate for a specific application. Although naturally occurring membranes exist, membranes used in industrial applications are normally synthetic and may be polymeric (i.e. totally organic or organic/inorganic combinations such as in mixed matrix membranes) or totally inorganic. Both polymeric and inorganic membranes can be classified as isotropic or anisotropic. Isotropic membranes include porous and non-porous (dense) membranes while anisotropic membranes can be asymmetric (formed by phase inversion) or a thin film composite (with a top separation layer attached to a porous supporting layer). Properties of the membrane material such as the molecular structure of the polymer(s) and the microscopic morphology (which can also be influenced by the fabrication process) dictate the membrane separation performance. Based on the low cost of raw commodity polymers and their versatility for fabrication and scale-up, polymeric membranes are significantly cheaper than inorganic membranes (Baker, 2012).

Porous membranes (whether polymeric or inorganic) generally separate on the basis of molecular size in microporous membranes or perhaps Knudsen diffusion in mesoporous membranes. Permeation in porous membranes might be enhanced through surface diffusion in the pores. Non-porous membranes generally rely on a molecular, atomic or ionic solution-diffusion mechanism that might be enhanced through a facilitated transport mechanism. Non-porous polymeric membranes generally involve molecular transport of the more selective gas but non-porous inorganic membranes generally require formation of an atomic or ionic species on the feed side of the membrane (e.g. atomic or ionic hydrogen in H₂ selective metal membranes) that recombines to form the original gas molecule (in this case H₂) on the permeate side of the membrane.

Gas separation membrane technology emerged as a commercial process on the industrial scale in the 1980s (Kesting et al., 1993). In 1980, the first industrial application was a H₂ separation process that used Permea's Prism membranes. Cellulose acetate membranes were applied to remove CO₂ from natural gas by the mid-1980s and production of pure N₂ from air with polymeric gas separation membranes has been widely undertaken since the 1990s.

Gas separation membranes have not yet been applied at commercial scale for CCS but on-going research is progressing to field testing (TRL 2 to TRL 6) in a range of applications. At the current time, the major applications under development involve: (1) separation of CO₂ from gases produced from combustion and gasification processes at power plants, refineries and other industrial sites; (2) separation of CO₂ from methane sources such as natural gas, coal seam gas and biogas; (3)

separation of O₂ from air and other gas streams for combustion and oxidation processes to enhance the CO₂ concentration in the final gas stream. Each application requires a tailored membrane and gas separation process matched to the gas composition and conditions.

Recent key projects developing membranes and modules for CO₂ separation include Membrane Research Technology (MTR), NanoGLOWA, the Carbon Capture Project (CCP) and the CO2CRC. The MTR membrane is a multi-layer composite flat sheet membrane housed in a spiral wound module (Merkel et al., 2010). The NanoGLOWA composite hollow fiber Diffusion Transport Membrane (DTM) was tested with artificial flue gas and compared with the performance of a commercial PPO membrane module in a power plant (Huibers et al., 2011). CCP3 tested a Pall metallic composite membrane consisting of a micron-thin layer of palladium alloy deposited on a porous stainless steel support for CO₂ separation from syngas (CCP3, 2014). CO2CRC has tested commercial gas separation membranes for pre-combustion (Clare Anderson et al., 2011) and post-combustion capture (Qader A et al., 2011) and also developed their own hollow fibre membranes for flue gas separation (Wang Y et al., 2014). Various inorganic membranes made from ceramic materials or Pd and its alloys have been investigated at laboratory and pilot scale for hydrogen separation due to advantageous material properties such as tolerance of harsh conditions (Adhikari et al., 2006). Oxygen (OTM) or ion (ITM) transport membranes are an active area of research for a range of stand-alone and integrated applications for separating oxygen from air for combustion and partial oxidation processes (Dyer et al., 2000, Griffin et al., 2003). Air Products & Chemicals have demonstrated the use of dense ceramic membranes at industrial scale to deliver 5 TPD of oxygen for over 515 days (Repasky et al., 2012). Praxair is developing their ceramic OTM for CO₂ capture from gasified coal syngas and natural gas derived syngas (Kelly, 2014).

CO₂ emissions from combustion power plant and industrial flue gases represent the largest sources for capture. Although membrane development for pre-combustion (hydrogen separation) and oxy-fuel (nitrogen separation) are important in advancing the deployment of CCS, our focus in this paper will be CO₂ gas separation membranes as they represent the bulk of the near term opportunities.

5.1 Performance of inorganic membranes for CO₂ capture

Inorganic membranes can be made from ceramic materials, carbon, silica, zeolite, various oxides (alumina, titania, zirconia) and metals such as palladium, silver and their alloys. Table 15 provides a comparison of some of the major types of inorganic membranes best suited to large-scale CCS applications. Advantages of inorganic membranes include temperature stability, resistance towards solvents, well-defined stable pore structure, and the possibility of sterilization. Dense inorganic membranes are primarily used for highly selective separation of gases such as hydrogen and oxygen. However, dense membranes have limited industrial application due to their low permeability compared to porous inorganic membranes. Therefore, porous membranes dominate the current inorganic membrane market. Inorganic membranes are usually substantially more expensive than polymeric membranes and this has hindered application for large-scale CCS, especially if there is not a valuable product (e.g. H₂, O₂, CH₄) to offset the capture cost. The high cost of inorganic membranes is related not only to the high cost of the membrane and module materials (especially for metal membranes with costs for Pd-alloy based membranes reactors reported in the range US\$ 4800-7200/m²) (Dolan, 2010) but also to the low packing density of the modules and the complexity of fabrication which hinders scaling up (Baker, 2012).

Table 15. Comparison of inorganic materials for large-scale CO₂ capture

Membrane Type	Structure	Application	Advantages/Cost	TRL	Reference
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Silica	Amine functionalized silicas coated on a α -alumina or γ -alumina support; also anisotropic metal oxide silicas	CO_2/H_2 and CO_2/N_2	High selectivity/Medium to high cost	2/3	(Pera-Titus, 2013, Wang Y et al., 2014),
Zeolites	Thin zeolite layer deposited on a support such as porous α -alumina or stainless steel with well-defined pore structure	CO_2/CH_4	Very high selectivity and high permeability along with good thermal, mechanical, chemical stability/High cost	2/3	(Pera-Titus, 2013)
Carbon molecular sieve	Porous random networks typically produced by pyrolysis of thermosetting polymers under controlled conditions	CO_2/CH_4	Good thermal and chemical stability/High to very high cost	2/3	(Brunetti et al., 2010)
Metal	Palladium and alloys in dense or composite formats (Pd on tantalum or vanadium support film)	H_2 separation	High selectivity, high temperature tolerance/Very high cost	3/4	(Baker, 2012)
Ceramic	Anisotropic perovskites and fluorites	O_2/N_2	High selectivity, high temperature tolerance, lower energy consumption than cryogenic separation/High to very high cost	2-6	(Leo et al., 2009, Smart et al., 2011)

There are several approaches for reducing the costs of inorganic membranes in order to be able to take advantage of their superior characteristics. A simple option is to develop membranes from cheap inorganic materials (e.g. cheap naturally occurring zeolites or carbon sources). Composite membranes also offer the potential to reduce the overall membrane cost while improving permeability. For metal membranes this can be done by coating a thin layer of palladium on a tantalum or vanadium support film (Peachey et al., 1996). For silica, zeolite and ceramic membranes, the selective separating layer can be fabricated on top of a more open and cheaper support layer (Pera-Titus, 2013, Wang et al., 2014). Figure 20 shows two examples of inorganic membrane structures.

Figure 20. (a) Anisotropic cobalt oxide silica membranes (Wang et al., 2014) (b) Nano composite MFI-zeolite-alumina hollow fibre membranes (Pera-Titus et al., 2009).

5.2 Performance of polymeric membranes for CO_2 capture

The low cost of polymeric membranes and their versatility for fabrication and design makes them an attractive option for large-scale CCS applications. Polymeric membrane materials commonly used in

industry are mostly glassy polymers such as polysulfone, cellulose acetate, polyimides, polycarbonate, polyphenylene oxide. A glassy polymer is defined as one in which the temperature where the structure changes from the rigid glassy state to the flexible rubber state is much higher than the ambient temperature. Rubbery polymers such as poly(dimethyl siloxane) (silicone rubber) have also been used in industrial scale. The total membrane area used in industrial gas separation technology is in the order of $10^7 \text{ m}^2/\text{year}$ (Baker, 2012).

Recent research and development in identifying suitable polymeric materials for CO_2 separation has focussed on advanced polymers, polymer and copolymer blends, polymeric based mixed-matrix membranes and polymer inclusion membranes (Han et al., 2011, Dong et al., 2013). Membranes under development need to pass the hurdles of cost and complexity of fabrication to be considered suitable for large-scale commercial deployment for CO_2 capture.

Polymer blends present a means for achieving good separation and permeability at reduced cost compared to advanced polymers (Zhang et al., 2013). The copolymer used should possess “hard” and “soft” blocks. The glassy (“hard”) polymer segments form a structural frame and provide mechanical support. If the “hard” block consists of high temperature polymers such as polyimides, it can also improve thermal resistance. The rubbery (“soft”) segments should form continuous micro-domains, where the flexible chain structure allows easy transportation of gases; hence providing permeability. The right ratio of “hard” and “soft” blocks provides the best membrane performance (Reijerkerk et al., 2011).

Mixed matrix membranes (MMMs), where inorganic fillers are embedded in a polymer matrix, provide the opportunity to combine the superior performance of inorganic materials with the handling properties of polymeric materials. However, issues related to the stability of the membrane over time and homogeneous dispersion at high filler content and the adhesion between heterogeneous phases still need to be resolved (Dong et al., 2013).

Most polymeric membranes used in industrial applications are fabricated with the phase inversion technique, which results in integrally skinned asymmetric membranes as shown in Figure 21 (a). The transport of gas species in the thin selective skin layer of these membranes plays the main role in controlling the separation between gas species while the micro-porous sub-structure provides mechanical strength and contributes additional resistance to the overall gas permeation. The phase inversion technique provides a simple rapid technique for producing cheap commodity membranes in either flat sheet or hollow fibre configuration.

Thin dense selective skin layer ($0.1 \sim 0.5 \mu\text{m}$)

Figure 21. SEM image of UNSW fabricated Matrimid® asymmetric hollow fibre membrane and a composite hollow fiber (Dong et al., 2010a).

Composite membranes possess an asymmetric structure where a thin dense top-layer is supported by a porous sub-layer (Figure 21 (C)). The two layers can originate from different materials and are prepared via separate steps that increase the complexity and cost of membrane fabrication. The advantage of composite membranes is that each layer can be optimized independently to obtain optimal membrane performance with respect to selectivity, permeability and chemical and thermal stability. Furthermore, the top-layer of such membranes can be made from a material that is difficult to use in the phase inversion technique.

5.3 Considerations for large-scale implementation

Engineering design

Factors that influence the performance of a gas separation membrane system include the properties of the membrane (i.e. selectivity and permeability/permeance) in the specific application, the physical properties and the chemical composition of the feed, and, adequate engineering design including module configuration, stage cut and flow management. Other factors such as pre-treatment of the feed stream before entering the membrane process, the operational protocol (such as cleaning and maintenance frequency and intervals) also influence system performance.

The first consideration for the engineering design of membrane systems is the module configuration. Common configurations include hollow fiber, spiral wound and flat sheet modules. Hollow fibers are the dominant configuration covering about 80% of the entire membrane market with spiral wound modules making up most of the rest. Determined mostly by their fabrication simplicity and packing density (Table 16), the cost for hollow fiber modules is significantly lower than for spiral wound modules (Baker, 2012). It should however be noted that the cost of the membrane is only a fraction of the cost of the overall system.

Table 16. Packing density of typical membrane module configurations (Baker, 2012)

Module type	Packing density (Membrane surface/module volume)	Indicative membrane cost
Plat and frame	100-400 m ² /m ³	US\$50-200/m ²
Spiral wound	300-1,000 m ² /m ³	US\$5-100/m ²
Hollow fibre	6-10,000 m ² /m ³	US\$5-10/m ²

Operating mode must also be considered in process design. Pressurised feed is used for feed streams that are already at medium to high pressure. Thus gas separation membrane processes are well suited to natural gas separation and other high pressure industrial separations such as steam-methane reforming. For post-combustion flue gases or other industrial gases at or close to atmospheric pressure including oxygen separation from air, operation of the membrane system at high feed pressure requires very large compressors that impose very high energy usage, thereby reducing the competitiveness of gas separation membrane processes for post-combustion capture of flue gases. A significant decrease in energy usage would be achieved with multistage compressors. In addition, utilising turbine expanders on the high-pressure stream exiting the membrane system might be able to recover up to 80 % of the energy, which could be used to provide some of the gas compression requirements (Follmann et al., 2011).

Recent research has suggested other ways of reducing energy usage and system cost by careful design of membrane cascades. For example, utilizing the incoming combustion air as a sweep gas to generate the driving force for a first stage gas separation membrane step offers significant savings in overall cost (Merkel et al., 2010). Alternatively use of vacuum permeate might be more cost effective (Ho et al., 2009). However, vacuum operation currently faces industrial limitations due to the large footprint of pumps compared to compressors and the relatively low energy efficiency of vacuum systems when a high vacuum is required.

Other major considerations for process design include the pressure ratio (feed pressure/permeation pressure) and the stage cut (permeate flow/feed flow) for multi-step and multi-stage system design.

Pre-treatment of the feed stream for removal of particulates along with dehydration to avoid water condensation in the membrane system is also very important for successful operation (Piroux et al., 2004).

Membrane material selection

The selection of membrane materials with good separation properties does not guarantee successful large-scale implementation in industry. For membrane technology to become commercially viable for CO₂ capture or enrichment, membranes should possess sustainable performance over long-term operation. To date, most of the investigations of long-term performance of membranes are limited to a few commodity polymers (e.g. polyimides, polyethersulfone, polysulfone, cellulose acetate). For new materials, research in this field remains scarce even though such information will be important for large-scale implementation. Important considerations for sustainable performance of polymeric materials include physical ageing of the membrane and plasticization as well as the effect of other components in the feed gas on membrane characteristics. For inorganic membranes to achieve their potential for large-scale CCS applications, the major issues include sealing of the membrane modules to allow continuous operation especially at high temperature (up to 1000 °C), membrane tolerance to the thermal gradient across the membrane to prevent cracking, and, chemical stability to gas components (e.g. perovskite tolerance to H₂) (Krishnan et al., 1994). For thin composite metal membranes, it is vital to reducing surface poisoning effects (e.g. by a carbon-containing source) (Gabbitto et al., 2009).

Physical ageing is often observed in glassy polymers because they are not in thermodynamic equilibrium below their glass transition, so they undergo a slow approach towards equilibrium (Struik, 1977). Ageing causes a slow reduction in polymer free volume that provides passage for gas molecules, reducing membrane permeability over time. Different membranes age differently (Bartos et al., 1990, Chung et al., 1999, Dorkenoo et al., 1999, Kim et al., 2006, Pfromm et al., 1995). Ageing is also thickness dependent (McCaig et al., 2000a, McCaig et al., 2000b, Punsalan et al., 2005), which means that asymmetric hollow fibres with an ultra-thin skin layer could experience more severe ageing than dense films. Commonly reported ageing studies were conducted at constant temperature, zero stress and under no influence from any other external conditions. Under industrial plant operating conditions such as repeated start up and shut down or ambient temperature changes, physical ageing could potentially accelerate.

Plasticization is another phenomenon observed for glassy polymer membranes. When the feed stream contains a plasticizer, such as CO₂ or water, the membrane swells due to sorption of the plasticizer and interaction between it and the polymer. As a result, the permeation of other gases accelerates leading to a reduction in selectivity (Ismail et al., 2002). Plasticization by CO₂ normally occurs when the partial pressure of CO₂ reaches the plasticization pressure as shown in Figure 22 (Dong et al., 2011). Similar to physical ageing, plasticization is thickness dependent (Huang et al., 2007, Jordan et al., 1990, Pfromm et al., 1995, Punsalan et al., 2005, Krause et al., 2001) and becomes more pronounced as the thickness of the membrane decreases. Therefore asymmetric hollow fibres with a thin skin layer may suffer more from plasticization than dense films. For applications in which the combination of the concentration of CO₂ and total pressure is low (e.g. syngas, post-combustion flue gas), the CO₂ partial pressure might not reach the plasticization pressure. However, long operating times may cause plasticization over time. Thermal annealing (Chung et al., 2003b, Kuroda et al., 1989a, Kuroda et al., 1989b, Zhou et al., 2003), chemical cross-linking (Bos et al., 1998b) and blending with a secondary polymer with higher plasticization resistance (Bos et al., 1998a) may alleviate plasticization.

Figure 22. CO₂ permeation isotherm as a function of feed pressure (pure CO₂ feed stream) (Dong et al., 2011).

Other components in the raw feed gas may compete with CO₂, thereby decreasing permeability, and altering separation performance in both polymeric and inorganic membranes. Some of these may also enhance plasticization and physical ageing in polymeric membranes.

Water vapour is an often overlooked component in many gas mixtures that is known to have a much stronger influence on membrane permeability and performance in polymer membranes than other minor components due to competitive sorption, plasticization and ageing (Chern et al., 1983). In addition, unless the temperature of the feed gas is controlled above the dew point, water will condense on polymeric and inorganic membrane surfaces and inside any porous structures, causing severe reduction in permeance and selectivity (Wang Y et al., 2014).

The presence of SO_x (SO₂ and SO₃) in conjunction with water vapour may form acids. This can be particularly problematic within the free volume of polymer membranes, causing damage to the membrane structure and increasing the fractional free volume and permeability (Scholes et al., 2009). In addition, permeation of SO₂ through polymeric membrane is generally faster than CO₂ due to the higher critical temperature of SO₂ that leads to a higher affinity. As a consequence, many polymeric membranes display a SO₂/CO₂ selectivity in the range of 5-25 (Scholes et al., 2009). The presence of SO₂ can also lead to plasticization.

NO_x in combination with water vapour may also form acid that may degrade membranes. Tests of glassy polymeric membranes and composite hollow fiber membranes in the presence of NO have shown a small degree of reduction in CO₂ permeance and CO₂/N₂ selectivity.

5.4 Economic considerations

Early studies of post-combustion CO₂ capture using membranes estimated costs of above US\$80/t CO₂ avoided, which were typically 30% higher than for a comparable amine chemical absorption process at that time (Hendriks, 1994, Feron, 1992). This was due to the high capital and operating costs associated with compressors needed for both the concentrated product stream and the low pressure and purity flue gas. For these designs in which the flue gas needed to be compressed to 15-20 bar, the membranes units themselves only accounted for less than 20% of the total equipment

costs. Meanwhile compressors and expanders contributed over 50% to the equipment costs and also 50% to the energy penalty.

Figure 23. Effect of membrane selectivity on CO₂ capture cost for NGCC flue gas (Merkel et al., 2010).

In contrast, more recent studies have recommended the use of a vacuum membrane system which is predicted to achieve a reduction in the total cost of capture by about 35% due to the lower capital costs and a reduction in the energy penalties to below 35% of those for high pressure feed gas systems (Favre, 2007, Ho et al., 2008b). Because the membranes make up 50-60% of the equipment cost in this design, it will be important that new membranes are designed to minimise the size and cost of the membranes as well as the auxiliary compressors and vacuum pumps. Work undertaken by Merkel et al. (Merkel et al., 2010) and Ho et al. (Ho et al., 2008b) for both the vacuum and the high pressure system has shown that increasing the CO₂/N₂ selectivity beyond values of about 30 or 40 does not achieve a significant cost benefit for post-combustion capture of CO₂ from either NGCC or coal-fired power plant flue gas (Figure 23 and Figure 24). On the other hand, for a single stage membrane system, increasing the membrane CO₂ permeability has a much larger effect on the costs, due to the larger contribution of the membrane to the equipment costs. However, beyond 300 Barrer (or 3000 GPU) cost benefits are predicted to be insignificant. For membranes with high permeance (values of 1000 GPU or more) and moderate CO₂/N₂ selectivity of 50, the resulting cost of post-combustion capture is in the range of US\$25-40/t CO₂ avoided with energy penalties of 16-30% (Scholes et al., 2010, Merkel et al., 2010, Ho et al., 2008a). Details about other assumptions used in estimating to these costs can be found in Table 17. At these costs, membrane separation has the potential to be competitive with state-of-the-art amine absorption processes.

Figure 24. Effect of membrane selectivity on CO₂ capture cost for a coal fired power plant flue gas (Ho et al., 2008b) .

Also shown in Table 17 are details of estimated costs for membrane-based pre-combustion capture and oxygen enrichment processes. For pre-combustion capture, studies by Bracht et al. (Bracht et al., 1997), Koc et al. (Koc et al., 2012) and Siefert et al. (Siefert et al., 2013) indicate that using inorganic membranes in a water shift reactor coupled with CO₂ recovery at an IGCC power plant has a cost comparable to conventional solvent absorption using Rectisol.

For an integrated oxyfiring natural gas power cycle based at a thermal bitumen extraction plant, Bolea et al. (Bolea et al., 2013) have shown that using OTMs resulted in higher costs than using a cryogenic ASU. In contrast, (Möller et al., 2006) estimated that an integrated OTM-NGCC power plant (Advanced Zero Emissions Plant) would have capture costs that are competitive with post-combustion amine solvent capture. Praxair's inorganic OTM has been reported to have capture costs less than \$40/t CO₂ avoided with a cost of electricity around 32-42% greater than for an air fired power plant without capture (Kelly, 2014).

Table 17. Summary of cost estimated for selected membrane-based CO₂ capture and enrichment processes

	Post-combustion CO ₂ /N ₂ separation				Pre-combustion CO ₂ /H ₂ separation			Oxygen enrichment (O ₂ /N ₂ separation)		
	Ho et al. (Ho et al., 2008b)	Ho et al. (Ho et al., 2008b)	Merkel et al. (Merkel et al., 2010)	Scholes et al. (Scholes et al., 2013)	Bracht et al. (Bracht et al., 1997)	Koc et al., 2012 (Koc et al., 2012)	Siefert et al. (Siefert et al., 2013)	Kelly, 2014 (Kelly, 2014)	Möller et al. (Möller et al., 2006)	Bolea et al. (Bolea et al., 2013)
Plant type	Supercritical bituminous coal	Supercritical bituminous coal	NGCC	Supercritical bituminous coal	IGCC	IGCC	IGCC	Praxair advanced oxyfiring power cycle (coal firing)	NGCC Advanced Zero Emissions Plant	SAGD – thermal bitumen extraction process
Membrane system	Vacuum membrane	Vacuum membrane	Vacuum membrane + cryogenic	Vacuum membrane + cryogenic	WGS + membrane reactor	WGS + membrane reactor	WGS + membrane reactor	OTM	OTM	OTM
Comments	Base case*	Improved membrane	Base case membrane	3 stage membrane base case	Inorganic membrane	Pd/alloy membrane	Pd membrane, OTM for O ₂ separation	-	Base case	Base case – natural gas-fired co-generation
Net power output before capture (MW _e)	500	500	600	500	379	550	808 (with capture)	-	400	Fuel input before capture - 76
Energy penalty (%)	28	19	16	30	6%	-	-	-	38	Fuel input with OTM – 90 MW
CO ₂ recovery	90	90	90	90	88	98	100	-	100	-

(%)										
Membrane price (US\$/m ²)	50	50	50	50	-	US\$1795/ft ²	US\$4800/m ² (Pd) US\$1500/m ² (OTM)	-	€45k/MWth	US\$350/kW (OTM)
Plant operating life (years)	25	25	25	25	-	40	25	-	-	-
Capacity factor (%)	85	85	85	85	-	80	80	-	-	90
Fixed charge factor or discount rate (%)	7 (real)	7 (real)	-	7 (real)	-	9 (nominal)	7 (real)	-	10	-
CO ₂ avoided cost (US\$/ton CO ₂ avoided)	54	25	32	31-32	-	-	-	38-39	-	92
LCOE without capture (US\$/MWh)	34	34	40	40	€78.7	-	50	-	€39.5	-
LCOE with capture (US\$/MWh)	-	-	-	-	€86.7	99.7 [#]	~58	-	€54	-

^ Steam-assisted gravity drainage

*Low permeability and low selectivity membrane

US\$25/t CO₂ tax included

5.5 Development outlook for membrane based CO₂ capture systems

This section provides an overview of the major areas that are likely to be at the forefront of gas separation membrane CCS R&D for the next 10 years. Gas separation membranes are not always going to be the best choice for CO₂ capture or enrichment. The choice of technology will depend on factors including the feed gas composition, temperature, pressure and volume. Other site-specific factors that will affect the technology choice include available land space, auxiliary services, the degree of integration with other process equipment and whether the plant is new build or retrofit. Cost, of course, is always an important decision variable. Many of the membranes and membrane systems currently under development are likely to decrease in cost over time with technology development especially if production and installation techniques can achieve economies of scale at larger installation sizes needed for full scale CCS applications and with greater market demand for numbers of installations.

Innovative improvements to gas separation membrane system design and integration for specific applications are needed but these need to show significant improvement over existing gas separation membrane systems in general and the specific innovations for CO₂ capture and enrichments applications that have been identified over the last 10 years. In this regard, it is important to note that gas separation membrane system design is already quite mature. So it is more likely that the largest R&D improvements in the next 10 years will come from materials and module development where there has been much less research to date that has progressed to commercial scale for CCS applications.

Thus, we finish this section with an assessment of the best opportunities for materials for membrane development, a range of which are shown in more detail in Table 18. The materials in this table have been selected as examples of 'best in class' performance for a range of commodity (i.e. existing commercially available) polymers and newer polymers with superior performance to commodity polymers but still only available at laboratory scale. Commodity polymers shown in the table remain of interest because of their ready availability and potentially lower cost but their performance needs to be further enhanced in order to meet large-scale application needs. The laboratory polymers shown in the table are of interest because of their clearly superior performance at laboratory scale but they need further development and testing to prove their potential for large-scale application.

In general, development of membranes and membrane systems for CO₂ capture should aim for high permeability and moderate selectivity with sustainable separation performance and integrity for the selected industrial application. Membrane systems for CO₂ enrichment, as in H₂ and O₂ separation, should aim to be efficient, stable and affordable with good performance at both high and moderate temperatures, and with long-term reliability under real operating conditions. Polymeric membranes need to withstand membrane ageing and plasticization especially in the presence of water vapour and other contaminants. Both polymeric and inorganic membranes need to be thermally and chemically stable over long time periods. All membranes need to be able to be manufactured in a way that is easy to scale up, has the least fabrication complexity and is made from the cheapest possible precursor materials (e.g. using new cheaper alloys for thin selective layers for metal membranes or commodity polymers and commodity polymer fabrication methods for polymeric membranes (Criscuoli et al., 2001).

More specifically, post-combustion capture at power and industrial plants faces challenges because of the large gas volumes that need to be treated at low pressure and low to very low CO₂ concentration. This is especially the case for gas-fired non-recycling turbines. Membranes for post-combustion capture therefore need high CO₂ permeance (around 1000 GPU) to be economically competitive with other separation technologies such as amine-based solvent capture (Merkel et al., 2013, Carapellucci et al., 2004). For pre-combustion capture at power and industrial plants,

membranes with moderate CO₂ permeance and good selectivity, as well as temperature tolerance are required (Scholes et al., 2010). Due to the high pressure (normally > 40 bar), natural gas purification requires a membrane with high selectivity as well as tolerance to plasticization and swelling caused by sorption of CO₂ and water (Baker et al., 2008). The presence of H₂S, CO₂ and water in biogas make it very corrosive and require the use of suitable membrane and membrane module materials (Baker et al., 2008). Although membranes already exist for production of nitrogen or oxygen from air with high purity, further improvements are needed to balance the trade-off between permeability and selectivity to achieve the optimum economic performance (Baker, 2012). Due to the similar size of N₂ and O₂ molecules, membranes with very high selectivity are required.

Many of these developments would be fast-tracked with the availability of better membrane performance data (permeability and selectivity as a minimum). Much of the data in Table 18 for selectivity and permeability/permeance has only been estimated from data for pure gases measured at small scale in the laboratory. Usually both of these factors will be lower for mixed-gas permeation experiments. Performance with real industrial feed gases may also be different to both pure and mixed gas results in the laboratory, either increasing or decreasing depending on the effect of other components in the feed gas.

Laboratory based testing with mixed gases is a crucial step in membrane development in order to properly understand and design around interaction effects. However, laboratory testing is not sufficient for commercial development. Field-testing with real industrial gases is essential because there are many minor components that cannot be replicated in the laboratory. It is also difficult to simulate start-up, shut-down and other operational cycles and disturbances in the laboratory. Therefore, testing and demonstrating membrane performance with real industrial gas streams is probably the most pressing task for pilot tests in order to progress gas separation membranes towards large-scale industrial application for CO₂ capture and enrichment.

Table 18. Separation performance for selected membrane materials for CO₂ capture and enrichment

	Membrane material (Application)	CO ₂ or O ₂ permeability or permeance	CO ₂ or O ₂ selectivity	Synthesis at Scale/Cost	Tested in Field/Pilot	Material maturity	TRL	References
Polymeric Dense film	Matrimid (CO ₂ /CH ₄)	6 ~ 10 Barrer	25 ~ 30	Tons/Low cost	Yes	Commodity polymer	5	(Tin et al., 2003, Chung et al., 2003a, Perez et al., 2009, Peter et al., 2009)
	Polysulfone (CO ₂ /CH ₄)	4 ~ 6 Barrer	22 ~ 25	Tons/Low cost	Yes	Commodity polymer	8	(McHattie et al., 1991, Barbari et al., 1989)
	Poly(ethylene oxide) (CO ₂ /N ₂)	8 ~ 50 Barrer	40 ~ 140	Tons/Low cost	Yes	Commodity polymer	5	(Lin et al., 2004)
	PIM (CO ₂ /N ₂)	>2000 Barrer	>90	Grams/High cost	No	Lab scale synthesis	2/3	(Budd et al., 2005)
	6FDA-durene (CO ₂ /N ₂ , CO ₂ /CH ₄)	>400 Barrer	10 ~ 15	Grams/High cost	No	Lab scale synthesis	2/3	(Lin et al., 2000, Tanaka et al., 1992)
	Polyactive (CO ₂ /N ₂)	>100 Barrer	20 ~ 50	Tons/Medium cost	Yes	Commodity membrane	5	(Car et al., 2008)

						product ¹		
	Polyethersulfone (CO ₂ /CH ₄)	30 ~ 80 GPU	15 ~ 25	Tons/Low cost	Yes	Commodity polymer	5	(Wang et al., 1996, Wang et al., 2000)
	MMM MOF and ZIF (CO ₂ /N ₂)	30 GPU	4	Grams/kg/Potentially high cost	No	Lab scale synthesis	3	(Pera-Titus, 2013)
	MMM MOF and ZIF (H ₂ /CO ₂)	300 GPU	4.5	Grams/kg/Potentially high cost	No	Lab scale synthesis	3	(Pera-Titus, 2013)
Polymeric Hollow fibre	Matrimid (CO ₂ /N ₂ , CO ₂ /CH ₄)	10 ~ 12 GPU	6 ~ 10	Tons/Low cost	Yes	Commodity polymer	3/4	(Dong et al., 2010b)
	PEBAX [®] composite membrane (CO ₂ /N ₂)	17 ~ 40 GPU	17 ~ 30	Tons/Low cost	Yes	Commodity polymer	7	(Liu et al., 2004)
	6FDA-durene (CO ₂ /CH ₄)	>900 GPU	2 ~ 7	Grams/High cost	No	Lab scale synthesis	3	(Chung et al., 2000)
	Polyphenolene Oxide (CO ₂ /N ₂)	15 GPU	25-70	Tons/Low cost	Yes	Commercial membrane product	9	(Huibers et al., 2011)
	Composite HF with SPEEK as selective layer (CO ₂ /N ₂)	Aiming at 370 GPU	Varied	Tons/Low cost	Yes	Commercial hollow fiber as support + SPEEK coating	9	(Huibers et al., 2011)
Inorganic Dense film	SiO ₂ (low T CO ₂ /N ₂)	300-1000 GPU	10-14	Grams/High cost	No	Lab scale synthesis	3	(Pera-Titus, 2013)
	SiO (high T H ₂ /CO ₂ separation)	1-2400 GPU	6-150	Grams/High cost	No	Lab scale synthesis	3	(Pera-Titus, 2013)
	Zeolite (CO ₂ /N ₂)	2-8 GPU	3.3-7	Grams/High cost	No	Lab scale synthesis	3	(Pera-Titus, 2013)
	Zeolite (H ₂ /CO ₂)	1200 GPU	2.5	Grams/High cost	No	Lab scale synthesis	3	(Pera-Titus, 2013)
	Tubular BSCF Perovskite (O ₂ /N ₂)	1.5 ml/(cm ² .min) (~0.3 GPU ¹)	100	Grams/High cost	No	Lab scale synthesis	3	(Wang et al., 2004)
	Hollow fibre BSCF Perovskite (O ₂ /N ₂)	5-8 ml/(cm ² .min) (~1-2 GPU ¹)	>99	Grams/High cost	No	Lab scale synthesis	3	(Schiessel et al., 2005, Liu et al., 2005)
	Flat sheet LSCF Perovskite (O ₂ /N ₂)	3.2 ml/(cm ² .min) (~0.6 GPU ¹)	>99	Grams/High cost	No	Lab scale synthesis	3	(Kusaba et al., 2006)
	Fluorite (O ₂ /N ₂)	0.05 ml/(cm ² .min) (~0.01 GPU ¹)	>99	Grams/High cost	No	Lab scale synthesis	3	(Fagg et al., 2007)

Notes: ¹ Estimated GPU at 1 atm and 25 °C. Actual operating conditions and permeance may vary. GPU is equivalent to Barrer divided by membrane thickness (m) and multiplied by 2.95x10¹³.

6. Conclusion

The main conclusion from this review is that certain emerging CO₂ capture processes have rapidly increased their Technical Readiness Level since the publication of the IPCC SRCCS (2005), reaching pilot scale demonstration at the MW_{th} range at industrially relevant environments (TRL5-6). This level of maturity has validated a substantial quantity of new knowledge obtained at lab scales. Key design issues of full CO₂ capture systems by chemical looping, calcium looping, low temperature solid sorbents and membranes are now much better understood. It has been shown that many of these technologies can exploit the experience of highly similar technologies in that are commercially available in the chemical and power industries. As a result, detailed scaled up exercises and first approximations to the cost structure of these emerging technologies have been published, confirming process viabilities at full scale and potential for relevant cost reductions. Therefore, it is widely accepted within the different R&D communities and within their industrial developers, that there is a real chance for some of these technologies to become major technology competitors if there is ever a market for CCS.

Further progress is possible in all the reviewed technology routes by encouraging a competitive but sustained R&D effort on those CO₂ capture routes that have shown the fastest progress in recent years. Also by keeping the door open for new breakthroughs in the fields of functional materials, reactor improvements and process design that may lead to 2nd or 3rd generation of these emerging CO₂ capture technologies.

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