

Edited by Tomas R. Reina, José A. Odriozola,  
and Harvey Arellano-Garcia

# Engineering Solutions for CO<sub>2</sub> Conversion





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*Tomas R. Reina*

*José A. Odriozola*

*Harvey Arellano-Garcia*

**WILEY-VCH**

## **Editors**

### **Dr. Tomas R. Reina**

University of Surrey  
Department of Chemical & Process  
Engineering  
388 Stag Hill  
GU2 7XH Guildford, Surrey  
United Kingdom

### **Prof. José A. Odriozola**

Universidad de Sevilla  
Inorganic Chemistry Department  
4 San Fernando Street  
41004 Sevilla  
Spain

### **Prof. Harvey Arellano-Garcia**

University of Surrey  
Department of Chemical & Process  
Engineering  
388 Stag Hill  
GU2 7XH Guildford, Surrey  
United Kingdom

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## 1

## CO<sub>2</sub> Capture – A Brief Review of Technologies and Its Integration

Mónica García<sup>1</sup>, Theo Chronopoulos<sup>2</sup>, and Rubén M. Montañés<sup>3</sup>

<sup>1</sup>International Energy Agency- Greenhouse Gas R&D Programme (IEAGHG), Pure Offices, Hatherley Lane, Cheltenham GL51 6SH, United Kingdom

<sup>2</sup>128/15 Hoxton Street, N1 6SH, London, United Kingdom

<sup>3</sup>Energy Technology, Chalmers University of Technology, Department of Space, Earth and Environment, Hörsalsvägen 7B, Gothenburg SE-412 96, Sweden

### 1.1 Introduction: The Role of Carbon Capture

The Intergovernmental Panel for Climate Change (IPCC) recently released the special report on 1.5C [1] and pointed out the need to implement all available tools to cut down CO<sub>2</sub> emissions. Energy efficiency, fuel switching, renewables, and carbon capture represent the largest impact on CO<sub>2</sub> emission reduction in power and industrial sectors. Carbon capture represents a contribution of 23% in the “Beyond 2 degrees scenario” (B2DS) modeled by the International Energy Agency (IEA)<sup>1</sup> and has other interesting characteristics that increase its value beyond its cost: (i) easiness to retrofit current power plants or industrial facilities,<sup>2</sup> (ii) simplicity to integrate that in the electricity grid and offer an interesting tool to cover the intermittency of renewables, (iii) ideal to cut down industrial process emissions that otherwise cannot suffer deep reductions, and (iv) current carbon budgets rely on negative emissions to compensate the use of fossil fuels [1]. Carbon capture combined with bioenergy (BECCS) can provide negative emissions at large scale in an immediate future.

CO<sub>2</sub> capture (also called CO<sub>2</sub> sequestration or carbon capture) involves a group of technologies aiming to separate CO<sub>2</sub> from other compounds released during the production of energy or industrial products, obtaining a CO<sub>2</sub>-rich gas that can be stored or used for the obtention of valuable products. The main classification of CO<sub>2</sub> capture technologies relies on where in the process the CO<sub>2</sub> separation occurs. For the power sector, it can be divided into pre-, oxy-, and post-combustion. For the industrial sector, the classification is similar, although their integration would be different. In addition, other new arrangements are emerging.

1 <https://www.iea.org/etp/explore/> (visited in January 2019).

2 Under specific arrangements.

## 1.2 CO<sub>2</sub> Capture Technologies

### 1.2.1 Status of CO<sub>2</sub> Capture Deployment

GCCSI reported in 2018 23 large-scale CCS facilities in operation or under construction globally, summing up 37 MtCO<sub>2</sub> per year. This wide range of facilities shows the versatility of CO<sub>2</sub> capture processes.<sup>3</sup>

In the power sector, the United States is leading the implementation deployment, although Europe has the highest CO<sub>2</sub> capture capacity. The Boundary Dam project (Canada) and Petra Nova (USA) are pioneers in reaching commercial scale. Moreover, based on the successful results of the Boundary Dam project, a CO<sub>2</sub> capture facility has been planned for the Shand power facility (Canada), incorporating not only learnings from the Boundary Dam but also enhanced thermal integration and tailored design. The results show a significant cost reduction [2]. Also in Canada, the Quest project completes the list of Canadian CCS projects in operation [3] and The National Energy Laboratory (NET) power project recently appeared in the United States as a potential significant reduction on CO<sub>2</sub> capture costs [4].

In the industrial sector, cement, steel, refining, chemicals, heavy oil, hydrogen, waste-to-energy, fertilizers, and natural gas have been identified by the Carbon Sequestration Leadership Forum (CSLF; <https://www.cslforum.org>) as the main intensive emitter industries. As it is highlighted, the Norcem Brevik plant [5, 6], LEILAC [7] (cement production), and Al Redayah (steel production) are on the way to start running carbon capture systems in industrial facilities at pilot and large scales.

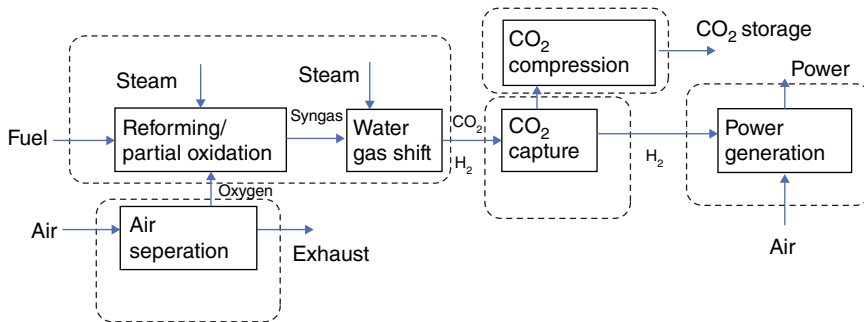
### 1.2.2 Pre-combustion

Pre-combustion systems can be applied to natural gas combined cycles (NGCC) or integrated gasification combined cycle (IGCC) (Figure 1.1), where a syngas, comprising mainly CO and H<sub>2</sub>, feeds a gas turbine (GT) combined cycle system to produce electricity. The potential advantages are higher conversion efficiencies of coal to electricity and cheaper removal of pollutants [8]. The syngas, based on the water shift reaction, can be converted into CO<sub>2</sub> and H<sub>2</sub>O. This mixture is typically separated with physical solvents (as described in Section 1.2.4), membranes, or sorbents. However, hybrid technologies can also be used. Depending on the technology, further post-treatment would be needed to avoid degradation and loss of efficiency.

The main theoretical advantage of pre-combustion is the production of hydrogen, which will add value to the business model, and a lower energy penalty compared to using the traditional chemical absorption within a post-combustion configuration. However, large projects demonstrated that this difference is only 1–2%, as reported by National Energy Technology Laboratory (NETL) [9].

The most notable pre-combustion project was the Kemper County IGCC plant in the United States, which stopped its operation in 2017. This demonstration facility

3 The Global Status of CCS, GCCSI 2018 <https://indd.adobe.com/view/2dab1be7-edd0-447d-b020-06242ea2cf3b>.



**Figure 1.1** Diagram of pre-combustion capture for power generation in IGCC. Source: Adapted from Jansen et al. [72].

would place this arrangement at high TRL, while other testing campaigns would reach up to a TRL of 6.

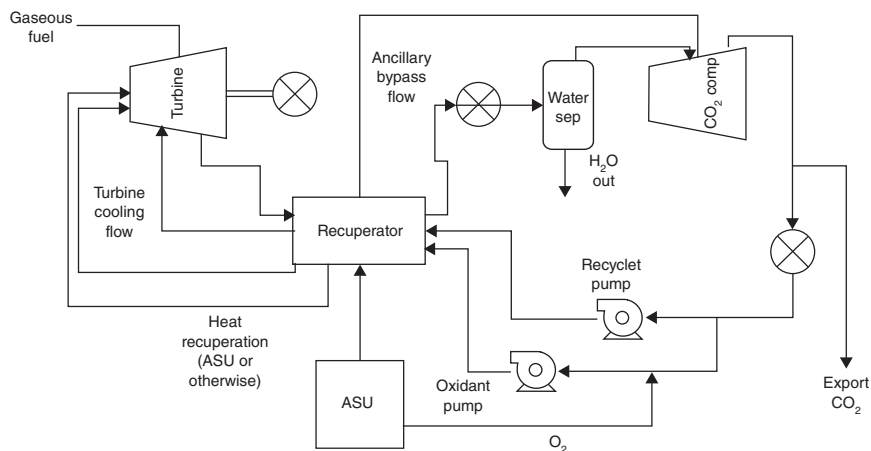
### 1.2.3 Oxyfuel

In the oxyfuel process, the air is split into nitrogen and oxygen, generally using an air separation unit (ASU), for the combustion of fuel with nearly pure oxygen. The consequence is a higher flame temperature and a highly concentrated CO<sub>2</sub> stream (60–75%, wet and might contain impurities and incondensable components) that can be further purified to meet the final use specifications. The CO<sub>2</sub>-rich gas is typically recirculated to manage the unstable flame and its high temperature. Nowadays, the progress on oxyfuel combustion is focused on the reduction of air separation costs and the enhancement of process configuration to reduce capture costs. Further information can be found, for example, in Ref. [10]. Based on the current progress, the most advanced arrangements can be assessed as TRL 7.

An advanced oxyfuel process, called the Allam cycle (Figure 1.2), is being tested at large scale as part of the NET Power project in the United States [4]. This involves oxyfuel combustion and a high-pressure supercritical CO<sub>2</sub> working fluid in a highly recuperated Brayton cycle, aiming to reduce CO<sub>2</sub> capture costs and prove stable operation. Based on that, there is a potential to progress to a TRL of 7 once the facility is fully operational.

### 1.2.4 Post-combustion

Post-combustion refers to the group of technologies able to separate CO<sub>2</sub> from the flue gas emitted during the fuel combustion and/or other reactions in the industrial sector. This indicates that those systems are mainly installed as additional equipment downstream in new plants or during the retrofitting of the existing facilities. The latter represents the main advantage of post-combustion technologies compared to pre- or oxy-combustion, as a fundamental redesign or complex integration with the existing facilities would be minimal.



**Figure 1.2** Process schematic of a simplified commercial scale natural gas Allam cycle. Source: Adapted from Allam et al. [4].

#### 1.2.4.1 Adsorption

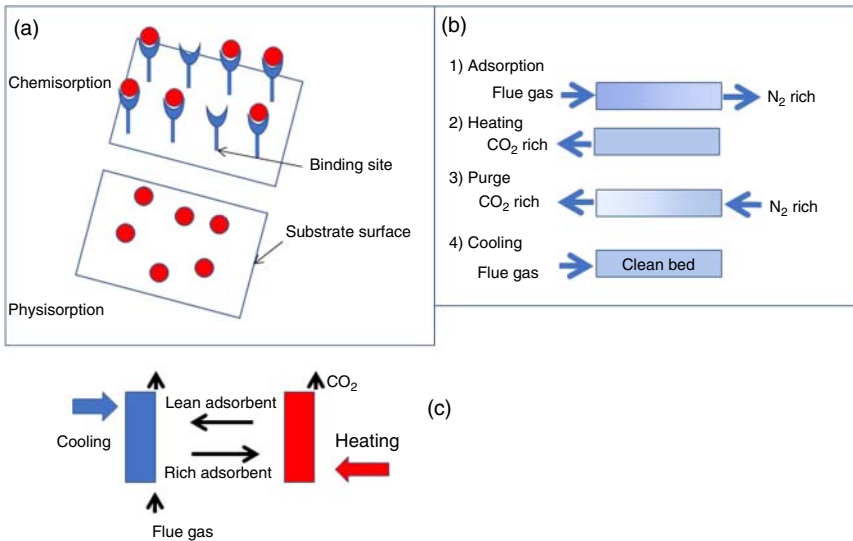
Adsorption refers to the uptake of CO<sub>2</sub> molecules onto the surface of another material. Based on the nature of interactions, adsorption can be classified into two types: (i) physical adsorption and (ii) chemical adsorption. In physical adsorption, the molecules are physisorbed because of physical forces (dipole–dipole, electrostatic, apolar, hydrophobic associations, or van der Waals) and the bond energy is 8–41 kcal mol<sup>−1</sup>, while in chemical adsorption, the molecules are chemisorbed (chemical bond; covalent, ionic, or metallic) and the bond energy is about 60–418 kcal mol<sup>−1</sup> [11].

A theoretical advantage of adsorption against other processes is that the regeneration energy should be lower compared to absorption because the heat capacity of a solid sorbent is lower than that of aqueous solvents. However, other parameters, such as working capacity and heat of adsorption, should also be considered [12]. The higher the heat of adsorption, the stronger the interaction between the CO<sub>2</sub> molecules and adsorbent-active sites and thus the higher the energy demand for the regeneration. The potential disadvantages for adsorbents include particle attrition, handling of large volumes of sorbents, and thermal management of large-scale adsorber vessels.

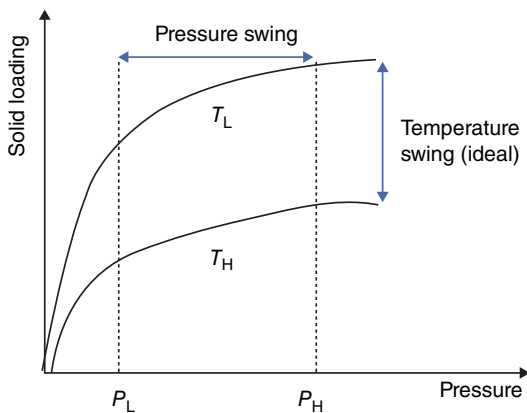
Solid sorbents can be classified according to the temperature range where adsorption is performed. Low-temperature solid adsorbents (<200 °C) include carbon-based, zeolite-based, metal–organic framework (MOFs)-based, several alkali metal carbonate-based, and amine-based solid adsorbents. Intermediate-temperature (200–400 °C) solid adsorbents include hydrotalcite-like compounds or anionic clays, while high-temperature (>400 °C) sorbents refer to calcium-based adsorbents and several alkali ceramic-based adsorbents.

Usually, adsorption takes place in packed or fluidized beds, as can be seen in Figure 1.3. For the packed bed case, the adsorbent is loaded into a column, the flue gas flows through the void spaces between the adsorbent particles, and CO<sub>2</sub>





**Figure 1.3** The adsorption process: (a) difference of physisorption and chemisorption, (b) a packed bed configuration, and (c) a fluidized bed configuration. Source: Adapted from Global CCS Institute (<https://www.globalccsinstitute.com/archive/hub/publications/29721/co2-capture-technologies-pcc.pdf>).



**Figure 1.4** Comparison of TSA and PSA for the regeneration of solid adsorbents. H = high; L = low. Source: Adapted from Rackley [73].

gets adsorbed onto the surface of the particles. In fluidized beds, the flue gas flows upward through a column above the minimum fluidization velocity and the adsorbent particles are as such suspended in the gas flow. Regardless of the process configuration, the adsorbent selectively adsorbs CO<sub>2</sub> from the flue gas and is subsequently regenerated to complete the cyclic adsorption process.

Cyclic adsorption processes alternate between the adsorption and desorption modes of operation. Based on the intensive variable that is cycled, the adsorption processes are broadly classified as pressure swing adsorption (PSA) or temperature

swing adsorption (TSA), as can be seen in Figure 1.4. If the cycle switches between adsorption at atmospheric pressure and desorption under vacuum, then it is called vacuum swing adsorption (VSA). Pressure vacuum swing adsorption (PVSA) cycles have an adsorption step above atmospheric pressures and desorption under vacuum [13].

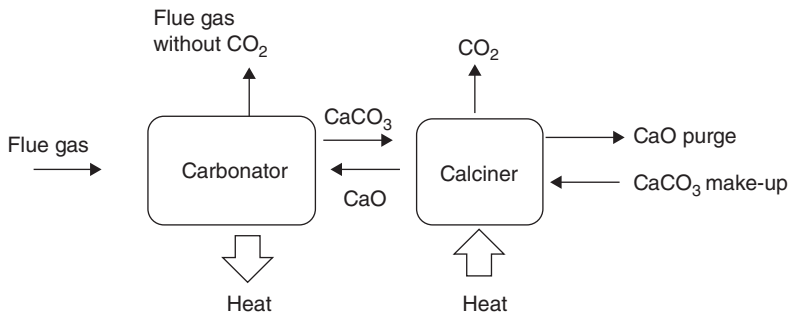
In a packed bed configuration, regeneration is accomplished by heating the CO<sub>2</sub>-loaded adsorbent to liberate CO<sub>2</sub>. During this time, the flue gas is diverted to a second packed bed, which continues to adsorb CO<sub>2</sub> from the gas. By alternating the flue gas between two packed beds that alternatively undergo absorption and regeneration in a cycle, CO<sub>2</sub> can be continually removed from the flue gas. In a fluidized bed, the sorbent is circulated between an absorber vessel where it contacts the flue gas and a regenerator vessel where it is heated to liberate gaseous CO<sub>2</sub>.

Usually, the PSA process is preferred to other cyclic operations when the process is carried out at elevated pressures. Otherwise, when the concentration of the adsorbate is low (0–15 vol%), or when the process is at low pressure, other options such as TSA may need to be considered. For a low-concentration adsorbate, the PSA technology may result in a much longer desorption step, whereas for low-pressure processes, the installation should also include additional vacuum pumps and compressors, both resulting in a more complicated process, increased capital cost, and reduced efficiency [8]. A potential option that could overcome these issues is vacuum pressure swing adsorption (VPSA).

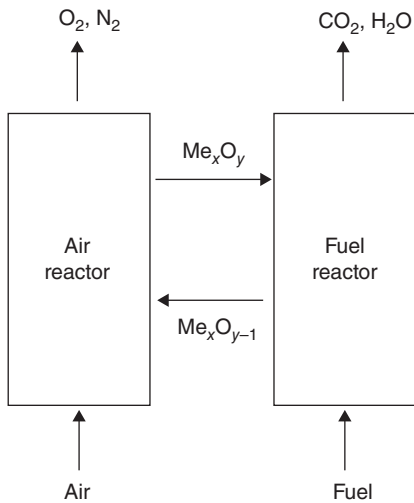
TSA can work both for low and elevated pressures; however, it is usually preferred when the adsorption step is carried out at a low temperature. Consequently, the main advantage of TSA over PSA is its ability to separate efficiently strong-bonded adsorbates onto adsorbents, as for the case of chemisorption. However, a major drawback of TSA is the high energy intensity of the desorption process compared to PSA. Other alternatives to TSA include microwave swing adsorption (MSA) [14] and electric swing adsorption (ESA) [15] that could offer potential energy savings and faster heating rates; however, these technologies are still at low technology readiness level (TRL).

Generally, TSA is usually preferred for post-combustion CO<sub>2</sub> capture at low temperature and atmospheric pressure, while PSA usually is the right choice for pre-combustion CO<sub>2</sub> capture at elevated temperatures, as in the case for an IGCC plant configuration. As a post-combustion arrangement, PSA and TSA are assessed as TRL 6.

Adsorption equilibria, kinetics, and regeneration ability are key factors to evaluate the performance of an adsorbent. Fast adsorption/desorption kinetics, influenced by functional groups present, as well as the pore size and distribution in the support, are essential for an efficient CO<sub>2</sub> adsorption process and control of the cycle time and the required amount of adsorbent. Other selection criteria include high CO<sub>2</sub> selectivity, mechanical strength after multi-cycling, chemical stability/tolerance to impurities, high availability, and, lastly, low costs.



**Figure 1.5** Calcium looping system as post-combustion configuration. Source: Adapted from Abanades [16].



**Figure 1.6** Chemical looping combustion.  $\text{Me}_x\text{O}_y/\text{Me}_x\text{O}_{y-1}$  denotes the recirculation oxygen carrier material. Source: Adapted from Abanades et al. [17]. © Elsevier.

#### 1.2.4.2 High-Temperature Solids Looping Technologies

The most common types of high-temperature solids looping technologies are calcium and chemical looping combustion. Calcium looping uses CaO as a sorbent, which produces CaCO<sub>3</sub> at approximately 650 °C (Figure 1.5). Chemical looping is a two-step conversion process where the fuel reacts with almost pure O<sub>2</sub> as in the oxyfuel process, while a metal oxide acts as an oxygen carrier and reacts with the fuel, obtaining CO<sub>2</sub> and water (Figure 1.6). In both cases, the metal oxide or CaO is regenerated.

Note that calcium looping can be considered as post-combustion or pre-combustion, while chemical looping can be considered as oxy-combustion or pre-combustion depending on the configuration [16].

Because of the high operation temperature, the advantage of this process is the potential recovery of energy for steam production, which can be used for additional power production and reduce the efficiency penalty in the power plant.

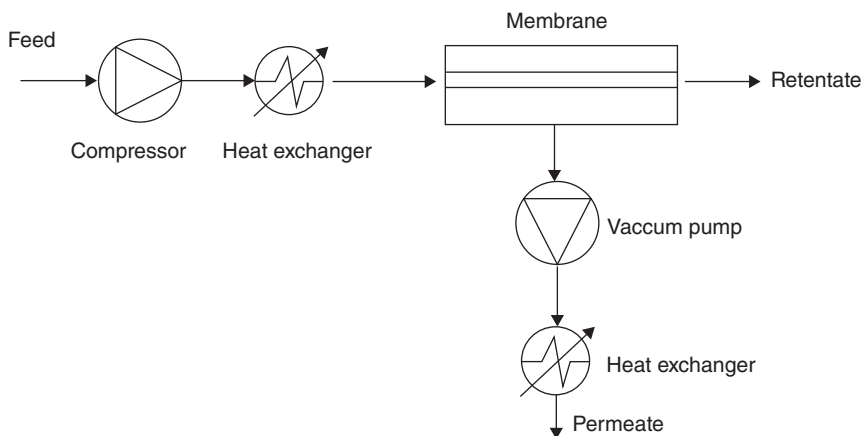
Calcium looping has shown a significant evolution over the past 15 years from lab scale to pilot testing, reaching a TRL of 6. The main research focus to cut down the costs over the next years is on the sorbent, reactors (configurations and interconnections), and process designs [17]. If used in the industrial sector, calcium looping can be beneficially integrated in the cement production facility because of the use of solids from the capture system in the production. In this regard, the CLEANKER project aims to scale up a calcium looping process in a cement production environment, which will increase the TRL of this technology up to 7.<sup>4</sup>

Chemical looping has reached a TRL of 6 as oxyfuel arrangement while a TRL of 3 as pre-combustion system. The main research areas on chemical looping are focused on the reactor design, oxygen carrier development, and prototype testing. Moreover, more than a thousand materials have been tested at the laboratory scale. At a larger scale (0.3–1 MW), the accumulated operational experience is more than 7000 hours [17]. A detailed review of the main process routes under development within the chemical looping systems is included in Ref. [17].

#### 1.2.4.3 Membranes

Membranes are porous structures able to separate different gases at different rates because of their different permeation [8]. These can be used not only in post- and pre-combustion processes but also in oxyfuel for oxygen separation. In post-combustion, the main interest in these systems is their low energy requirements compared to the traditional chemical absorption process.

The energy needs are reduced to those from the compressor and vacuum pump. Moreover, membrane systems are easy to start and operate, have no emissions associated, and are modular, offering installation advantages [8]. However, the separation mechanism of membranes is based on the difference of CO<sub>2</sub> partial pressure. In post-combustion, because of the relative low CO<sub>2</sub> concentration in the flue gas to



**Figure 1.7** Scheme of a single-stage membrane system. Source: Adapted from Mores et al. [18].

<sup>4</sup> <http://www.cleanker.eu>.

**Table 1.1** Advantages of each type of membrane [21].

Type of membrane	Advantages
Ceramic	Good selectivity–permeability Easier to manufacture larger areas
Polymeric	Good thermal stability and mechanical strength
Hybrids	Aiming to show the advantages of both ceramic and polymeric membranes

Source: Adapted from Wang et al. [21].

be treated (approximately 4–12% for power plants), this driving force would not be enough to achieve high CO<sub>2</sub> capture ratios through simple configurations. However, membranes could offer advantages for partial capture arrangements and generally more complex arrangements are used to reach a full capture rate (90%). In pre-combustion, because of the higher partial pressure of CO<sub>2</sub> in the gas to be treated, membranes can be more effective. In any case, the gas containing CO<sub>2</sub> must be cooled down to meet the temperature limitations of the membrane [18] and that could be a drawback (Figure 1.7).

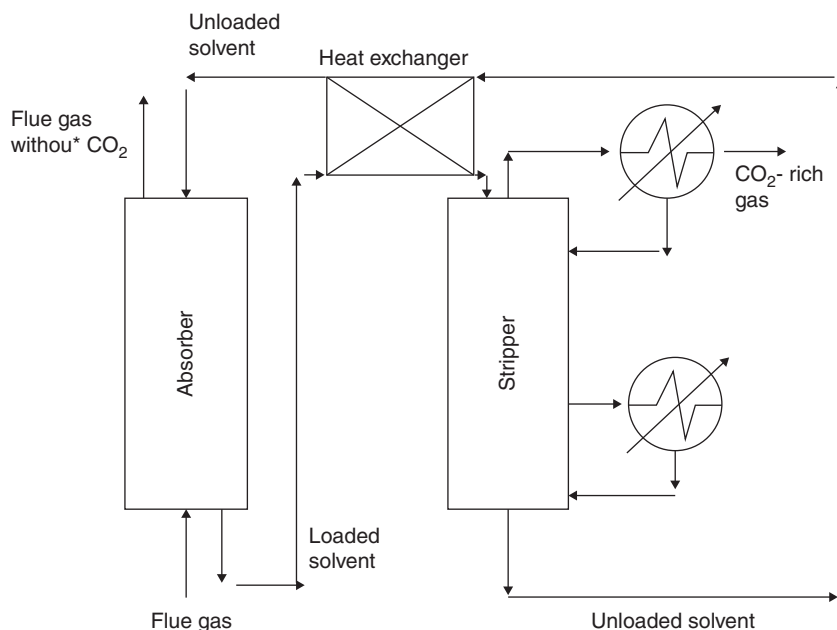
There are two main characteristics to define a membrane material for CO<sub>2</sub> capture: permeability, which will impact on the CO<sub>2</sub> separation ratio and selectivity, which will define the CO<sub>2</sub> concentration in the output gas. From a techno-economic perspective, the optimum values for selectivity and permeability would be a function of the gas to be treated, as studied in Ref. [19]. The ratio of the permeability to the thickness of the membrane will be of high importance as that will characterize the permeance (commonly measured as gas permeation units [GPU]). To maximize the permeance without impacting the mechanical stability, the membranes are typically a dense layer supported by a porous layer [20].

The membrane materials can be divided into ceramic, polymeric, and hybrid (Table 1.1). Moreover, the design of the membrane-based system will be a key factor on the separation process. Firstly, the membrane module will be the key factor. The main modules for polymeric membranes are described as a spiral wound, a hollow fiber, and an envelope [21].

The majority of the membranes used currently for post-combustion are based on polymeric materials [20], and a large list of polymers have been studied in the literature, including polyimides, polysulfones, and polyethylene oxide. The most advanced processes have reached currently a TRL of 6. Because of the modularity membranes offer, although sometimes predicted, it is not clear if there will be a fast development toward higher TRLs [21].

#### 1.2.4.4 Chemical Absorption

The basic configuration of chemical absorption (Figure 1.8) includes the reaction of a liquid solvent with CO<sub>2</sub> in a column called absorber at a relatively low temperature, 40–60 °C, and its desorption in another column called desorber or stripper, generally at a high temperature, 100–140 °C. It must be noted that process modifications and solvent enhancements might modify those process conditions.



**Figure 1.8** General chemical absorption configuration

The absorption of CO<sub>2</sub> into liquid solvents takes place by three phenomena: chemical reaction, physical absorption, and diffusivity. Depending on the compound and the conditions, one phenomenon will be predominant over the others.

Chemical solvents are more attractive candidates for typical post-combustion processes, with relatively low partial pressures of CO<sub>2</sub> (10–15% in coal power plants and 4–8% for gas-fired power plants). Chemical absorption follows a standard configuration such as in Figure 1.8. However, new configurations have appeared to enhance the process, increase the efficiency, and/or decrease the capture costs.

Chemical absorption with amines is by far the most advanced carbon capture process and the only one that reached a TRL of 9 [2]. The most tested solvent is aqueous monoethanolamine (MEA) solution, although it does not represent any more the benchmark solution as consolidated alternatives show enhanced properties. Two large-scale facilities have used enhanced systems, the Boundary Dam Capture plant [2] and Petra Nova. One of the main pathways to get more efficient chemical absorption processes and cut down costs is the development of new solvents. However, many solvents are emerging and only few have been tested at large scale, maintaining the TRL of other new systems still low. A review of commercial solutions and relevant projects can be found, for example, in Ref. [22]. The main criteria for the selection of a solvent are included in Table 1.2.

Primary amines are of high interest because of their fast reaction with CO<sub>2</sub>. However, the main drawback is their high energy consumption for the solution regeneration. Several alternatives are emerging to decrease such penalty, the most common one being the use of tertiary amines. However, the CO<sub>2</sub> absorption in tertiary amines

**Table 1.2** Desired solvent properties and its impact on the absorption process [75].

Solvent property	Impact on the absorption process
High capacity and low heat of absorption	It is linked to the energy requirements per ton of CO <sub>2</sub> , but the absorption capacity is connected to heat (thermodynamics) and independent variation is limited
High mass transfer and chemical kinetics	It reduces equipment size or the capacity by operating near the equilibrium limit
Low viscosity	It reduces the pumping costs and potentially increases the mass transfer and the heat transfer rate
Low degradation tendency	It reduces the solvent make-up and the regenerator can operate at higher pressure/temperature, increasing the thermal efficiency
Low toxicity/environmentally friendly	It becomes more important if toxic by-products are released during volatility losses
Cost and availability	It will impact on reaching commercial scale
Low fouling tendency	It will impact on the operation

Source: Adapted from Mathias et al. [75].

is much slower. Consequently, other alternatives are emerging, such as the use of blends combining primary and tertiary amines (commonly called “promoted tertiary amines” or “activated tertiary amines”). Numerous alternatives have emerged during the past years; perhaps it is difficult to establish the best alternative.

A potential substitute of traditional solvents is the use of compounds that, at unloaded or loaded conditions, separate into two phases, called biphasic solvents. There are two types of biphasic solvents, namely, liquid–liquid or solid–liquid, depending on the phases in solution. The main advantage is that only one phase needs to be regenerated, and consequently, the stripper size is reduced, and the energy consumption is potentially lower. Consequently, numerous biphasic solvents have been studied in the literature (e.g. in Ref. [23]).

Another strategy is to add enzymes, such as carbonic anhydrase (CA) [24]. CA increases the kinetic constant of the absorption of CO<sub>2</sub> in aqueous amine and dilute carbonate solutions by catalyzing the CO<sub>2</sub> hydration. The impact will depend on the compounds in solution, as the regeneration of the enzyme regeneration rate will vary. The challenges enzymes offer are their pH and thermal stability, lifetime, and sensitivity to pollutants such as SO<sub>x</sub> and NO<sub>x</sub>.

At lower development stage, solvents can be encapsulated in thin polymer shells and be considered as a bed of capsules containing the solvent. Capsules must be permeable enough to allow carbon dioxide to get in contact with the solvent but strong

enough to resist the high regeneration temperatures during a number of cycles [25]. The benefit of this configuration is to increase the surface area of the solvent in contact with the flue gas and avoid issues related to viscosity and precipitation.

Recently, ionic liquids (ILs) are of great interest. These are composed of ions and are at liquid state below 100 °C. If the melting point is below the room temperature, these are referred as room temperature ionic liquids (RTILs). These solvents are recognized by their low vapor pressure, high thermal and chemical stability, nonflammability, and high viscosity. These properties open new possibilities for the solvent regeneration at different pressures and temperatures, which can be optimized accordingly. Some ILs show a high absorption capacity, although the viscosity could be decremental for the mass transfer.

Physical solvents are characterized for the high physical solubility of CO<sub>2</sub> in these and are especially interesting for flue gas with high CO<sub>2</sub> content [26]. There are commercial processes based on this principle, such as Rectisol®, Selexol®, Purisol®, Morphysorb®, and Fluor®, particularly effective at high concentrations of acid gas, high pressure, and low temperature [27] and are characterized by their low vapor pressure, low toxicity, and low corrosion [15].

An emerging pathway is the use of hybrid solvents, solutions containing amine/s and organic compound/s with or without the presence of water, the former called as water-lean solvents. The goal is to maintain an enhanced physical absorption by substituting partial/totally the water content and maintaining a considerable chemical reaction by keeping the amine in the solution. It is known that at low concentration of the amine(s), the physical solubility plays an important role and the diffusivity can also become an important factor in viscous solutions. The enhanced solubility of CO<sub>2</sub> in organic solvents, compared to water, has been widely studied in the past [28–31], and this presents advantages in its application in chemical absorption. During the desorption, the main energy penalty is due to the water evaporation. Decreasing the water content will decrease this energy penalty. Partial and total substitution of water by organic solvents has been considered as an alternative to decrease the steam consumption in the desorber. However, as studied in Ref. [32], the absorption kinetics would just be favorable, compared with aqueous amine solutions, at certain conditions of pressure and temperature in the absorber. The total substitution of water in water-lean solvents will limit the reactions that take place in solution: hydrolysis will not occur and the carbamate and bicarbamate ions will be nonexistent [33]. However, the net benefit in the energy consumption when using water-lean solvents is not yet clear, as discussed in Ref. [34].

#### **1.2.4.4.1 Advances on Process Configurations**

As mentioned previously, chemical absorption is the most advanced technology, reaching commercial status (TRL 9). However, there are still barriers that slow down its application in industrial and power sectors. Cost is one of the challenges to overcome and energy consumption has a strong contribution. The development of new solvents and improvements on the process flow sheet and/or its integration in the industrial or power facility could reduce this energy consumption.



The common process modifications can be divided as in Ref. [35]: (i) absorption enhancement, (ii) heat integration, and (iii) heat pumps. Perhaps these can also be classified by their purpose, as in Ref. [36]: (i) increase of rich solvent loading, (ii) reduction of the specific reboiler duty, or (iii) combination of both. The enhancement on the absorption and desorption processes and its impact on costs will depend on other factors such as the solvent and the facility. The modifications on the stripper to reduce energy consumption are being considered for the next generation of post-combustion processes' configurations with advanced solvents (e.g. as in Ref. [37]).

### 1.2.5 Others CO<sub>2</sub> Capture/Separation Technologies

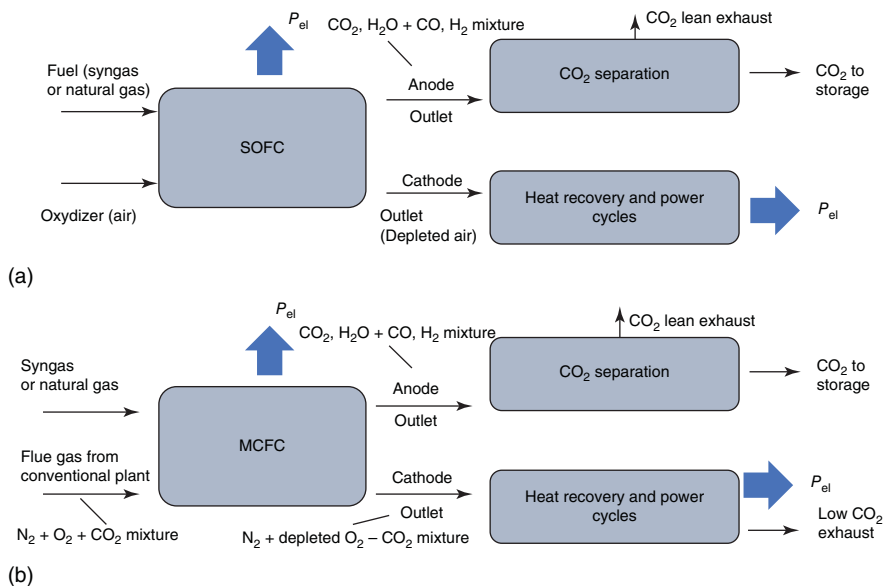
Other CO<sub>2</sub> capture/separation technologies such as electrochemical, cryogenic separation, liquefaction, microbial/microalgae, or direct air separation are described in the literature.

Hybrid technologies have been studied in the past years, aiming to achieve higher capture rates and/or sum up the advantages of each CO<sub>2</sub> capture technology. The hybrid processes can be classified into absorption-based, adsorption-based, membrane-based, and cryogen-based hybrid processes. The integration of membranes into the absorption process (such as in the membrane contractor arrangement), catalysis process, and cryogenic process has progressed over the past years. However, the majority of the results are based on simulations or small-scale testing campaigns, and the real value of using two technologies is not clear [38].

Within the range of emerging technologies, electrochemical separation has had a fast development over the past years and, potentially, will continue in this pathway. The following Section 1.2.5.1 will be focused on fuel cells because of the growing expectation on this electrochemical separation technology for its integration in power plants.

#### 1.2.5.1 Fuel Cells

Fuel cells convert chemical energy of a gaseous fuel directly into electricity and heat. The fuel is oxidized electrochemically, which leads to lower exergy losses compared to direct combustion. In general, fuel cells are classified by the electrolyte material and their operating temperature (Figure 1.9). Low-temperature fuel cells (100–250 °C) include alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), and proton exchange membrane fuel cells (PEMFCs), while high-temperature fuel cells (600–900 °C) refer to Molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs). Because of the high temperature at which MCFCs and SOFCs operate, natural gas reformation and the subsequent shift reaction can be performed in the fuel cell itself. MCFCs and SOFCs are most appropriate for stationary power production at scales ranging from a few hundred kilowatts up to a few megawatts because of their high electrical efficiencies and the ability for cogeneration of electricity and heat [39]. Moreover, SOFCs and MCFCs are more fuel flexible and are not poisoned by carbon monoxide and carbon dioxide.



**Figure 1.9** Two main options for CO<sub>2</sub> capture using fuel cells. (a) The FC oxidizes a fuel taking oxygen from air and later separating CO<sub>2</sub> from the anode effluent. (b) The MCFC concentrates the CO<sub>2</sub> in flue gas from a conventional power plant from the cathode inlet to the anode outlet, while also oxidizing a portion of additional fuel. Source: Adapted from [11].

When MCFCs/SOFCs are fueled with natural gas or syngas, CO<sub>2</sub> capture can be implemented at different points, for example, after the fuel cell (“post-anode capture”). Alternatively, H<sub>2</sub> can be produced by reforming/partial oxidation of natural gas or coal gasification upstream the fuel cell and CO<sub>2</sub> can be removed after syngas is shifted by means of physical solvents, membranes, or adsorbents – “pre-anode CO<sub>2</sub> capture,” similar to pre-combustion.

Fuel cells generally operate with an approach that is similar to the “oxyfuel” concept, oxidizing fuel with oxygen extracted from air while generating power and releasing concentrated effluents at the anode outlet (Figure 1.9). This kind of power cycles generally require an integration with custom-tailored gas turbine cycles, often operating at unconventional turbine inlet temperatures and pressure ratios, either using natural gas as a fuel or coal through integrated gasification fuel cell (IGFC) concepts. Because most fuel is oxidized in the fuel cell to allow a high CO<sub>2</sub> capture efficiency, the fuel cell (FC) generates the majority of the cycle power output. The alternative option offered by MCFCs is shown at the bottom of Figure 1.9, where the fuel cell can operate “draining” CO<sub>2</sub> from the cathode inlet stream, receiving the flue gases of a conventional power plant. In this configuration, the fuel cell operates with a post-combustion approach, although also oxidizing a minor portion of additional fuel with the same “oxyfuel” features discussed above.

The parameters affecting the selection of operating conditions of the SOFC/MCFC are stack size, heat transfer rate, voltage output and cell life, load requirement, and