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CO₂ Capture – A Brief Review of Technologies and Its Integration

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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 CO₂ emissions. Energy efficiency, fuel switching, renewables, and carbon capture represent the largest impact on CO₂ 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)¹ and has other interesting characteristics that increase its value beyond its cost: (i) easiness to retrofit current power plants or industrial facilities,² (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.

CO₂ capture (also called CO₂ sequestration or carbon capture) involves a group of technologies aiming to separate CO₂ from other compounds released during the production of energy or industrial products, obtaining a CO₂-rich gas that can be stored or used for the obtention of valuable products. The main classification of CO₂ capture technologies relies on where in the process the CO₂ 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 CO₂ Capture Technologies

1.2.1 Status of CO₂ Capture Deployment

GCCSI reported in 2018 23 large-scale CCS facilities in operation or under construction globally, summing up 37 MtCO₂ per year. This wide range of facilities shows the versatility of CO₂ capture processes³.

In the power sector, the United States is leading the implementation deployment, although Europe has the highest CO₂ 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 CO₂ 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 CO₂ 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 H₂, 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 CO₂ and H₂O. 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>).

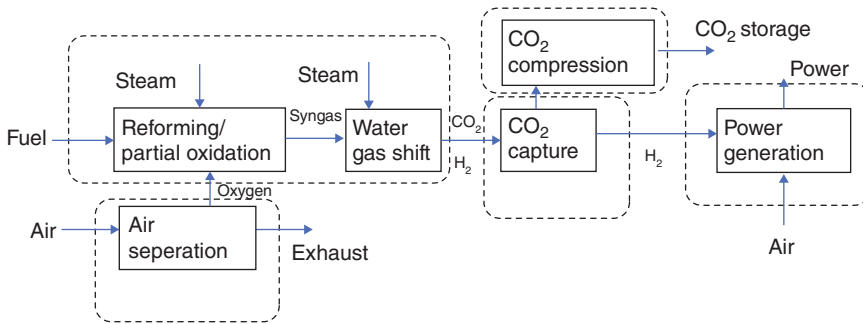


Figure 1.1 Diagram of pre-combustion capture for power generation in IGCC. Source: Adapted from Jansen et al. [72].

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 CO₂ stream (60–75%, wet and might contain impurities and incondensable components) that can be further purified to meet the final use specifications. The CO₂-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 CO₂ working fluid in a highly recuperated Brayton cycle, aiming to reduce CO₂ 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 CO₂ 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.

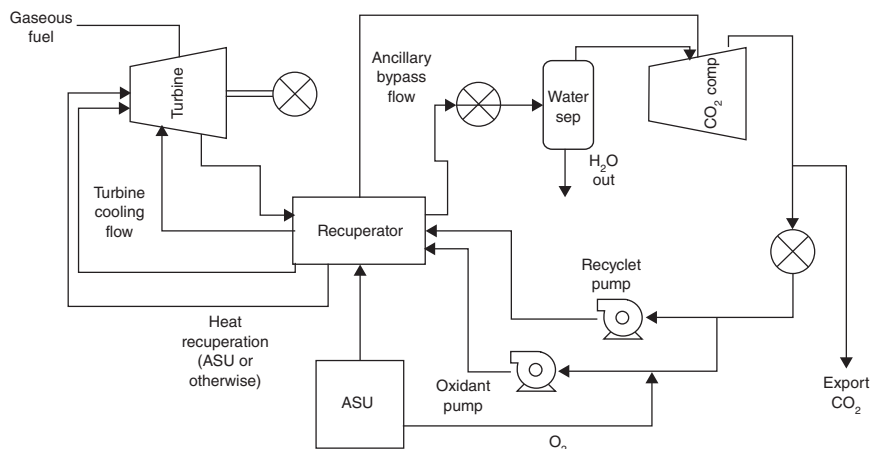


Figure 1.2 Process schematic of a simplified commercial scale natural gas Allam cycle. Source: Adapted from Allam et al. [4].

1.2.4.1 Adsorption

Adsorption refers to the uptake of CO₂ 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^{−1}, while in chemical adsorption, the molecules are chemisorbed (chemical bond; covalent, ionic, or metallic) and the bond energy is about 60–418 kcal mol^{−1} [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 CO₂ 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 CO₂

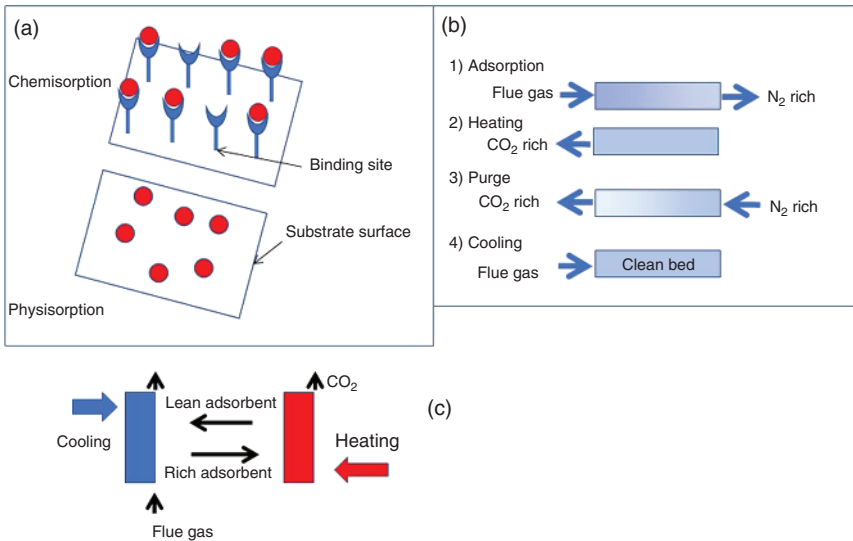


Figure 1.3 The adsorption process: (a) difference of physisorption and chemisorption, (b) a packed bed configuration, and (c) a fluidized bed configuration. Source: Adapted from Global CCS Institute (<https://www.globalccsinstitute.com/archive/hub/publications/29721/co2-capture-technologies-pcc.pdf>).

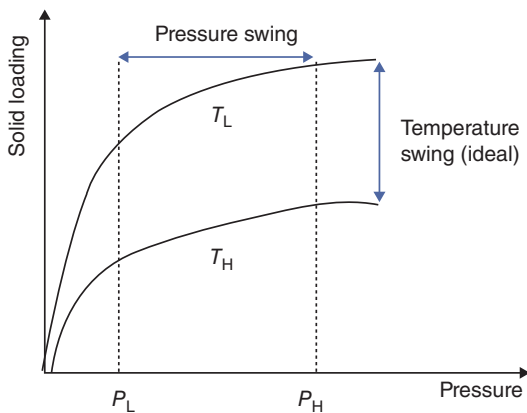


Figure 1.4 Comparison of TSA and PSA for the regeneration of solid adsorbents. H = high; L = low. Source: Adapted from Rackley [73].

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 CO₂ 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 CO₂-loaded adsorbent to liberate CO₂. During this time, the flue gas is diverted to a second packed bed, which continues to adsorb CO₂ from the gas. By alternating the flue gas between two packed beds that alternatively undergo absorption and regeneration in a cycle, CO₂ 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 CO₂.

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 CO₂ capture at low temperature and atmospheric pressure, while PSA usually is the right choice for pre-combustion CO₂ 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 CO₂ adsorption process and control of the cycle time and the required amount of adsorbent. Other selection criteria include high CO₂ selectivity, mechanical strength after multi-cycling, chemical stability/tolerance to impurities, high availability, and, lastly, low costs.

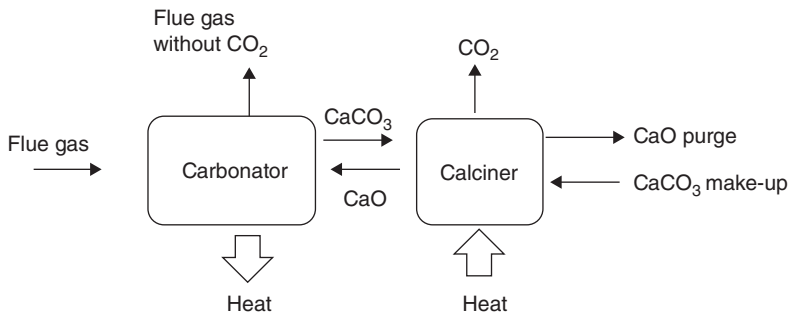


Figure 1.5 Calcium looping system as post-combustion configuration. Source: Adapted from Abanades [16].

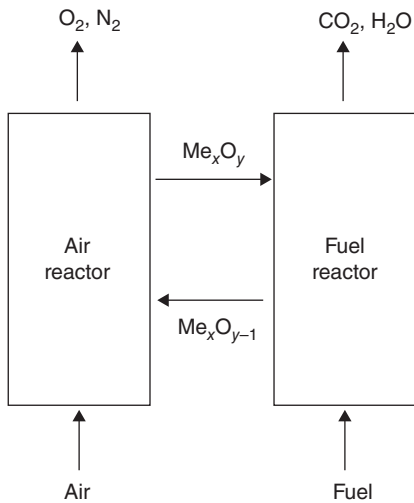


Figure 1.6 Chemical looping combustion. $\text{Me}_x\text{O}_y/\text{Me}_x\text{O}_{y-1}$ denotes the recirculation oxygen carrier material. Source: Adapted from Abanades et al. [17]. © Elsevier.

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 CaCO₃ at approximately 650 °C (Figure 1.5). Chemical looping is a two-step conversion process where the fuel reacts with almost pure O₂ as in the oxyfuel process, while a metal oxide acts as an oxygen carrier and reacts with the fuel, obtaining CO₂ 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 7⁴.

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 CO₂ partial pressure. In post-combustion, because of the relative low CO₂ concentration in the flue gas to

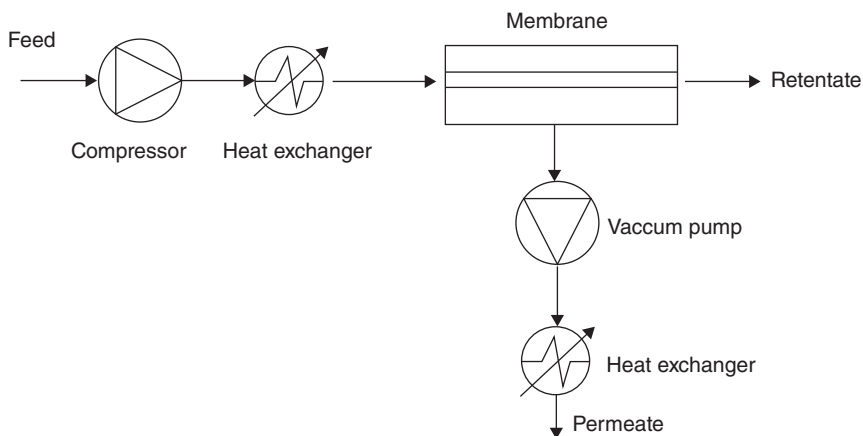


Figure 1.7 Scheme of a single-stage membrane system. Source: Adapted from Mores et al. [18].

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 CO₂ 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 CO₂ in the gas to be treated, membranes can be more effective. In any case, the gas containing CO₂ 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 CO₂ capture: permeability, which will impact on the CO₂ separation ratio and selectivity, which will define the CO₂ 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 CO₂ 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.

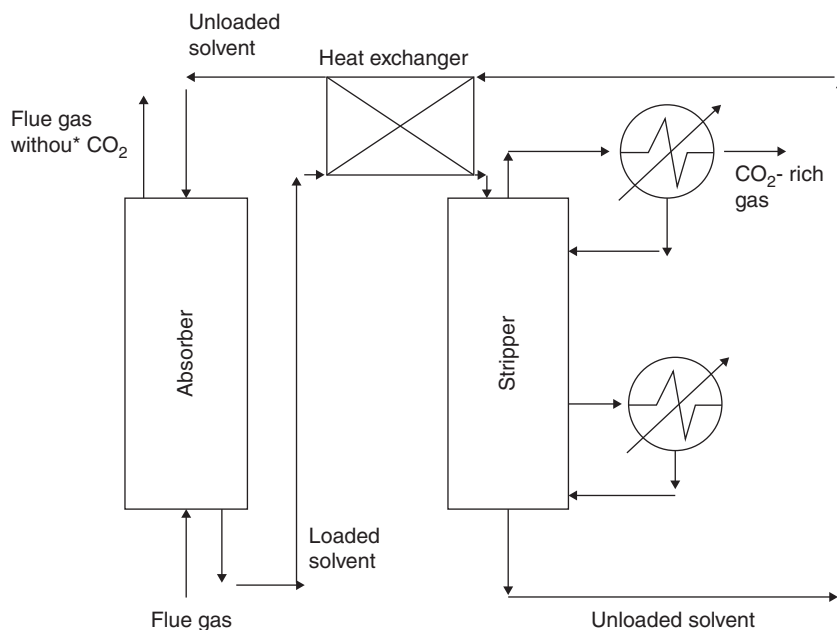


Figure 1.8 General chemical absorption configuration

The absorption of CO₂ 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 CO₂ (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 CO₂. 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 CO₂ 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 ₂ , 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 CO₂ in aqueous amine and dilute carbonate solutions by catalyzing the CO₂ 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_x and NO_x.

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 CO₂ in these and are especially interesting for flue gas with high CO₂ 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 CO₂ 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 CO₂ Capture/Separation Technologies

Other CO₂ 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 CO₂ 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.

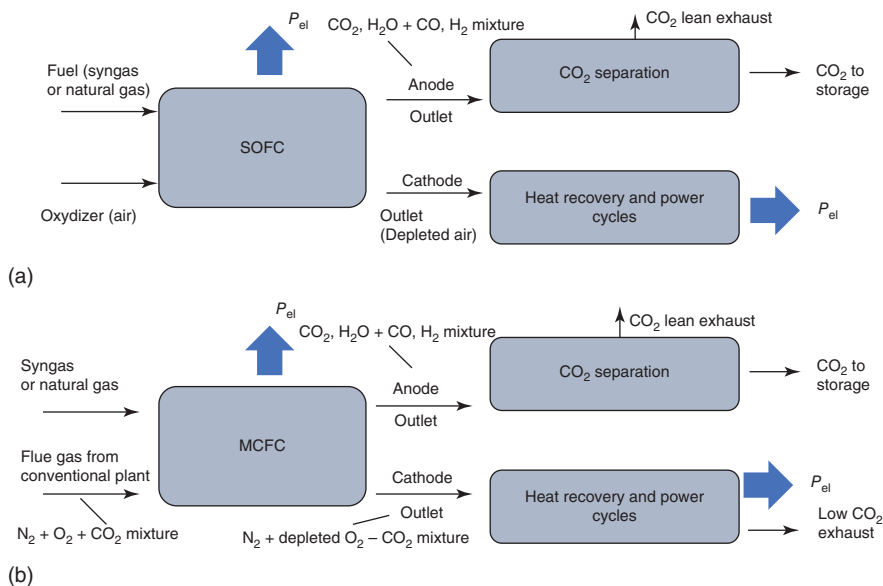


Figure 1.9 Two main options for CO₂ capture using fuel cells. (a) The FC oxidizes a fuel taking oxygen from air and later separating CO₂ from the anode effluent. (b) The MCFC concentrates the CO₂ in flue gas from a conventional power plant from the cathode inlet to the anode outlet, while also oxidizing a portion of additional fuel. Source: Adapted from [11].

When MCFCs/SOFCs are fueled with natural gas or syngas, CO₂ capture can be implemented at different points, for example, after the fuel cell (“post-anode capture”). Alternatively, H₂ can be produced by reforming/partial oxidation of natural gas or coal gasification upstream the fuel cell and CO₂ can be removed after syngas is shifted by means of physical solvents, membranes, or adsorbents – “pre-anode CO₂ 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 CO₂ 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” CO₂ 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

cost. The main operating conditions are pressure, fuel utilization factor at the anode and O₂/CO₂ utilization factor (for SOFC and MCFC cases, respectively) at the cathode, voltage, current density, and temperature. The optimization of the process configuration in conjunction with optimal operating parameters is critical to minimize stack degradation, which directly impacts the performance and life of the FC.

Currently, the main challenges for stationary fuel cells are cost and cell durability. For the IGFC system, the gas cleaning process adds another energy barrier to its power generation.

1.2.5.1.1 Solid Oxide Fuel Cells (SOFCs)

Adams et al. [40] divided SOFC systems for CO₂ capture into first- and second-generation systems as a function of the operating pressure of the SOFC. Low-pressure, first-generation SOFC systems are the most promising option for SOFC commercialization at large scale (100 MW or greater) in the short term. Several process configurations and design options are possible (Figure 1.10), although those generally follow the same pattern and offer some flexibility to select the optimum combination of variables such as gas clean-up/reforming, water gas shift (WGS), CO₂ capture technology, and heat recovery.

Second-generation SOFC systems are high-pressure SOFCs with separate streams for the anode and cathode exhausts. This arrangement promotes the use of an SOFC system that captures and compresses CO₂ at significantly reduced costs and minimum complexity via “pre-anode” and/or “post-anode” capture.

In the pre-anode CO₂ capture process, syngas is generated at high pressure through high pressure coal gasification or by reforming the natural gas available from a natural gas pipeline at high pressure. Similar to the above cases, the syngas can be optionally shifted using the WGS reaction, creating a stream of steam, H₂, and CO₂. Up to about 90% of the CO₂ can then be recovered from the syngas (or shifted syngas) using absorption or adsorption technologies.

The post-anode CO₂ capture has been extensively studied in SOFC IGCC and natural gas cycles. A simple IGFC system is similar to an IGCC system, but the gas turbine (GT) power island is replaced by a FC island. Some system configurations still have a gas or steam turbine to utilize the extra heat. “Post-anode” CO₂ capture can be applied via CO₂ separation from H₂O via H₂O condensation (or via cooling, knockout, and additional drying) and can effectively result in a 100% CO₂ removal. A separation system that uses condensation followed by a cascade of flash drums can be used to produce CO₂ at high enough purity for pipeline transport at the SOFC anode exhaust pressure.

1.2.5.1.2 Molten Carbonate Fuel Cells (MCFCs)

The MCFC can be used to separate CO₂ thanks to the functional reactions that occur inside the cell. By sending flue gas from a power plant to the cathode, the CO₂ from the flue gas is selectively separated and concentrated at the anode, in a mixture of water and small amounts of unreacted hydrogen and methane. The “cleaner flue gas” is delivered to the atmosphere with up to 70% less CO₂ content, which is transferred to the MCFC anode exhaust stream where it can be separated much more

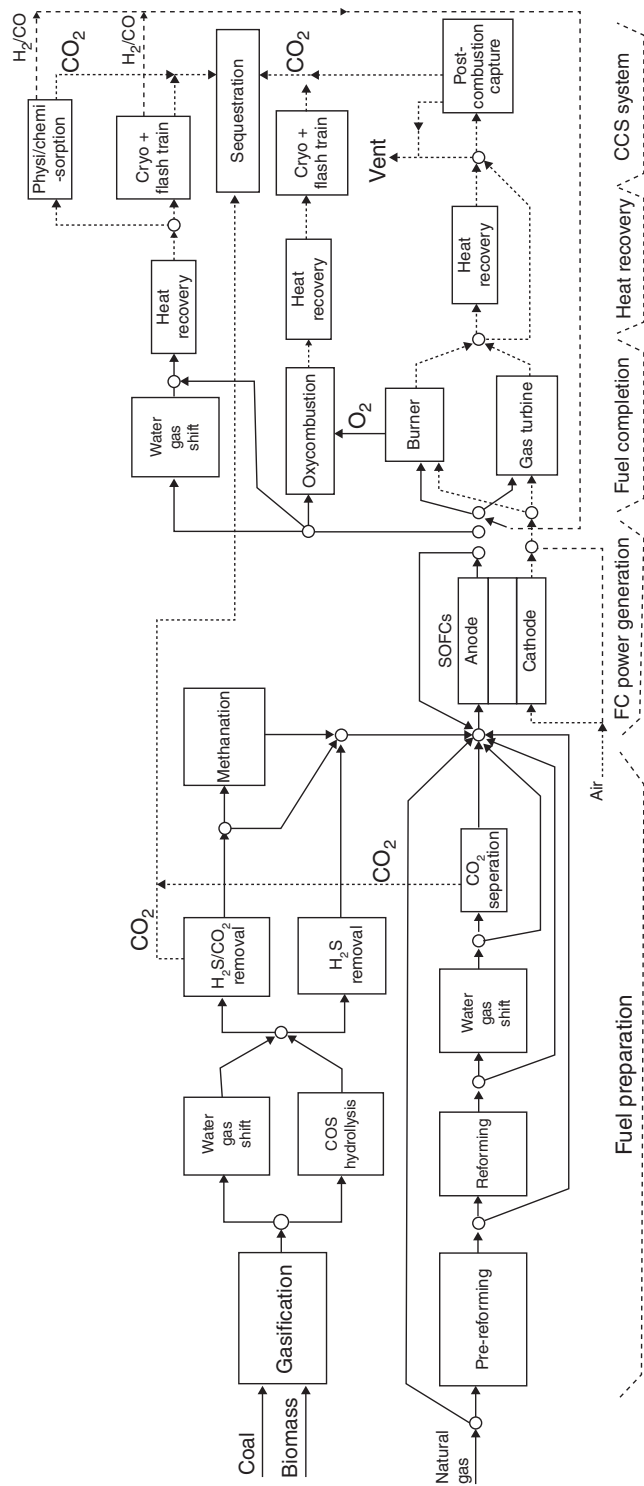


Figure 1.10 Superstructure of SOFC – CO₂ capture process configurations. Source: Adams et al. [40].

effectively, resulting in a high-purity CO₂ flow. The main advantage in this process is that extra power is generated because the MCFC will be fueled and operated normally to carry out the separation, and it increases the overall efficiency of the power plant and compactness of the post-combustion unit, while reduces the energy penalty. The modularity feature of MCFC systems allows to tailor the installation to the capture needs or gradually increases the size of the capture unit.

One example of an MCFC and CO₂ capture system was developed by Fuel Cell Energy (FCE), namely, the Combined Electric Power and Carbon-dioxide Separation (CEPACS). In the process of capturing >90% CO₂. In this configuration, the system can generate up to 351 MWe additional power (net AC), after compensating for the auxiliary power requirements of CO₂ capture and compression⁵.

1.3 Integration of Post-combustion CO₂ Capture in the Power Plant and Electricity Grid

A key aspect of thermal power plants is their carbon intensity (CO₂ emitted per unit of energy generated, generally expressed as kg CO₂/MWh). Nowadays, the global average is around 500 kgCO₂/MWh, which must be reduced to 100 kgCO₂/MWh by the late 2030s to be consistent with a 2 °C climate pathway [36]. Even if combined cycle thermal power plants can be considered as low carbon alternatives in some scenarios, in the mid-to-long term, it might be required to further decarbonize the existing units by retrofitting them with CCS or by building novel designs with low CO₂ emissions. As demonstrated at commercial scale, post-combustion CO₂ capture can significantly reduce the carbon intensity of thermal power plants [2]. Table 1.3 compares the carbon intensity of thermal power plants with and without CCS.

1.3.1 Integration of the Capture Unit in the Thermal Power Plant

In principle, the key integration aspects of the power plant and the capture unit are the flue gas, emitted by the power plant and sent to the capture unit, and the energy requirements of the chemical absorption/desorption process, provided by the power plant to the capture unit (Figure 1.11). Figure 1.11 shows a simplified schematic of a power plant integrated with a post-combustion CO₂ capture system. The main energy and mass integration flows are described. Fuel and air are used in the combustion process, providing heat to produce steam in the power cycle. The flue gas from the combustion is sent to the CO₂ capture unit and leaves it lean in CO₂. A CO₂ rich stream is produced in the CO₂ capture plant and sent to conditioning, transport, and storage. Heat in the form of steam is provided from the power plant and is returned back as water condensate. Electricity from the power plant is utilized to run the auxiliary systems of the capture unit, including the flue gas fan, cooling, and solvent circulation pumps. Higher levels of process integration between the power plant and the capture unit can be considered, as explained in [41].

5 (<https://www.netl.doe.gov/project-information?p=FE0026580>).

Table 1.3 Low heat value (LHV) efficiency, carbon intensity, and energy penalty in coal- and gas-based thermal power plants with CCS [43, 54, 76].

	Carbon intensity (kg CO ₂ /MWh)	LHV efficiency (%)	Efficiency reduction (%)
Pulverized coal subcritical	700–1000	30–47	—
Combined cycle	350–450	56–62	—
Pulverized coal with CCS at 90% capture rate	130	25–42	5–7
Combined cycle with CCS at 90% capture rate	40–50	50–54	6–8

Source: Adapted from Adams and Mac Dowell [43], Gonzalez-Salazar et al. [54], Kvamsdal et al. [76].

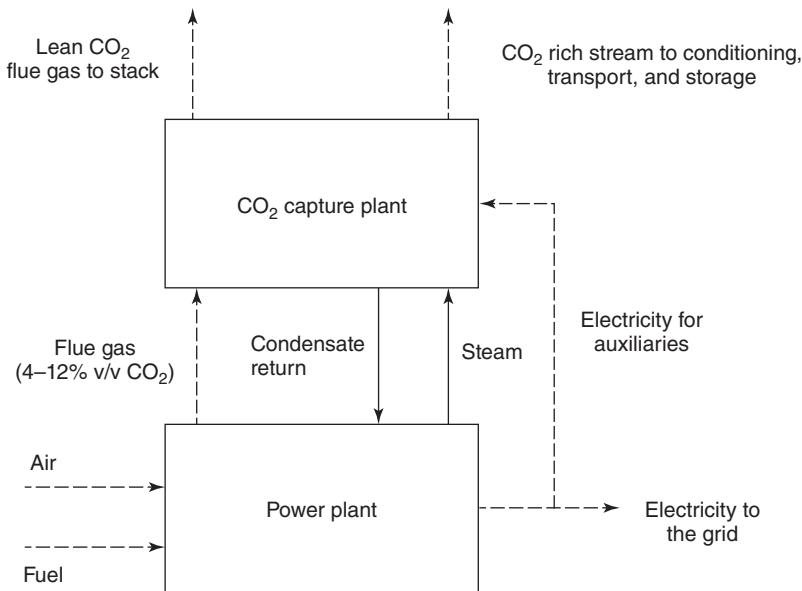


Figure 1.11 Schematic integration of a power plant with a post-combustion CO₂ capture system.

The energy required to run the chemical absorption–desorption process in the capture unit process is mainly due to the (i) mechanical work to drive the flue gas fan to compensate the pressure drop induced by direct contact cooler, absorber column, and water wash sections and ducting; (ii) mechanical work to drive the pumps for cooling water and solvent circulation pumps; (iii) steam for solvent reclaiming because of its degradation in order to keep the solvent fresh and contaminant free; and (iv) steam to feed the reboiler duty: regenerate the solvent, generate stripping vapors, heat up the solvent to saturation conditions, and evaporate the water.

The flue gas is sent to the capture unit and additional pressure drop is imposed, which is a function of the thermal power plant unit, its equipment for emissions control, and the boiler type. In gas plants, the heat recovery steam generator in the exhaust gas generally imposes the additional pressure drop downstream the gas turbine (in the order of 20–40 mbar [8]), and in boilers (coal/oil/gas fired), a fan is commonly used to keep it under slightly sub-ambient pressure. The main flue gas line equipment inducing pressure drop would be as follows [42]:

- The particle removal system (electrostatic precipitator [ESP]).
- The flue gas desulfurization (FGD) unit (if existing).
- The NO_x scrubber (if required) 2–7 mbar [42].
- The bypass stack and damper if installed to bypass the capture unit.
- Flue gas recirculation ducting and/or bypass (if utilized).
- Direct contact cooler, absorber column, and water washes 6–80 mbar [43].
- Absorber duct and stack.

In general, a fan will be required to overcome those pressure drops, whose size will depend on the volumetric flow and pressure drop. In combined cycle thermal power plants, most of the pressure drop might be overcome by raising the back pressure of the gas turbine. However, in boilers, the pressure drop is generally overcome by one or more fans [43].

The extraction of steam from the power plant steam turbine could cover the requirements in the capture system. This strategy will reduce the power output at a lower degree than the amount of heat extracted because the exergy content of the steam is just a fraction of the heat [41]. When the extracted steam is superheated (typically at higher steam pressure), it is normally cooled down by high-pressure water injection. The heat content of the steam can be fully utilized or part of it is returned via the condensate recirculation to the power plant. The steam extraction design depends on the specific configuration and power plant unit, level of process integration, and steam requirement in the reboiler (also function of the solvent characteristics), which has been extensively discussed in the literature [44–46].

In order to compensate for the efficiency reduction in power generation introduced by the CO₂ capture and conditioning processes, several studies have been conducted to increase the efficiency of the integrated process. Increasing process integration within the capture unit itself might lead to reduced specific reboiler duty, for example, by using lean vapor recompression, absorber intercooling, or solvent split flow to stripper [41, 47]. In addition, studies have shown the potential to reduce the specific reboiler duty by using a technique called exhaust gas recirculation (EGR), which consists of recirculating part of the CO₂-rich stream to increase the partial pressure of the exhaust [48] using supplementary firing to increase the partial pressure of CO₂ [49] and/or even integrating part of the reboiler duty in the power plant [50]. These options can lead to lower capital and operational costs at the expense of higher integration between the power plant and the capture unit under operation.

1.3.2 Flexible Operation of Thermal Power Plants in Future Energy Systems

Thermal power plant operation is highly coupled to the operation of power systems and power markets. Flexible operation of thermal power plants has become an important issue in the past decades because the increased integration of renewables CCS must operate accordingly (e.g. [51]). In decarbonized power systems, thermal power plants must be operated in cycling mode in order to cope with variability in demand and generation [52, 53], following the main patterns:

- *Efficiency at part load:* In power systems with high penetration of renewables, it is expected that thermal power plants will be operated during a significant number of hours at part load [52, 54, 55]. However, at part load, the efficiency of thermal power generation is generally reduced and specific emissions at minimum compliant load increase. Thermal power plant developers are striving to reduce minimum compliant load level (to minimize economic losses at times when marginal costs of operation are higher than electricity prices) and increase part load efficiency. Design and operation should take into consideration the part load performance of thermal power plants with CCS. An important aspect is to keep minimum specific reboiler duty and an economically suitable capture rate in the capture unit over the whole load range [43, 44, 56, 57].
- *More frequent changes in load:* Faster ramping can be valuable for thermal power plants in order to be more competitive in day-ahead power markets and balancing markets [54, 55] and the different time scales required for ramping the power plant load and the capture plant will be the key. Generally, thermal power plant load change is characterized by stabilization times in the order of 5–10 minutes, while the capture unit can take up to several hours [54] to stabilize under load changes because of the inertia of the chemical process [58–60]. Efforts are being made to develop operational and control strategies to improve the stabilization time and reduce the specific reboiler duty under transient conditions [57, 61–63].
- *More frequent start-up and shutdown events:* The start-up and shutdown increase CO₂ emissions during start-up and fuel utilization without any significant power output from the power plant. Efforts are being made in order to reduce the start-up time to provide power on demand and/or reduce emissions during start-up [64]. Because the start-up of amine-based post combustion CO₂ capture is time and energy intensive, minimizing the start-up time and emissions during the start-up sequence might be relevant.

Several operational strategies are proposed to operate thermal power plants with CCS in flexible operation mode, being the main purpose to change the power output of the power plant by changing the operational conditions of the integrated process. The main goal from the power operator perspective is to maximize the profits, while from the power system operator perspective, the power plant would be providing variation management to the power system to accommodate the variability of renewables. In addition, flexible operation of post-combustion capture might be required when integrated within industrial processes because of the inherent variability of the

industrial process operations, such as in primary steelmaking [65]. The main strategies proposed for power plants with a carbon capture system can be summarized as follows:

- Allowing the thermal power plant to follow load changes. The capture unit follows the power plant load change [58, 59].
- Varying the CO₂ capture rate, depending on CO₂ costs and electricity prices [51]. In such case, the solvent regeneration is variable, using the large amount of loading capacity and large inventories of solvent as CO₂ storage [66]. At times with high electricity prices, the steam is used for power production, while the regeneration takes place at low electricity prices.
- Turning on-and-off the capture unit or flue gas bypass. The flue gases sent to the capture unit are bypassed to the stack of the power plant so that partial or no CO₂ is being captured. Part of the flue gas is vented to the atmosphere. This allows part of the steam used for solvent regeneration to be used for power production in the steam turbine. This option might be viable in scenarios in which CO₂ emission costs or prices are low.
- Providing solvent storage to decouple plant operation from the capture unit. The capture rate is kept constant and the solvent is stored in tanks. The regeneration energy is shifted to times when electricity prices are low. Solvent storage can incur in significant capital expenditure required for solvent storage, which could be favorable in scenarios with high CO₂ emission costs.

1.4 CO₂ Capture in the Industrial Sector

The industrial sector was responsible for almost 25% of the CO₂ emissions in 2014. CO₂ is emitted on the fuel combustion, intrinsic reactions and indirectly on the use of electricity. IEA predicted a required reduction on the CO₂ emissions of 3–6 Gt/yr to achieve the 2 degrees scenario (2DS) or B2DS. Although other measures such as increasing energy efficiency, developing new production process, using renewable energy or fuel switching, will reduce CO₂ emissions, still there is a significant amount of CO₂ from the process that can be only reduced through CO₂ capture [20]. To achieve the B2DS, the contribution of CCS is estimated as 23%.

All the available CO₂ capture technologies can be potentially installed in industrial facilities. However, while certain industries would have similar or even more favorable characteristics for the implementation of carbon capture utilisation and storage (CCUS) compared to power plants, the design of CO₂ capture systems must be tailored for each facility. The heat and energy integration will be site specific and, together with the composition and CO₂ emission stacks, will impact on the optimum capture rate and the CO₂ avoidance cost.

An exhaustive description of the integration of certain CO₂ capture technologies in the cement sector can be found, for example, in Refs. [67, 68]. A large scale chemical absorption system will be installed in the Norcem Brevik facility, after other

technologies (solid sorbents and membranes) were tested at smaller scale [6]. Oxy-fuel has been included in the Front End Engineering Design (FEED) studies within the European climate research alliance (ECRA) project and the LEILAC project will test the Calix technology (direct separation) [7]. Other technologies, such as chilled ammonia, membrane-based capture combined with liquefaction, and calcium looping were studied, for example, in the CEMCAP project at modeling scale [69]. Moreover, partial capture configurations for several industries are being studied by the CO2STCAP project [70] and the CLEANKER project will scale up the calcium looping up to a TRL of 7⁶.

The peculiarity of the steelmaking sector is the heterogeneity of production processes that will be more or less dependent on the electricity grid. At large scale, the most significant project is the Al Reyadah in Abu Dhabi, where CO₂ is captured in the steam methane reforming (SMR) for H₂ production to be used in a direct reduction iron (DRI) process. A recent cost review identified promising CO₂ capture solutions for this sector, perhaps at lower TRL and potentially with less accurate cost figures [71]. Other projects are advancing on CO₂ capture technologies applied to the steelmaking sector. For example, the C4U project will test high-temperature solid sorbents, aiming to reach a TRL of 7 once the demonstration facility is fully operational. Additionally, the STEPWISE project will advance on the testing of the sorption-enhanced water gas shift technology, reaching a TRL of 7 once it operates successfully, while the 3D project will test an advanced solvent in a steel mill⁷.

Other sectors such as refining, hydrogen, natural gas, heavy oil, fertilizer productions, and waste-to-energy are important and are being considered for further study, for example, by the CSLF.

1.5 Conclusions

In this chapter, the main CO₂ capture systems applied to the industrial and power sectors have been described, covering a wide range of TRLs. Chemical absorption as post-combustion arrangement was further discussed, including advanced process configurations and its integration in the power plant and electricity grid.

Based on the information from the literature, Figure 1.12 aims to provide an overview of the current TRLs of the different CO₂ capture technologies applied to the power and industrial sectors. Note that differences on the TRL definitions from different sources can impact on the TRL assessment. Additionally, several systems can vary and it would be reflected in their TRL. For example, chemical absorption systems have reached their maximum TRL when commercial solvents are used. However, emerging solvents might be at a much lower TRL. Similar limitations of those estimations can be seen, for example, in the use of different absorbents, different types of membranes or using novel O₂ separation process for oxyfuel. Moreover, in the case of the industrial sector, the TRL is also dependent on the industry. For example, while a system has been tested within a cement production facility, it might not have been used in the iron and steel production environment.

⁶ (www.cleanker.eu).

⁷ <https://3d-ccus.com/>

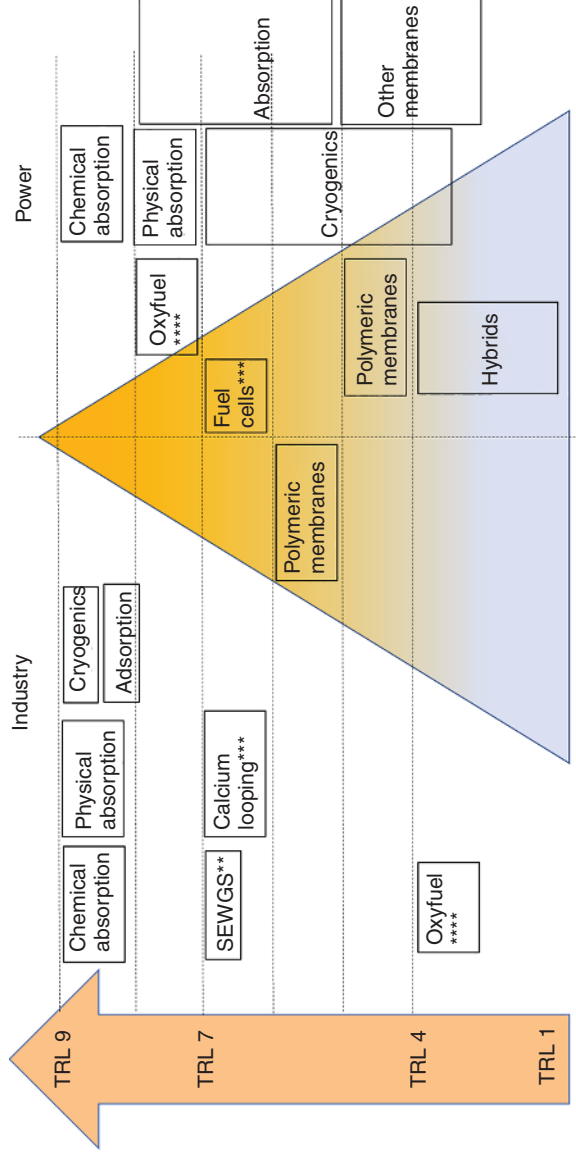


Figure 1.12 Review of current TRL of different CO₂ capture technologies. *The prediction of the TRL of fuel cells is based on the project implemented in Alabama by ExxonMobil and Fuel Cell Energy partnership using MCFC. **SEWGS = Sorption-enhanced water gas shift. This prediction is based on the expected outcome of the STEPWISE project. ***The prediction of the calcium looping technology on the industrial sector is based on the expected outcome of the CLEANER project. ****Oxyfuel is considered here as the combustion with almost pure oxygen. Other configurations of, for example, chemical looping, cryogenics, membranes (oxygen separation), among others, can be considered as part of the oxy-combustion technologies.

In addition, in some industries, there could be a wide range of production processes, which impact on the CO₂ emitted and composition of the flue gas, and will be considered when assessing the TRL at the relevant environment.

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