An overview of current status of carbon dioxide capture and storage technologies

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\textbf{A B S T R A C T}

Global warming and climate change concerns have triggered global efforts to reduce the concentration of atmospheric carbon dioxide (CO\textsubscript{2}). Carbon dioxide capture and storage (CCS) is considered a crucial strategy for meeting CO\textsubscript{2} emission reduction targets. In this paper, various aspects of CCS are reviewed and discussed including the state of the art technologies for CO\textsubscript{2} capture, separation, transport, storage, leakage, monitoring, and life cycle analysis. The selection of specific CO\textsubscript{2} capture technology heavily depends on the type of CO\textsubscript{2} generating plant and fuel used. Among those CO\textsubscript{2} separation processes, absorption is the most mature and commonly adopted due to its higher efficiency and lower cost. Pipeline is considered to be the most viable solution for large volume of CO\textsubscript{2} transport. Among those geological formations for CO\textsubscript{2} storage, enhanced oil recovery is mature and has been practiced for many years but its economical viability for anthropogenic sources needs to be demonstrated. There are growing interests in CO\textsubscript{2} storage in saline aquifers due to their enormous potential storage capacity and several projects are in the pipeline for demonstration of its viability. There are multiple hurdles to CCS deployment including the absence of a clear business case for CCS investment and the absence of robust economic incentives to support the additional high capital and operating costs of the whole CCS process.

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1364-0321/\textcopyright 2014 Published by Elsevier Ltd.
1. Introduction

Rapid economic growth has contributed to today’s ever increasing demand for energy. An obvious consequence of this is an increase in the use of fuels, particularly conventional fossil fuels (i.e. coal, oil and natural gas) that have become key energy sources since the industrial revolution. However, the abundant use of fossil fuels has become a cause of concern due to their adverse effects on the environment, particularly related to the emission of carbon dioxide (CO₂), a major anthropogenic greenhouse gas (GHG). According to the Emission Database for Global Atmospheric Research [1], global emission of CO₂ was 33.4 billion tonnes in 2011, which is 48% more than that of two decades ago. Over the past century, atmospheric CO₂ level has increased more than 39%, from 280 ppm during pre-industrial time [2] to the record high level of 400 ppm in May 2013 with a corresponding increase in global surface temperature of about 0.8°C [3]. Without climate change mitigation policies it is estimated that global GHG emission in 2030 will increase by 25–90% over the year 2000 level, with CO₂-equivalent concentrations in the atmosphere growing to as much as 600–1550 ppm [4].

The Intergovernmental Panel on Climate Change (IPCC) 5th Assessment Report (AR5) issued in 2013–14 confirmed the 4th Assessment Report’s assertion that global warming of our climate system is unequivocal and is associated with the observed increase in anthropogenic greenhouse gas concentrations [2,5]. Furthermore, it is mentioned that 1983–2012 was likely the warmest 30 years period of the last 1400 years in Northern Hemisphere. The same IPCC report (AR5) indicates that to avoid the worst effects of climate change occurring, it is necessary to keep the temperature rise less than 2°C relative to preindustrial levels and that CO₂ emissions should be reduced globally by 41–72% by 2050 and by 78–118% by 2100 with respect to 2010 levels [5]. Although there was not any binding agreement on CO₂ emission control in the last United Nations Climate Change Conference (COP19) held in November 2013 in Warsaw, Poland, participating countries unanimously looked forward a green economy leading to sustainable development. The IPCC has conducted a comprehensive review on various CCS technologies providing a valuable reference for researchers and policy makers in developing their GHG emission reduction program [6]. However, most of the information can be dated back to 2005 or before and there are a lot of changes since then. Moreover, reviews in literature only account for separate aspects of the CCS technology chain, with a focus on either capture, transport, storage or environmental impact [7–13]. The purpose of this paper is to provide a holistic review on the state of the art of CCS technologies and various relevant aspects, including CO₂ capture (Section 3), separation (Section 4), transport (Section 5), utilization (Section 6), storage (Section 7), life cycle GHG assessment (Section 8), and leakage and monitoring (Section 9). An updated status and outlook for CCS projects together with a discussion on the barriers for commercial deployment (Section 10) will also be provided.

2. Approaches to mitigate global climate change

Different approaches are considered and adopted by various countries to reduce their CO₂ emissions, including

- improve energy efficiency and promote energy conservation;
- increase usage of low carbon fuels, including natural gas, hydrogen or nuclear power;
- deploy renewable energy, such as solar, wind, hydropower and bioenergy;
- apply geoengineering approaches, e.g. afforestation and reforestation; and
- CO₂ capture and storage (CCS).

Table 1 compares the application areas, advantages and limitations of these different approaches. Some of these approaches deal with source emissions reduction, such as adopting clean fuels, clean coal technologies, while others adopt demand-side management, i.e. energy conservation. Each approach has intrinsic advantages and limitations that will condition its applicability. It is unlikely that adopting a single approach or strategy can adequately meet the IPCC goal of CO₂ reduction, i.e. 50–85% by 2050 from 2000 levels, and therefore, a complimentary portfolio of CO₂ emission reduction strategies needs to be developed. Amongst the different approaches, CCS can reduce CO₂ emissions (typically 85–90%) from large point emission sources, such as power production utilities, and energy intensive emitters, e.g. cement kiln plants. In this approach, CO₂ is first captured from the flue/fuel gases, separated from the sorbent, transported and then either stored permanently or reutilized industrially.

CCS includes a portfolio of technologies, involving different processes for CO₂ capture, separation, transport, storage and monitoring that are separately discussed in the following sections.

3. CO₂ capture technologies

CO₂ is formed during combustion and the type of combustion process directly affects the choice of an appropriate CO₂ removal process. CO₂ capture technologies are available in the market but are costly in general, and contribute to around 70–80% of the total cost of a full CCS system including capture, transport and storage [14]. Therefore, significant R&D efforts are focused on the reduction of operating costs and energy penalty. There are three main CO₂ capture systems associated with different combustion processes, namely, post-combustion, pre-combustion and oxyfuel combustion. These three technologies are shown in Fig. 1 and discussed in the following sections.

3.1. Post-combustion

This process removes CO₂ from the flue gas after combustion has taken place. Post-combustion technologies are the preferred
option for retrofitting existing power plants. The technology has been proven at small-scale with CO2 recovered at rates up to 800 t/day [15]. However, the major challenge for post-combustion CO2 capture is its large parasitic load. Since the CO2 level in combustion flue gas is normally quite low (i.e. 7–14% for coal-fired and as low as 4% for gas-fired), the energy penalty and associated costs for the capture unit to reach the concentration of CO2 (above 95.5%) needed for transport and storage are elevated [16–18]. The U.S. National Energy Technology Laboratory estimated that CO2 post-combustion capture would increase the cost of electricity production by 70% [19]. A recent study reported that the cost of electricity would increase by 32% and 65% for post-combustion in gas and coal-fired plants, respectively [20]. It has been identified that 16 large scale integrated CCS projects are currently operating or under construction but two of them are of post-combustion technology [21].

### Table 1
Summary of CO2 reduction strategies.

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Application area/sector</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhance energy efficiency and energy conservation</td>
<td>Applied mainly in commercial and industrial buildings.</td>
<td>Energy saving from 10% to 20% easily achievable.</td>
<td>May involve extensive capital investment for installation of energy saving device.</td>
</tr>
<tr>
<td>Increase usage of clean fuels</td>
<td>Substitution of coal by natural gas for power generation.</td>
<td>Natural gas emits 40–50% less CO2 than coal due to its lower carbon content and higher combustion efficiency; cleaner exhaust gas (lower particulates and sulfur dioxide emissions).</td>
<td>Higher fuel cost for conventional natural gas. Comparable cost for shale gas.</td>
</tr>
<tr>
<td>Adopt clean coal technologies</td>
<td>Integrated gasification combined cycle (IGCC), pressurized fluidized bed combustor (PFBC) etc. to replace conventional combustion.</td>
<td>Allow the use of coal with lower emissions of air pollutants.</td>
<td>Significant investment needed to roll out technologies widely.</td>
</tr>
<tr>
<td>Use of renewable energy</td>
<td>Hydro, solar (thermal), wind power, and biofuels highly developed.</td>
<td>Use of local natural resources; no or low greenhouse and toxic gas emissions.</td>
<td>Applicability may depend on local resources availability and cost. Power from solar, wind, marine etc. are intermittent and associated technologies are not mature; most current renewable energies are more costly than conventional energy.</td>
</tr>
<tr>
<td>Development of nuclear power</td>
<td>Nuclear fission adopted mainly in US, France, Japan, Russia and China. Nuclear fusion still in research and development phase.</td>
<td>No air pollutant and greenhouse gas emissions.</td>
<td>Usage is controversial; development of world's nuclear power is hindered due to the Fukushima Nuclear Accident in 2011, e.g. Germany will phase out all its nuclear power by 2022.</td>
</tr>
<tr>
<td>Afforestation and reforestation</td>
<td>Applicable to all countries.</td>
<td>Simple approach to create natural and sustainable CO2 sinks. It can reduce vast amount of CO2 with capture efficiency &gt; 80%.</td>
<td>CCS full chain technologies not proven at full commercial scale.</td>
</tr>
<tr>
<td>Carbon capture and storage</td>
<td>Applicable to large CO2 point emission sources.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 1. CO2 capture technologies.](image-url)
3.2. Pre-combustion

In this process, the fuel (normally coal or natural gas) is pre-treated before combustion. For coal, the pretreatment involves a gasification process conducted in a gasifier under low oxygen level forming a syngas which consists mainly of CO and H₂ and is mainly free from other pollutant gases (Eq. 1). The syngas will then undergo water gas shift reaction with steam forming more H₂ while the CO gas will be converted to CO₂ (Eq. 2):

\[
\text{Coal} \xrightarrow{\text{gasification}} \text{CO} + \text{H}_2
\]  

(1)

\[
\text{CO} + \text{H}_2 \text{O} \xrightarrow{\text{water--gas shift}} \text{H}_2 + \text{CO}_2
\]  

(2)

\[
\text{CH}_4 + \text{H}_2 \text{O} \xrightarrow{\text{reform}} \text{CO} + \text{H}_2
\]  

(3)

The high CO₂ concentration ( > 20%) in the H₂/CO₂ fuel gas mixture facilitates the CO₂ separation [18], and typical CO₂ separation methods are discussed in Section 4. Subsequently, the H₂ is burned in air producing mainly N₂ and water vapor. Pre-combustion capture can be applied to Integrated Gasification Combined Cycle (IGCC) power plants using coal as fuel, but this will incur an efficiency loss of 7–8% [15,22]. EPRI and US DOE have developed a roadmap of IGCC technology developments that can potentially improve the IGCC efficiency matching or exceeding the current IGCC technology without capture [22].

Natural gas, as it mainly contains CH₄, can be reformed to syngas containing H₂ and CO (Eq. (3)). The content of H₂ can be increased by the water gas shift reaction (Eq. (2)) and the rest of the process is similar to that described above for coal [23]. Hoffmann et al. [24] conducted a performance and cost analysis on advanced combined cycle gas turbine plants operated by natural gas with a pre-combustion CO₂ capture system and obtained a CO₂ capture efficiency of 80% with the cost of CO₂ avoided reaching $29/t CO₂ for an advanced design concept.

3.3. Oxyfuel combustion

In oxyfuel combustion, oxygen, instead of air, is used for combustion. This reduces the amount of nitrogen present in the exhaust gas that affects the subsequent separation process. Substantial reduction in thermal NOₓ is another advantage of this process [25]. With the use of pure oxygen for the combustion, the major composition of the flue gases is CO₂, water, particulates and SO₂. Particulates and SO₂ can be removed by conventional electrostatic precipitator and flue gas desulfurization methods, respectively. The remaining gases, contain high concentration of CO₂ (80–98% depending on fuel used [26]), can be compressed, transported and stored. This process is technically feasible [25] but consumes large amounts of oxygen coming from an energy intensive air separation unit [27]. This results in high cost and the energy penalty may reach over 7% compared with a plant without CCS [28,29]. Also, high SO₂ concentration in the flue gas may intensify the system's corrosion problems. At present, there is no full scale oxyfuel-fired projects in the range of 1000–2000 MWth under development but a few sub-scale commercial demonstration plants are under development worldwide such as the 25 MWe and 250 MWe oxy-coal units proposed by CS Energy and Vattenfall, respectively [29].

3.4. Comparison of different combustion technologies for CO₂ capture

Table 2 compares the three CO₂ capture technologies described above. Pre-combustion is mainly applied to coal-gasification plants, while post-combustion and oxyfuel combustion can be applied to both coal and gas fired plants. Post-combustion technology is currently the most mature process for CO₂ capture [26,30]. On the cost side, Gibbins and Chalmers [31] compared the three technologies for both gas and coal-fired plants (Table 3). They reported that for coal-fired plants the pre-combustion technology presented the lowest cost per tonne of CO₂ avoided, while the post-combustion and oxyfuel technologies are of similar costs. However, for gas-fired plants, the cost per tonne of CO₂...
avoided for the post-combustion capture was almost 50% lower than the other two capture technologies. Moreover, the post-combustion CO₂ capture is normally the least efficient option, with an energy penalty of about 8% and 6% for the coal-fired and gas-fired plants, respectively [32).

4. CO₂ separation technologies

This section describes the main CO₂ separation technologies that can be applied to isolate the CO₂ from the flue/fuel gas stream prior to transportation. Advanced technologies, such as wet scrubber, dry regenerable sorbents, membranes, cryogenics, pressure and temperature swing adsorption, and other advanced concepts have been developed. These technologies are compared in Table 4 and discussed below.

4.1. Absorption

A liquid sorbent is used to separate the CO₂ from the flue gas. The sorbent can be regenerated through a stripping or regenerative process by heating and/or depressurization. This process is the most mature method for CO₂ separation [30]. Typical sorbents include monoethanolamine (MEA), diethanolamine (DEA) and potassium carbonate [33]. Among the various aqueous amines, such as MEA and DEA, Veawab et al. [34] found that MEA is the most efficient one for CO₂ absorption with efficiency over 90%. Subsequently, Aaron et al. [35] conducted a review on various CO₂ capture technologies and concluded that the most promising method for CO₂ capture for CCS is absorption using MEA. An absorption pilot plant with 1 t CO₂/h was constructed and successfully tested together with the post-combustion capture technology for a coal-fired power plant using a solvent containing 30% MEA [36]. Some other sorbents, such as piperazine and anion-functionalized ionic liquid have also received attention in recent years [37]. Piperazine has been found to react much faster than MEA, but because it has a larger volatility of concentration. Environmental impacts related to sorbent regeneration are required. Environmental impacts related to sorbent degradation have to be understood.

### Table 3
Cost comparison for different capture processes [211]. Costs include CO₂ compression to 110 bar but excluding storage and transportation costs.

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Parameter</th>
<th>Capture technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>No capture</td>
<td>Post-combustion</td>
<td>Pre-combustion</td>
</tr>
<tr>
<td>Coal-fired</td>
<td>Thermal efficiency (% LHV)</td>
<td>44.0</td>
</tr>
<tr>
<td>Capital cost ($/kW)</td>
<td>1410</td>
<td>1980</td>
</tr>
<tr>
<td>Electricity cost ($/kWh)</td>
<td>5.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Cost of CO₂ avoided ($/t CO₂)</td>
<td>–</td>
<td>34</td>
</tr>
<tr>
<td>Gas-fired</td>
<td>Thermal efficiency (% LHV)</td>
<td>55.6</td>
</tr>
<tr>
<td>Capital cost ($/kW)</td>
<td>500</td>
<td>870</td>
</tr>
<tr>
<td>Electricity cost ($/kWh)</td>
<td>6.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Cost of CO₂ avoided ($/t CO₂)</td>
<td>–</td>
<td>58</td>
</tr>
</tbody>
</table>

### Table 4
Comparison of different separation technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>– High absorption efficiency (&gt; 90%).</td>
<td>– Absorption efficiency depends on CO₂ concentration.</td>
<td>[30,33,35]</td>
</tr>
<tr>
<td>Adsorption</td>
<td>– Process is reversible and the absorbent can be recycled.</td>
<td>– Require high temperature absorbent.</td>
<td>[43–45,212]</td>
</tr>
<tr>
<td>Chemical looping combustion</td>
<td>– CO₂ is the main combustion product, which remains unmixed with N₂, thus avoiding energy intensive air separation.</td>
<td>– Process is still under development and there is no large scale operation experience.</td>
<td>[58–60]</td>
</tr>
<tr>
<td>Membrane separation</td>
<td>– Process has been adopted for separation of other gases.</td>
<td>– Operational problems include low fluxes and fouling.</td>
<td>[35,61,63,213]</td>
</tr>
<tr>
<td>Hydrate-based separation</td>
<td>– Small energy penalty.</td>
<td>– New technology and more research and development is required.</td>
<td>[13,19,67,68]</td>
</tr>
<tr>
<td>Cryogenic distillation</td>
<td>– Mature technology.</td>
<td>– Only viable for very high CO₂ concentration (&gt; 90% v/v).</td>
<td>[72,74]</td>
</tr>
</tbody>
</table>
less problem as compared to those that amine is facing with degradation.

4.2. Adsorption

In contrast to absorption processes where use a liquid absorbent, a solid sorbent is used to bind the CO2 on its surfaces. Large specific surface area, high selectivity and high regeneration ability are the main criteria for sorbent selection. Typical sorbents include molecular sieves, activated carbon, zeolites, calcium oxides, hydroxides and lithium zirconate.

The adsorbed CO2 can be recovered by swinging the pressure (PSA) or temperature (TSA) of the system. Atmosphere containing the CO2-saturated sorbent. PSA is a commercial available technology for CO2 recovery from power plants that can have efficiency higher than 85% [43,44]. In this process, CO2 is preferentially adsorbed on the surface of a solid adsorbent at high pressure, which will swing to low pressure (usually atmospheric pressure) to desorb the adsorbent and release CO2 for subsequent transport. In TSA, the adsorbed CO2 will be released by increasing the system temperature using hot air or steam injection. The regeneration time is normally longer than PSA but CO2 purity higher than 95% and recovery higher than 80% can be achieved [45]. Operating cost of a specific TSA process was estimated to be of the order of 80–150 US $/tonne CO2 captured [46]. Finally, the use of residues from industrial and agricultural operations to develop sorbents for CO2 capture has attracted significant attention to reduce the total costs of capture [47–50].

4.3. Chemical looping combustion

A metal oxide is used as an oxygen carrier instead of using pure oxygen directly for the combustion as in the case of oxyfuel combustion. During the process the metal oxide is reduced to metal while the fuel is being oxidized to CO2 and water. The metal is then oxidized in another stage and recycled in the process. Water, the process by-product, can be easily removed by condensation, while pure CO2 can be obtained without consumption of energy for separation. There are a wide variety of metal oxides that are of low-cost and suitable for this process including Fe2O3, NiO, CuO and Mn2O3. The effectiveness of different metal oxides in this process has been studied by various researchers [51–56]. Adánez et al. [54] found that support inert materials can be used to optimize the performance of the metal oxides, but the choice of inert material will depend on the type of metal oxide used. Lyngfelt et al. [57] studied experimentally the feasibility of chemical looping in a boiler with a design of two interconnected fluidized beds. This technology has been reviewed recently by Lyngfelt and Mattisson [58]. Both Lyngfelt and Mattisson [58] and Adanez et al. [59] found that this process is a very promising technology for CO2 capture. Erlich et al. [60] compared the CO2 separation of IGCC using pre-combustion with that of chemical looping combustion and found that the net plant efficiency of the latter is 2.8% higher than the former case.

4.4. Membrane separation

Membranes can be used to allow only CO2 to pass through, while excluding other components of the flue gas. The most important part of this process is the membrane which is made of a composite polymer of which a thin selective layer is bonded to a thicker, non-selective and low-cost layer that provides mechanical support to the membrane [61]. This method has also been used to separate other gases such as O2 from N2, and CO2 from natural gas. Through the development of high efficient membranes, Audus [62] and Gielin [63] achieved a CO2 separation efficiency from 82% to 88%. The development of ceramic and metallic membranes [35] and polymeric membranes [64] for membrane diffusion could produce membranes significantly more efficient for CO2 separation than liquid absorption processes. Brunetti et al. [65] conducted a general review on current CO2 separation technology using membranes and compared with other separation technologies such as adsorption and cryogenic. It pointed out that the performance of a membrane system is strongly affected by the flue gas conditions such as low CO2 concentration and pressure, which are the main hurdles for applying this technology. Furthermore, Bernardo et al. [66] revealed that although there are significant developments in gas separation membrane systems, they are still far away to realize the potentialities of this technology.

4.5. Hydrate-based separation

Hydrate-based CO2 separation is a new technology by which the exhaust gas containing CO2 is exposed to water under high pressure forming hydrates. The CO2 in the exhaust gas is selectively engaged in the cages of hydrate and is separated from other gases. The mechanism is based on the differences of phase equilibrium of CO2 with other gases, where CO2 can form hydrates easier than other gases such as N2 [67].

This technology has the advantage of small energy penalty (6–8%) [19] and the energy consumption of CO2 capture via hydrate could be as low as 0.57 kWh/kg-CO2 [67]. Improving the hydrate formation rate and reducing hydrate pressure can improve the CO2 capture efficiency [67]. Tetrahydrofuran (THF) is a water-miscible solvent, which can form solid clathrate hydrate structures with water at low temperatures. So the presence of THF facilitates the formation of hydrate and is frequently used as a thermodynamic promoter for hydrate formation. Englezos et al. [68] found that the presence of small amount of THF substantially reduces the hydrate formation pressure from a flue gas mixture (CO2/N2) and offers the possibility to capture CO2 at medium pressures. Recently, Zhang et al. [69] studied the effects and mechanism of the additive mixture on the hydrate phase equilibrium using the isochoric method and confirmed the effect of THF on hydrate formation. US DOE considers this technology to be the most promising long term CO2 separation technology identified today and is currently in the R&D phase [19,70,71].

4.6. Cryogenic distillation

Cryogenic distillation is a gas separation process using distillation at very low temperature and high pressure, which is similar to other conventional distillation processes except that it is used to separate components of gaseous mixture (due to their different boiling points) instead of liquid. For CO2 separation, flue gas containing CO2 is cooled to desublimation temperature (−100 to−135 °C) and then solidified CO2 is separated from other light gases and compressed to a high pressure of 100–200 atmospheric pressure. The amount of CO2 recovered can reach 90–95% of the flue gas. Since the distillation is conducted at extremely low temperature and high pressure, it is an energy intensive process estimated to be 600–660 kWh per tonne of CO2 recovered in liquid form [72]. Several patented processes have been developed and research has mainly focused on cost optimization [73,74]. The evaluation of low temperature processes for producing high purity, high pressure CO2 from oxyfuel combustion flue gas through simulation and modeling in Aspen HYSYS has also been investigated [75].
5. CO₂ transport

Once CO₂ is separated from the rest of the flue gas components it needs to be transported to the storage site or to the facilities for its industrial utilization. Whatever the chosen final fate of CO₂, a reliable, safe and economically feasible system of transport is a key feature of any CCS project. Depending on the volumes involved a variety of means of transport may be utilized, ranging from road tankers to ships and pipelines. A study related to CCS in the North Sea highlights that CO₂ transport by ship tanker, using technologies derived from the LPG carriers, is feasible and cost competitive with pipelines with a total cost ranging from 20 to 30 USD/tonne when more than 2 MtCO₂/year are transported within the distances involved in North Sea storage [76].

Pipelines are considered to be the most viable method for onshore transport of high volume of CO₂ through long distances as CCS would likely involve when widely deployed [77]. Pipelines are also the most efficient way for CO₂ transport when the source of CO₂ is a power plant which lifetime is longer than 23 years. For shorter period road and rail tankers are more competitive [78]. The cost of transport varies considerably with regional economic situation. A cost analysis in China shows that for a mass flow of 4000 t CO₂/day the use of ship tankers will cost 7.48 USD/tonne CO₂ compared with 12.64 USD/tonne CO₂ for railway tankers and 7.05 USD/tonne CO₂ for 300 km pipelines [79].

In order to optimize the mass/volume ratio CO₂ is carried as dense phase either in liquid or supercritical conditions. Supercritical is the preferred state for CO₂ transported by pipelines, which implies that the pipelines operative temperature and pressure should be maintained within the CO₂ supercritical envelop, i.e. above 32.1 °C and 72.9 atm. [80]. The typical range of pressure and temperature for a CO₂ pipeline is between 85 and 150 bar, and between 13 °C and 44 °C to ensure a stable single-phase flow through the pipeline [81]. The drop in pressure due to the reduction of the hydraulic head along the pipeline is compensated by adding recompression stations. Larger diameter pipelines allow lower flow rates with smaller pressure drop and therefore a reduced number of recompression stations; on the other hand larger pipelines are more expensive therefore a balancing of costs needs to be considered [81].

Impurities in the CO₂ stream represent a serious issue because their presence can change the boundaries of the pressure and temperature envelope within which a single-phase flow is stable. Moreover, the presence of water concentration above 50 ppm may lead to the formation of carbonic acid inside the pipeline and cause corrosion problems. Hydrates may also form that may affect the operation of valves and compressors. The estimated values of corrosion on the carbon steel commonly used for pipeline’s construction can be up to 10 mm/year [81,82].

Currently only a few pipelines are used to carry CO₂ and are almost all for EOR projects. The oldest is the Canyon Reef Carriers pipeline, a 225 km pipeline built in 1972 for EOR in Texas (USA). The longest is the 800 km Cortez pipeline which is carrying 20 million tonne/year of CO₂ from a natural source in Colorado to the oil fields in Denver City, Texas since 1983 [81].

CO₂ pipelines are mostly made of carbon steel and composed of insulated 12 m sections with crack arresters every 350 m and block valves every 16–32 km. The onshore pipelines are buried in trenches of about 1 m deep. Offshore pipelines in shallow water also need to be deployed in trenches as protection from fishing and mooring activities. Deep water pipelines generally do not need to be buried unless their diameter is below 400 mm [81,83].

The rate of accidents involving CO₂ pipelines is relatively low with a value of 0.30/year for every 1000 km calculated during the period 1990–2001 considered for an overall pipelines extension of 2800 km [84]. The enlargement of the pipelines network leads to an increase in the number of accidents up to 0.76/year for every 1000 km in 2002–2008 calculated over an overall pipeline length of 5800 km [85]. These values are still well below the ones involving pipelines for gas/oil or other hazardous fluids. However, the current CO₂ pipeline network is far smaller than that for gas/oil transport, and therefore, the statistical significance of these values is somewhat uncertain.

For commercial scale CCS projects an extensive network of CO₂ pipelines needs to be developed. An integrate network, where different sources will merge for their final transport to the storage areas, can reduce the total pipelines length by 25%, but it will require that all sources produce CO₂ stream with the same quality (e.g. pressure, T, water content) before being combined together [82]. When the flow managed through a network of pipelines increases there is an exponential decrease in the cost of transport; models highlight that the cost for transporting CO₂ along a 1000 km pipeline is around 8 USD/tonne for a mass flow of 25 MtCO₂/year with a further reduction down to 5 USD/tonne if the flow increases to 200 MtCO₂/year [86]. Further cost saving may be achieved from the reuse of existing gas pipelines but their suitability is to be verified. One of the biggest uncertainties is the effects on the pipelines’ integrity of long term exposure to CO₂ fluxes in terms of corrosion and potential brittle fractures propagation due to the sharp cooling of the pipelines in case of leak of supercritical CO₂ [87].

The pipelines have to be periodically monitored to assess their integrity and an accurate fiscal metering system is to be in place to assure the quantification of the stored fluxes. The equipment used for gas/oil pipelines need to be modified to withstand the challenging environment experienced inside a CO₂ pipeline. Poor lubrication capacity of CO₂, high chemical reactivity and high pressure may all affect the performance of both monitoring and metering equipment [88].

Other issues could arise from the trans-national transport of CO₂ and offshore storage due to legal aspects. The two key documents are the Convention for the Protection of the Marine Environment of the North East Atlantic (OSPAR Convention) and the London Protocol. These treaties do not allow waste dumping in marine environment and they also limit the cross border transport of pollutants. In 2007 the OSPAR Convention was amended allowing sub-seabed CO₂ storage and entered into force following the needed ratification by seven countries on 23 June 2011. In 2006 an amendment was made to Annex 1 of the London Protocol allowing CO₂ to be injected in sub-seabed geological formations. Being an amendment to an Annex it does not need to be ratified and entered in force on 10 February 2007, 100 days after being proposed as for rules of the London Protocol. A second amendment was proposed in 2009 in order to remove the restriction for cross border transport of CO₂ for geological storage; this is an amendment to the Protocol itself and therefore needs to be ratified by two-thirds of the 42 contracting parties. So far only Norway and the UK have ratified the document [89]. CO₂ transport for EOR is allowed under existing legislation both in USA [85] and Europe [89], but there is no guarantee that the same approach will be maintained for the far larger volumes needed to be transported for large scale CCS operations.

6. CO₂ utilization

After capture, the high CO₂ content stream can be transported for geological storage (see Section 7), or for CO₂ utilization. Kikuchi [90] evaluated the economic and technical aspects of large scale CO₂ recycling and proposed an integrated scheme for CO₂ recovery and reuse in industry, agriculture and energy production. A demonstration plant in Luzhou, China was recently commissioned


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that produces ammonia and urea using the CO₂ captured (160 t/day) from its production process [91]. CO₂ can also be used in other areas such as food beverages, refrigerants and fire extinguishing gases. Current CO₂ utilization accounts for only 2% of emissions, but forecasts predict chemical utilization could mitigate 700 megatons of CO₂ per year, far greater than the combined potential of nuclear, wind and cellulosic biofuel technologies [92]. Enhanced oil recovery (EOR) using CO₂ from capture processes can significantly increase CO₂ utilization [93], and this application is described in Section 7.1. Other related new sectors include the use of CO₂ as a cushion gas for energy storage [94]. CO₂ can be utilized through mineralization, a process based on the accelerated reaction of CO₂ with Mg/Ca rich silicate rocks or inorganic wastes to form stable carbonates which can be used [95]. The unfavorable kinetics of this process is overcome by (i) directly increasing the pressure and/or temperature or (ii) indirectly, by using aggressive leaching agents. Among the indirect routes, the pH swing has received significant attention as it allows the recyclability of the chemicals used during the process separation and recovery of pure products [96–104].

Large scale, economic photocatalytic conversion of CO₂ into methane (CH₄) and/or methanol (CH₃OH) represents a formidable scientific and technical challenge [105]. Recent progress in this area has focused mainly on the development of novel catalysts through advances in nanotechnology [106,107]. Few photocatalytic reactors have been tested for ultraviolet driven CO₂ reduction [108], and these generally operate as batch processes [109], with even more limited solar reactor studies published [110,111], predominantly operated in batch mode and within the context of wastewater treatment and air purification [112].

7. CO₂ geological storage

CO₂ can be stored into geological formations such as deep saline aquifers which have no other practical use, and oil or gas reservoirs. Geological storage is at present considered to be the most viable option for the storage of the large CO₂ quantities needed to effectively reduce global warming and related climate change [113–116]. A typical geological storage site can hold several tens of million tonnes of CO₂ trapped by different physical and chemical mechanisms [117]. Suitable geological sites for CO₂ storage have to be carefully selected. General requirements for geological storage of CO₂ include appropriate porosity, thickness, and permeability of the reservoir rock, a cap rock with good sealing capability, and a stable geological environment [118]. Requirements such as distance from the source of CO₂, effective storage capacity, pathways for potential leakage and in general economic constraints may limit the feasibility of being a storage site. Bachu [119] described the criteria and approaches for selecting suitable geological sites for storing CO₂, including the tectonic setting and geology of the basin, its geothermal regime, hydrology of formation waters, hydrocarbon potential and basin maturity. In addition, economic aspects related to infrastructure and socio-political conditions will also affect the site selection. Furthermore, although techniques for geological storage can be derived from existing processes, mostly enhanced oil recovery (EOR) projects, there is no real experience yet at commercial scale, and the potential long term environmental effects of large amounts of CO₂ stored is also limited.

Three different geological formations are commonly considered for CO₂ storage: depleted (or nearly depleted) oil and gas reservoirs, unmineable coal beds, and saline aquifers. Deep ocean storage is also a feasible option for CO₂ storage although environmental concerns (such as ocean acidification and eutrophication) will likely limit its application. It has been shown that CO₂ storage potential can reach 400–10,000 GT for deep saline aquifers compared with only 920 GT for depleted oil and gas fields and > 15 GT in unmineable coal seams [120]. Different geological settings have different criteria of consideration for their reliability as CO₂ storage areas and these are discussed below.

7.1. Enhanced oil recovery (EOR) in oil and gas reservoirs.

CO₂ can be injected into depleted (or nearly depleted) oil/gas reservoirs to increase their pressure and provide the driving force to extract residual oil and gases, while the injected CO₂ remains stored there permanently. Up to 40% of the residual oil left in an active reservoir can be extracted after primary production [121]. In fact, fluids injection methods have been widely used in the oil and gas extraction industry for decades to enhance the recovery of the residual oil and gases. Therefore, there is an economical incentive for injecting CO₂ (recovered from an associated capture process) into depleted oil and gas reservoirs in order to offset the high CCS cost commonly involved in the process. Technologies for injection of CO₂ for EOR are mature and there are studies on various aspects of EOR, such as migration simulation [122,123], geochemical modeling [124,125], and leakage/risk assessment [126].

Several EOR projects for CO₂ storage are ongoing, as shown in Table 5. The largest one is the Weyburn project that started in 2000 in the Weyburn oil reservoir in Saskatchewan, Canada. Although the aim of the project is not to investigate the potential for CO₂ storage, the reservoir is estimated to be able to store more than 30 million tonnes of CO₂ captured from a gasification plant in North Dakota, USA and transported to the site through a 320 km pipeline. A number of larger EOR projects with much larger storage capacity are planned (such as Hatfield and California DF2) and will be commissioned in the next few years. This will build confidence in operators for the feasibility of larger CO₂ storage demonstration projects.

7.2. Unmineable coal bed storage

CO₂ can be injected into deep coal beds to recover methane which is trapped in the porous structure of coal seams. This process, called CO₂ enhanced coal bed methane (CO₂-ECBM),
allows CO₂ to be stored in the void fraction made available by removal of the trapped methane in the coal seams. Extraction of coal bed methane (CBM) has been adopted in coal seams for many years and there are several commercial CBM extraction sites in the world, mostly in the USA (Table 6). White et al. [127] conducted a very comprehensive review on the CO₂ sequestration in deep unmineable coal beds with recovery of methane gas. Several key issues, such as estimation of potential storage capacity, storage integrity, physical and chemical processes, environmental health and safety, etc., were highlighted in their study.

CO₂ storage in deep unmineable coal bed with simultaneous methane gas recovery has been successfully carried out in several coal bed sites such as that in New Mexico, USA [128] and Alberta, Canada [129]. A list of CO₂-ECBM projects currently conducted or planned worldwide is shown in Table 6. The technology for CO₂-ECBM has additional economic incentives, and there are large coalbed methane resources worldwide, including China, Australia and the USA [130]. However, many of the coal seams (such as those in China and Western Europe) have low permeability that would make this process not applicable [128]. A field pilot test conducted at Yubari in Japan during the period of 2002–2007 indicated that reduction of permeability is one of the main technical issues to be solved in order to make large scale CO₂-ECBM economically viable [131].

### 7.3. Storage in saline aquifers

Deep aquifers at 700–1000 m below ground level often host high salinity formation brines [132]. These saline aquifers have no commercial value but can be used to store injected CO₂ captured from CCS process. Deep saline aquifers can be found in widespread areas both onshore and offshore and are considered to have enormous potential for storage of CO₂ [6]. Despite of the high potential for CO₂ storage, there are comparatively less knowledge about the CO₂ storage features of saline aquifers as compared to other geological sites such as coal seams and oil fields.

Different trapping mechanisms take place in saline aquifers when CO₂ is injected. The main features of these mechanisms are shown in Table 7, and a detailed review was published [133]. Yang et al. [115] conducted a review on the characteristics of CO₂ sequestration in saline aquifers, including CO₂ phase behavior, CO₂-water–rock interaction, and CO₂ trapping mechanisms that include hydrodynamic, residual, solubility and mineral trapping [61,129,134]. The parameters affecting mineral trapping of CO₂ sequestration in brines have been extensively investigated [135–138]. Recently, Szułczewski et al. [139] evaluated how pressure rises during injection and how CO₂ is trapped in the pore space of deep saline aquifers, which help the estimation of the CO₂ storage capacity.

Over the past two decades several pilot and commercial projects for CO₂ storage on saline or deep saline aquifers have been launched. Statoil’s Sleipner project in the North Sea, as part of a commercial natural gas operation, stores around 1 Mt CO₂/year in a deep saline aquifer hosted in the Utsira Sand formation, about 1000 m below the seafloor with an available volume for CO₂ storage in the order of 6.6 × 10⁶ m³ [140–142]. This project started in 1996 and is one of the earliest CCS projects. Other current and approved projects of different scales (i.e. commercial, pilot and demonstration) can be found in Rai et al. [143], Michael et al. [144] and Global CCS Institute [87], and are summarized in Table 8. It can be observed that previous and existing projects are of small CO₂ injection capacity (≤ 1.3 Mt/year) but future projects (such as the Gorgon and the Latrobe Valley projects in Australia) would have much larger CO₂ injection capacity (> 4.5 Mt/year).

White et al. [127] conducted a comprehensive review on the storage of the captured CO₂ in deep saline aquifers and commented that, with the experience gained in several concurrent projects, storage of CO₂ in deep saline aquifers is technically feasible, and can have little or no negative environmental impacts. Michael et al. [144] conducted a similar study based on the experience from existing storage operations and presented similar conclusions as White et al. [127]. These authors also discussed the importance of monitoring and verification, and pointed out that there are limited monitoring programs for existing projects, as well as limited data from post-injection monitoring of CO₂ behavior in the storage reservoir. Nevertheless, the experience gained in these operations helps to establish best practice guidelines for future CO₂ geological storage. More recently, Myer [116] reviewed the global status of geological CO₂ storage and indicated the lack of data on post-injection behavior inside the storage reservoir and the need for more field assessments on the processes that lead to plume stabilization and long term trapping.

### Table 6

List of current and planned CO₂-ECBM projects.

<table>
<thead>
<tr>
<th>Project Name</th>
<th>Location</th>
<th>Year of operation start</th>
<th>Max. CO₂ injection rate Mt/year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>San Juan Basin</td>
<td>New Mexico, USA</td>
<td>1996</td>
<td>0.1</td>
<td>[128,228,229]</td>
</tr>
<tr>
<td>Fenn Big Valley</td>
<td>Alberta, Canada</td>
<td>1998</td>
<td>0.02</td>
<td>[129,230]</td>
</tr>
<tr>
<td>Recopol</td>
<td>Poland</td>
<td>2003</td>
<td>400 t/year</td>
<td>[143]</td>
</tr>
<tr>
<td>Qinshui Basin</td>
<td>China</td>
<td>2003</td>
<td>0.01</td>
<td>[143]</td>
</tr>
<tr>
<td>Yubari</td>
<td>Japan</td>
<td>2004</td>
<td>0.004</td>
<td>[143]</td>
</tr>
<tr>
<td>Permian Basin</td>
<td>Texas, USA</td>
<td>2005</td>
<td>0.3</td>
<td>[219,220,231]</td>
</tr>
<tr>
<td>Farnham Dome/Uinta Basin</td>
<td>Utah, USA</td>
<td>2005</td>
<td>0.9</td>
<td>[216,232]</td>
</tr>
<tr>
<td>Hokkaido</td>
<td>Japan</td>
<td>2015</td>
<td>0.01</td>
<td>[143]</td>
</tr>
</tbody>
</table>

### Table 7

Types and mechanisms of CO₂ trapping in saline aquifers [61,129,134].

<table>
<thead>
<tr>
<th>Trapping mechanism</th>
<th>CO₂ trapping phase</th>
<th>Description of mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodynamic</td>
<td>Supercritical fluid</td>
<td>Undissolved CO₂ is trapped by overlying low-permeability caprock; CO₂ will be gradually dispersed.</td>
</tr>
<tr>
<td>Residual</td>
<td>Gas phase</td>
<td>CO₂ rises through water-saturated rock and displacing water from the pore space; the whole rock volume retains a residual saturation of CO₂.</td>
</tr>
<tr>
<td>Solubility</td>
<td>Dissolved liquid phase</td>
<td>CO₂ is dissolved in the formation brine water; a major trapping mechanism.</td>
</tr>
<tr>
<td>Mineral</td>
<td>Reacted solid phase</td>
<td>Dissolved CO₂ reacts with Ca, Fe, or Mg based mineral to form carbonate precipitates; not subject to leakage.</td>
</tr>
</tbody>
</table>
Deep ocean storage

Oceans cover more than 70% of Earth’s surface and are the biggest natural CO₂ sink. It is estimated that oceans contain about 38,000 Gt of carbon and take up carbon from the atmosphere at a rate of about 1.7 Gt annually. At the same time, oceans produce 50–100 Gt carbon (in the form of phytoplankton) annually, which is greater than the intake by terrestrial vegetation [145]. The carbon inventory in the ocean is enormous at about 50 times greater than that of our atmosphere [61]. At depths greater than 3 km, CO₂ will be liquefied and sunk to the bottom due to its higher density than the surrounding seawater [119,146]. Mathematical models suggest that CO₂ injected in this way could be kept underground for several hundred years [147]. House et al. [146] further showed that injecting CO₂ into deep sea sediments at a depth greater than 3 km can provide permanent geological storage of CO₂ even with large geomechanical perturbations. Therefore, deep ocean storage can present a potential sink for large amounts of anthropogenic CO₂. However, this approach is more controversial than other geological storage methods. Injecting large amounts of CO₂ directly into our oceans may affect the seawater chemistry (such as reducing its pH) causing ocean acidification, which may lead to disastrous consequences to the marine ecosystem [148]. Comparatively fewer studies have been conducted in this area, particularly on its effect on the marine ecosystem. Hall-Spencer et al. [149] studied the effect of ocean acidification on an ecosystem near volcanic CO₂ vents and concluded that ocean acidification will probably reduce the biodiversity and alter profoundly the ecosystems. Rodolfo-Metalpa et al. [150] also agreed that the ocean ecosystems’ resistance to acidification could be worsened by higher temperatures due to global warming. Espa et al. [151] and Caramanna et al. [152] carried out field studies in a volcanic island Panarea in Italy and laboratory investigations to examine the bubbles plumes effect due to sub-seabed CO₂ leakage. They found the development of a pseudo-convective cell around the rising plume forming vortices that act as a physical barrier inhibiting the interaction between the plume and the surrounding water. Moreover, the depth of the thermocline plays an important role in the diffusion of the CO₂ seepage through the overlying water column. This finding can be a useful guide for future studies on the acidification of surrounding water due to shallow water CO₂ leakage.

Although the IPCC has recognized the potential of ocean CO₂ storage, it also noted its local risks that may arise as mentioned above [6]. With the above ecological and environmental concerns, more studies in this area need to be conducted to establish its feasibility and long term effect on marine ecosystem before it can be fully implemented.

In-situ carbonation

Injected CO₂ reacts with the surrounding host rock and, in the presence of specific minerals, may generate carbonates [153]. This process may occur within mafic and ultramafic rocks such as basalts and Ophiolite suites [154]. Basalts are the most widely diffused rocks on the planet covering large areas of the continents and the oceans seafloor. Their potential for CO₂ storage is therefore very high even if technical issues and a limited knowledge of their stratigraphic setting at the level of details required for identifying the injection areas and their effective reactivity with CO₂ still limit their use [155,156].

Life cycle GHG assessment

The principal aim of CCS technologies is to reduce the CO₂ emissions from anthropogenic sources to the atmosphere. Most of the processes associated with CCS described in the previous sections would require the construction of infrastructure and installation of facilities (such as scrubbers, compressors and pipelines), additional use of chemicals (such as amine, hydroxide or zirconate), solid waste and wastewater disposal, etc. Energy would also be required for manufacturing, transporting, installing and operating of these facilities, and for producing chemicals, and thus, resulting in CO₂ emissions. Therefore, it is necessary to carry out a life cycle analysis (LCA) on GHG to determine whether or not a particular CCS technology can result in a net reduction in CO₂. This analysis is important, particularly for formulation of relevant CCS policy of a country. The Directive 2009/31/EC and the associated Guidance Document 1 is an example of how Europe is assessing the CO₂ Storage Life Cycle Risk Management [157].

Several LCA studies have been conducted regarding CCS, but mainly on coal-fired power plants and only including the capture unit [158–161]. Pehnt and Henkel [160] found that while there is an increase in cumulative energy demand for CCS, a substantial decrease in GHG emission is found for all the existing CO₂ capture approaches (i.e. post-combustion, pre-combustion, oxyfuel), as well as transport and storage in a depleted gas field. Odeh and Cockerill [159] conducted a LCA on the GHG emission of three types of fossil fuel power plants with and without CCS. They found that with a 90% CO₂ capture efficiency, life cycle GHG emissions are reduced by 75–84%. They also concluded that the global

### Table 8
Current and planned projects of CO₂ storage in saline aquifers.

<table>
<thead>
<tr>
<th>Project name</th>
<th>Location</th>
<th>Scale*</th>
<th>Year of injection start</th>
<th>Max. CO₂ injection rate Mt/year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alberta Basin</td>
<td>Alberta &amp; B.C. Canada</td>
<td>C</td>
<td>1990</td>
<td>0.1</td>
<td>[233,234]</td>
</tr>
<tr>
<td>Sleipner</td>
<td>North sea, Norway</td>
<td>D</td>
<td>1996</td>
<td>1.0</td>
<td>[184,235,236]</td>
</tr>
<tr>
<td>Frio</td>
<td>USA</td>
<td>P</td>
<td>2004</td>
<td>1.3</td>
<td>[143]</td>
</tr>
<tr>
<td>In Salah</td>
<td>Krechtiba, Algeria</td>
<td>D</td>
<td>2004</td>
<td>1.3</td>
<td>[237]</td>
</tr>
<tr>
<td>Snelfwit</td>
<td>Barents Sea, Norway</td>
<td>D</td>
<td>2008</td>
<td>0.7</td>
<td>[238,239]</td>
</tr>
<tr>
<td>MRCP- Michigan Basin</td>
<td>Gaylord, MT, USA</td>
<td>P</td>
<td>2008</td>
<td>0.2</td>
<td>[240,241]</td>
</tr>
<tr>
<td>MRCP-Cincinnati Arch</td>
<td>Kentucky, USA</td>
<td>P</td>
<td>2009</td>
<td>0.2</td>
<td>[242,243]</td>
</tr>
<tr>
<td>SECARB Early</td>
<td>Cranfield, MS, USA</td>
<td>D</td>
<td>2009</td>
<td>1.0</td>
<td>[244,245]</td>
</tr>
<tr>
<td>Mountaineer</td>
<td>West Virginia, USA</td>
<td>C</td>
<td>2009</td>
<td>0.1</td>
<td>[143,246]</td>
</tr>
<tr>
<td>MCSC Decatur</td>
<td>Decatur, IL, USA</td>
<td>D</td>
<td>2010</td>
<td>0.4</td>
<td>[247–249]</td>
</tr>
<tr>
<td>ZeroGen</td>
<td>Queensland, Australia</td>
<td>P</td>
<td>2012</td>
<td>0.7</td>
<td>[143,250]</td>
</tr>
<tr>
<td>Brindisi</td>
<td>Italy</td>
<td>P</td>
<td>2012</td>
<td>1.2</td>
<td>[143,251]</td>
</tr>
<tr>
<td>Gorgon</td>
<td>Barrow Island, WA, Australia</td>
<td>D</td>
<td>2014</td>
<td>4.5</td>
<td>[252,253]</td>
</tr>
<tr>
<td>Latrobe Valley</td>
<td>Victoria, Australia</td>
<td>C</td>
<td>2015</td>
<td>13</td>
<td>[143,254]</td>
</tr>
<tr>
<td>Nagaoka</td>
<td>Japan</td>
<td>P</td>
<td>2015</td>
<td>0.007</td>
<td>[144]</td>
</tr>
<tr>
<td>Edwardsport</td>
<td>Indiana, USA</td>
<td>P</td>
<td>2015</td>
<td>1.0</td>
<td>[255]</td>
</tr>
</tbody>
</table>

* C: commercial; P: pilot; D: demonstration.
warming potential is reduced when monoethanol amine (MEA) based CO2 capture system is employed. Khoo and Tan [158] carried out a detailed LCA on four CO2 recovery technologies, namely chemical absorption, membrane separation, cryogenics and pressure swing adsorption, combined with nine CO2 sequestration systems including six options of ocean sequestration (i.e. vertical injection, inclined pipe, pipe towed by ship, dry ice and gas lift advanced dissolution), and three types of geological sequestration (i.e. EOR, ECBM and saline aquifer). They found that the three geological storage methods induced the least environmental burdens and the deep saline aquifer option (Sleipner project with CO2 storage in the Utsira formation as an example) was the best. Geological formation induced the least environmental benefit due to its capability to prevent resource depletion. Recently, Singh et al. [162] conducted a LCA of a natural gas combined cycle power plant and found similar GHG reductions as those reported by Odeh and Cockerill [159]. However, a trade-off with other environmental impacts such as acidification, eutrophication and toxicity were found.

9. CO2 leakage and monitoring

One of the important aspects for geological storage is the potential leakage of the stored CO2 that would impair the effectiveness of the CO2 confinement and eventually lead to serious consequences on the surrounding environments, such as acidification and pollution induced by the mobilization of heavy metals [163]. Therefore, studies on leakage/risk assessment have also attracted much attention in CCS studies.

9.1. Potential leakages

There are two possible sources of CO2 leakage: CO2 transport facilities or the storage area. Several studies have been conducted to identify the effect of the atmospheric dispersion of CO2 due to leakage during transportation [164–166]. Dispersion models are normally used to study the plume dispersion due to a particular atmospheric condition and for assessing its effect to the environment. Comparatively, leakage from geological storage areas involves more complex situations and a number of studies have been conducted to assess this issue. There are two common sources of leakage from geological formations: leakage through caprock and leakage through permeable pathways. Normally the leakage through caprock will be slow and may take tens of thousands of years [167], while the leakage through permeable pathways can be faster causing more concerns to the operator [168]. Several studies have been conducted to model the effect of geological CO2 leakage [169–172]. Celia et al. [173] discussed some available analytical and numerical models, and data needed for estimation of CO2 leakage from geological sites. Nordbotten et al. [174] developed a semi-analytical solution for estimating CO2 leakage from injection well, leaky well, and multiple aquifers separated by impermeable aquitards. This served as a foundation for the later development of a novel framework for predicting the leakage from a large number of abandoned wells, and forming leakage paths connecting multiple subsurface permeable formations [175].

Investigations of gas leakage through the cap rock have been conducted by many researchers [176–178]. Li et al. [178] found that the cap rock sealing pressure should be determined before the start of the process, and should not be exceeded during the CO2 injection process to avoid CO2 migration to upper formations which could be more permeable allowing the CO2 to seep into the surrounding environment and, eventually, back to the atmosphere.

Wells (injection and abandoned) have been identified as the most probable leakage pathway. Therefore, maintaining the well-bore integrity is imperative to guarantee the isolation of geological formations, particularly in basins with a history of oil and gas exploration and production [179].

There are studies regarding the effects of CO2 leakage on human beings [180], plants [181] and marine ecosystems [148,172,182–184]. Due to the important consequences and effects of leakage on our environment, adequate monitoring is necessary in order to establish its potential long term effects on human and our environment, as described in the next section.

9.2. CO2 monitoring

The key feature for geological storage is that CO2 will be retained for extremely long periods, of the order of magnitude of 103 year, without any appreciable seepage back to the surface. Models show that a leakage rate above 0.1% per year will invalidate the effectiveness of CCS in global warming control [185]. Moreover, migration of the injected CO2 inside the storage volume should be monitored to assess that it will not interfere with the surrounding environment and in particular with the groundwater.

The monitoring strategy includes pre-injection, during injection and post-injection phases utilizing a suite of techniques aimed to assure the integrity of the reservoir, the absence of leakages, the quantification of the volumes of the stored CO2 and the identification of the geometry of the injected plume of CO2. Monitoring is also a key to verify the project’s aims, including its predicted performance and long term containment.

The variety of monitoring techniques can be grouped into several families, each one having its range of application in function of the data to be acquired and of the environmental condition of the storage area, as shown in Table 9.

Seismic monitoring: Both active and passive systems can be employed. For active seismic, an energy source is used to generate acoustic waves, which will be detected and interpreted to gain information about the underground geology of the storage area; while in passive seismic, the tremors and micro- earthquakes generated by the movement of fluids or by the formation of fractures are recorded by geophones. When used during the pre-injection phase these methods are aimed to identify the characteristics of the storage area and its structural integrity. During the injection and post-injection, seismic is applied to the monitoring of the evolution of the CO2 plume. 3D seismic generates a tri-dimensional image of the underground structures including the dimension of the injected plume of CO2. Time lapse or 4D monitoring is used to track the evolution through the time of the CO2 plume [186,187]. High quality 3D is able to identify CO2 bodies of mass above 106 kg at depths of 1–2 km with optimal results in off-shore monitoring where the presence of water as medium enhances the penetration of the seismic waves [187].

Geoelectrical methods: These are based on the variation of resistivity caused by the presence of CO2. When CO2 displaces fluids with higher conductivity, i.e. brines, the induced variation in resistivity can be measured giving information about the grade of CO2 saturation of the reservoir and the spatial distribution of the injected plume. The bigger the difference in conductivity between CO2 and displaced fluids, the stronger is the signal. Once CO2 is dissolved in water the difference in resistivity will drop below appreciable values, and therefore, this method is only valid for monitoring free CO2 before dissolution [188].

Temperature logs: A range of thermal processes are involved in CO2 injection (i.e. Joule–Thomson cooling, advective heat transfer,
Displacements. The injection of 3 Mt CO2 in the In Salah Gas Field can generate a certain degree of overpressure leading to deformation of the reservoir, mostly when the hydraulic conductivity is not very high, creating vertically elongated plumes generating a stronger signal than spread ones [187].

Most of the current storage practices/demonstration projects are related to EOR or ECBM, which are more financially viable and deep saline aquifers; demonstration in the latter two storage of CO2 for both inland and offshore storage; CCS is considered to be a crucial part of worldwide efforts to combat global warming by reducing greenhouse gas emission. It was estimated that about 100 CCS projects need to be implemented by 2020 and over 3000 by 2050 in order to reach the goal of restoring the global temperature by 2 °C [194]. Although some of the technologies regarding CCS have been proven, comprehensive CCS projects involving large scale capture and storage are not operational. According to the Global CCS Institute’s 2012 project survey 73 large scale integrated CCS projects have been identified around the world, only 15 of them are currently operating or in construction, capturing 35.4 Mt CO2 per year, and the rest of the projects are in the planning stage of development [21]. It has been noted that five power generation CCS projects were removed from the Institute’s 2011 listing.

IEA [165] pointed out a number of barriers of implementation of CCS, and recommended rules and standards for the transport and storage of CO2 as follows [31]:

- Lack of a market mechanism/incentive that is sufficiently large and long term enough to reward an entity with carbon reduction using CCS technologies;
- No mechanism to penalize those major CO2 emitting sources;
- Inadequate legal framework allowing transport and geological storage of CO2 for both inland and offshore storage;
- Most of the current storage practices/demonstration projects are related to EOR or ECBM, which are more financially viable but have limited CO2 storage capacity as compared to ocean and deep saline aquifers; demonstration in the latter two technologies need to be enhanced.

More recently DECC [195] identified a series of key points through the CCS chain to make its development an economically feasible solution:

- Identification of reliable storage sites with capability of switching between the sites in case a backup is needed;
- Use clusters of storage sites as “hubs” where different CO2 sources can be delivered thus reducing the cost by sharing the infrastructures;
- Develop a large scale network of pipelines with reduction of the transport costs following the increasing of the transported volumes;

### 10. Barriers and opportunities for commercial deployment

**Tracers:** Co-injection of specific compounds together with CO2 can generate a specific “fingerprint” of the stored CO2. These tracers can be detected even in very small concentration (ppm) allowing an identification of any seepage from the reservoir. SF6 and CH4 have been used as tracers in the storage of CO2 inside a depleted natural gas field and their presence was identified in samples collected from a monitoring well 700 m from the injection point about 150 days after the beginning of the injection, thus giving an estimate of the diffusivity of the CO2 inside the reservoir [191].

**Soil gas:** Monitoring the composition of the soil gas, and in particular the concentration of CO2, before the injection defines the baseline. Time lapse monitoring can be used during the injection and post-injection phases to assure the absence of CO2 seepage [192].

**Microbiology:** Samples of fluids and sediments can be collected before the injection for a baseline on biocenosis to be compared with the modification induced by the presence of CO2. Biological analysis is useful to identify biogeochemical processes which can affect the diffusion of CO2 within the reservoir [193].

### Table 9

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• Scaling up the CCS projects;
• Reduction in the energy penalty associated with capturing CO₂ from power plants;
• Assuring financial stability to the CCS projects by a regulatory and policy framework;
• Further explore the effectiveness of EOR in offsetting part of the costs associated with CCS;
• Identify other CO₂ sources than power generation which can be used for CCS.

There are no major technological barriers to the capture and geological storage of CO₂ for existing operation but noted that CCS is an energy intensive process that lowers the overall efficiency of the concerned energy/power generating systems. It is inevitable that the costs, both capital and operation, involved in plants equipped with CCS are much higher than those without capture due to the reduction in efficiency and additional capital cost for installing the capture, transport and injection facilities. The high cost of CO₂ capture, particularly for dilute streams like those from gas-fired power plants and industrial combustion processes is the major challenge of CCS [171]. Page et al. [196] compared the energy for CCS and efficiency penalty for different types of power plants and found that there are wide variations even for the same type of power plants. Part of the costs associated with CCS could be offset by using the CO₂ for economically productive application. EOR/ECBM in USA may allow the storage of up to 10,500 MtCO₂ generating revenue which should exceed the CCS costs; 78% of this low cost EOR is estimated to be used within a 20 years’ time. In China 5500 MtCO₂ can be used for 95% EOR within the first 20 years. Further 2000–2,500 MtCO₂ may be transported and stored at an average cost of 4.89 USD/tonne CO₂ for USA and 4.51 USD/tonne CO₂ for China. Adding the capture phase the overall cost will be increased from 40 USD/tonne CO₂ up to 70 USD/tonne CO₂ in China [197,198]. Considering CCS applied to power plants the cost of capture in USA will range from 4.5 USD/tonne CO₂ for coal based integrated gasification combined cycle power plant with EOR to 72.4 USD/tonne CO₂ for natural gas combined cycle with storage in saline formations [199].

Estimates of the total cost associated with CCS for electricity production are in the range of 60–100 USD/tonne CO₂, the recent reduction in price of natural gas is leading to lower cost for gas-fired power plants if compared with coal-fired ones [200]. In general, the cost of CO₂ capture is ~70–80% of the total costs of a carbon capture, transport and storage system [6,32]. Therefore, significant research efforts are underway to reduce the costs of capture. On the other hand study indicated that the cost of CO₂ avoided is from 23 to 92 USD for coal plants and from 67 to 106 USD for natural gas plants, which are much higher than other renewable energy technologies such as hydropower and onshore wind farms [89]. However, study indicated that with increased R&D and accumulation of experience in CCS technologies, the cost of CCS can be reduced by 50% between 2008 and 2020 [201].

A general bias of cost estimates in CCS is their large range of uncertainty, mostly due to the fact that so far no large scale power plant with integrated CCS is operating. The cost of the avoided CO₂ will also vary between the retrofitting of an existing power plant and a new one with built-in CCS; the retrofitting costs being higher mostly when considering coal-fired electricity generation. Moreover, a real reduction in atmospheric injection of CO₂ will be fully achieved only if a new CCS-equipped power plant is going to replace an older one. The development of a CO₂ tax aimed to penalize the CO₂ emitters will also play an important role in the overall cost estimates. Any cost comparison should be therefore carefully and critically addressed [202,203]. Kenney and Basu [204] identified a number of challenges that could hinder the achievement of a strategy for CO₂ reduction and highlight the importance of incentives to entice the engagement of countries.

Although much of the current discussion on CCS is focused on coal, a recent report by Green-Alliance [205] indicated that CCS could potentially be fitted on 50–100 GW of gas-fired capacity in Europe by 2030 with suitable policy action. Similarly, significant less attention has been paid to CCS for non-power applications, such as cement, steel and refinery, and hence there is relatively less knowledge about the required instrumentation and infrastructures for the deployment of CCS in the industrial sector [206,207].

Apart from conventional carbon capture and storage methods, there is increasing interest in some innovative ways of carbon reduction such as using biochar and biological CO₂ mitigation. Biochar (produced from pyrolysis of biomass) production and storage in soils can provide simultaneous benefits for carbon sequestration, provision of energy and soil conditioning that can restore degraded agricultural land and increase crop yields [208,209]. Its role for carbon sequestration was included in the Agenda for the 2009 UNFCCC Copenhagen climate change negotiations. In recent years microalgae has emerged as a promising option for biological CO₂ fixation and intensive research has been carried out to develop feasible systems for removing CO₂ from industrial exhaust gases. Lenton [210] conducted a review on land-based biological CO₂ removal and storage methods including biochar production and bioenergy with CO₂ capture and storage. The review suggests that there is already the potential to counterbalance land use change CO₂ emissions and by the end of the century, CO₂ removal could exceed CO₂ emissions, thus lowering atmospheric CO₂ concentration and global temperature. Although the above innovative mitigation technologies and measures may be able to break some of the barriers for commercial deployment of CCS systems, further R&D is needed on the optimal implementation plan and system.

11. Conclusions

In order to meet GHG emissions reduction target, a complimen-tary range of technological approaches, including improving energy efficiency and conservation, adopting clean fuels and clean coal technologies, developing renewable energy, and implementing CCS, has been considered by various countries according to their own circumstances. It is noted that CCS comprises a portfolio of technologies that can massively reduce CO₂ emissions, but CCS is yet to be widely deployed. This paper has reviewed various technologies and issues related to CO₂ capture, separation, transport, storage and monitoring. The selection of specific CO₂ capture technology heavily depends on the type of the plant and fuel used, where for gas-fired power plants, post-combustion capture technology was found generally to be the technology due to its lower cost. Absorption is the most mature CO₂ separation process, due to its high efficiency and lower cost; although issues related to environmental impact have to be fully understood.

The best option for CO₂ transport will depend on a variety of parameters including:

• Volumes of CO₂ to be transported;
• Planned lifetime of the CO₂ source (e.g. power plants, steel and cement factories);
• Distance between CO₂ source and storage area;
• Onshore vs. offshore transport and storage;
• Typology of transporting infrastructure available (i.e. road and rail networks, pipelines trunks, shipping docks facilities).

Pipeline is considered to be the most viable solution if large volumes of CO₂ are available for long time and if a trunk of
pipelines can be developed; further advantage is represented by the potential reuse of pipelines for gas or oil transport. In case of offshore storage shipping the CO₂ by tankers can be economically competitive due to the high capital costs involved in the deployment of submarine pipelines. The costs of intermediate storage facilities and suitable docking for the tankers should be addressed when ships are used as CO₂ carriers.

Four main types of geological formations are considered for CO₂ storage:

- Depleted oil and gas reservoirs;
- Unmineable coal beds;
- Saline aquifers;
- Basalts.

In case of storage in oil and gas reservoir the technology already used for enhanced oil recovery (EOR) is mature and has been practiced for many years using natural CO₂ sources and mostly on-shore. However, the economical feasibility of using captured CO₂ from anthropogenic sources for EOR has not been fully demonstrated yet mostly for offshore storage. The use of unmineable coal beds, eventually recovering methane by Enhanced Coal Bed Methane (ECBM) recovery, can be an option but it will make the coal used for CO₂ storage unavailable even if future mining technology and economical consideration should make it of commercial value. On the other hand, there are growing interests in CO₂ storage in saline aquifers, due to their enormous potential storage capacity and several projects are in development both onshore and offshore. Basalts represent an extremely large volume for CO₂ storage which will be fixed as carbonate minerals following chemical reaction with the minerals of the hosting rocks. A number of uncertainties ranging from the need of an extremely detailed knowledge of the stratigraphic structure of the basalt to be applied according to the special environmental conditions of the storage site.

Although technologies regarding the capture and storage of CO₂ exist, the overall cost of using current CCS procedures is still high and must be substantially reduced before it can be widely deployed. There are multiple hurdles to CCS deployment that need to be addressed in the coming years, including the absence of a clear business case for investment in CCS, and the absence of robust economic incentives to support the additional high capital and operating costs associated with CCS.

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