



ISSN (E): 2277- 7695
ISSN (P): 2349-8242
NAAS Rating: 5.03
TPI 2019; 8(11): 327-332
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www.thepharmajournal.com
Received: 17-09-2019
Accepted: 19-10-2019

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Present status of capture of carbon dioxide and its storage technologies: A review

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Abstract

Climate change has led to reduce the concentration of atmospheric carbon dioxide (CO₂). Carbon dioxide capture and storage (CCS) is considered a crucial strategy for meeting CO₂ emission reduction targets. In this paper, different aspects of CCS are reviewed and discussed including the state of the art technologies for CO₂ capture, separation, transport, storage, leakage, monitoring, and life cycle analysis. The selection of specific CO₂ capture technology heavily depends on the type of CO₂ generating plant and fuel used. Among those geological formations for CO₂ 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 CO₂ 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.

Keywords: Post-combustion, Pre-combustion, Oxyfuel combustion and Leakage and monitoring

Introduction

Speedy economic growth has led to today's ever increasing demand for energy. 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 profuse use of fossil fuels has caused adverse effects on the environment, particularly related to the emission of carbon dioxide (CO₂), a major anthropogenic greenhouse gas (GHG). The atmospheric CO₂ level has increased more than 39%, from 280 ppm during pre-industrial time to the record high level of 400 ppm in May 2013 with a corresponding increase in global surface temperature of about 0.8 °C. 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. The same IPCC report (AR5) indicates that to avoid the adverse effects of climate change occurring, it is necessary to keep the temperature rise less than 2 °C and that CO₂ emissions should be reduced globally by 41–72% by 2050 and by 78–118% by 2100 with respect to 2010 levels. 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, separation, transport, utilization, storage, life cycle GHG assessment and leakage and monitoring.

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. 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.

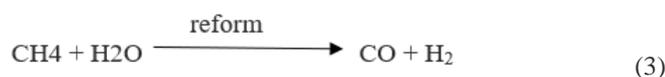
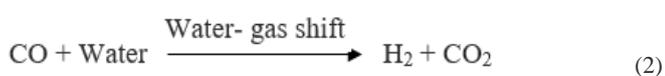
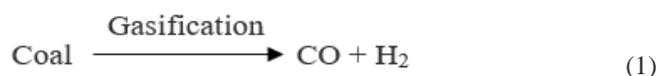
(a) Post-combustion

This process removes CO₂ from the flue gas after combustion has taken place. The technology has been proven at small-scale with CO₂ recovered at rates up to 800 t/day. 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.

(b) Pre-combustion

In this process, the fuel (normally coal or natural gas) is pre-treated before combustion. For coal, the pre-treatment 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):



The high CO₂ concentration (>20%) in the H₂/CO₂ fuel gas mixture facilitates the CO₂ separation. Subsequently, the H₂ is burned in air producing mainly N₂ and water vapor. 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 [4].

(c) 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 NO_x is another advantage of this process [4]. 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 [32]), can be compressed, transported and stored. This process is technically feasible [4] but consumes large amounts of oxygen coming from an energy intensive air separation unit [27]. 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.

Comparison of different combustion technologies for CO₂ capture

The comparison of three CO₂ capture technologies described below (Table 1). 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 [32, 3]. On the cost side, it was [11] compared the three technologies for both gas and coal-fired plants (Table 2) [11]. 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.

Table 1: Advantages and disadvantages of the different CO₂ capture technologies

Capture process	Application area	Advantages	Disadvantages
Post-combustion	Coal-fired and gas-fired plants	Technology more mature than other alternatives; can easily retrofit into existing plants.	Low CO ₂ concentration affects the capture efficiency.
Pre-combustion	Coal-gasification plants	High CO ₂ concentration enhance sorption efficiency; fully developed technology, commercially deployed at the required scale in some industrial sectors; opportunity for retrofit to existing plant.	Temperature associated heat transfer problem and efficiency decay issues associated with the use of hydrogen-rich gas turbine fuel; high parasitic power requirement for sorbent regeneration; inadequate experience due to few gasification plants currently operated in the market; high capital and operating costs for current sorption systems.
Oxyfuel combustion	Coal-fired and gas-fired plants	Very high CO ₂ concentration that enhances absorption efficiency; mature air separation technologies available; reduced volume of gas to be treated, hence required smaller boiler and other equipment.	High efficiency drop and energy penalty; cryogenic O ₂ production is costly; corrosion problem may arise.
Chemical looping combustion	Coal-gasification plants	CO ₂ is the main combustion product, which remains unmixed with N ₂ , thus avoiding energy intensive air separation.	Process is still under development and inadequate large scale operation experience.

Table 2: Cost comparison for different capture processes

Fuel type	Parameter	Capture technology			
		No capture	Post-combustion	Pre-combustion	Oxy-fuel
Coal-fired	Thermal efficiency (% LHV)	44.0	34.8	31.5	35.4
	Capital cost (\$/kW)	1410	1980	1820	2210
	Electricity cost (c/kWh)	5.4	7.5	6.9	7.8
Gas-fired	Cost of CO ₂ avoided (\$/t CO ₂)	–	34	23	36
	Thermal efficiency (% LHV)	55.6	47.4	41.5	44.7

	Capital cost (\$/kW)	500	870	1180	1530
	Electricity cost (c/kWh)	6.2	8.0	9.7	10.0
	Cost of CO ₂ avoided (\$/t CO ₂)	–	58	112	102

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. These technologies are compared in (Table 3) and discussed below.

Table 3: Comparison of different separation technologies

Technology	Advantage	Disadvantage
Absorption	<ul style="list-style-type: none"> – High absorption efficiency (>90%). – Sorbents can be regenerated by heating and/or depressurization. – Most mature process for CO₂ separation. 	<ul style="list-style-type: none"> – Absorption efficiency depends on CO₂ concentration. – Significant amounts of heat for absorbent regeneration are required. – Environmental impacts related to sorbent degradation have to be understood.
Adsorption	<ul style="list-style-type: none"> – Process is reversible and the absorbent can be recycled. – High adsorption efficiency achievable (>85%). 	<ul style="list-style-type: none"> – Require high temperature adsorbent. – High energy required for CO₂ desorption.
Chemical looping combustion	<ul style="list-style-type: none"> – CO₂ is the main combustion product, which remains unmixed with N₂, thus avoiding energy intensive air separation. 	<ul style="list-style-type: none"> – Process is still under development and there is no large scale operation experience.
Membrane separation	<ul style="list-style-type: none"> – Process has been adopted for separation of other gases. – High separation efficiency achievable (>80%). 	<ul style="list-style-type: none"> – Operational problems include low fluxes and fouling.
Cryogenic distillation	<ul style="list-style-type: none"> – Mature technology. – Adopted for many years in industry for CO₂ recovery. 	<ul style="list-style-type: none"> – Only viable for very high CO₂ concentration >90% v/v. – Should be conducted at very low temperature. – Process is very energy intensive.

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^[13]. 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^[18]. Some other sorbents, such as piperazine and anion-functionalized ionic liquid have also received attention in recent years. Piperazine has been found to react much faster than MEA, but because it has a larger volatility than MEA, its application in CO₂ absorption is more expensive and is still under development.

Moreover, amine emissions can degrade into nitrosamines and nitramines^[29], which are potentially harmful to the human health and the environment. Chilled ammonia process uses aqueous ammonium salts (such as ammonium carbonate) to capture CO₂ that can make use of waste heat to regenerate the CO₂ at elevated temperature and pressures to reduce downstream compression^[19]. This process will generate less problem as compared to those that amine is facing with degradation.

Adsorption

In contrast to absorption processes which 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, hydrotalcites and lithium

zirconate. The adsorbed CO₂ can be recovered by swinging the pressure (PSA) or temperature (TSA) of the system containing the CO₂-saturated sorbent. PSA is a commercial available technology for CO₂ recovery from power plants that can have efficiency higher than 85%^[23]. 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^[6]. 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^[22].

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. 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 membrane. It was^[12] achieved a CO₂ separation efficiency from 82% to 88%. Furthermore, it was revealed that although there are significant developments in gas separation membrane systems, they are still far away to realize the potentialities of this technology^[2].

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 2MtCO₂/year are transported within the distances involved in North Sea storage [30].

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 [12]. 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.

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. [16]. 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 [9].

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 [9].

Currently only a few pipelines are used to carry CO₂ and are almost all for EOR projects. 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 [14].

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 [10].

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.

CO₂ utilization

After capture, the high CO₂ content stream can be transported for geological storage or for CO₂ utilization. It was [17] 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. 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. Enhanced oil recovery (EOR) using CO₂ from capture processes can significantly increase CO₂ utilization [26].

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. 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.

Large scale, economic photocatalytic conversion of CO₂ into methane (CH₄) and/or methanol (CH₃OH) represents a formidable scientific and technical challenge. Recent progress in this area has focused mainly on the development of novel catalysts through advances in nanotechnology.

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. A typical geological storage site can hold several tens of million tonnes of CO₂ trapped by different physical and chemical mechanisms [7].

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. Requirements such as distance from the source of CO₂, effective storage capacity, pathways for potential leakage and in general economic constrains may limit the feasibility of being a storage site. The economic aspects related to infrastructure and socio-political conditions will also affect the site selection. 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.

Storage in saline aquifers

Deep aquifers at 700–1000 m below ground level often host high salinity formation brines. 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. 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. A review was conducted 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. The parameters

affecting mineral trapping of CO₂ sequestration in brines have been extensively investigated [31].

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 [8].

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 [20]. 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 [21], while the leakage through permeable pathways can be faster causing more concerns to the operator [5].

It was [21] 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 wellbore integrity is imperative to guarantee the isolation of geological formations, particularly in basins with a history of oil and gas exploration and production.

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. 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.

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 [1]. 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.

Remote sensing

The injection of large volumes of fluids in the reservoir, mostly when the hydraulic conductivity is not very high, can generate a certain degree of overpressure leading to deformation of the surface that can be detected by Interferometric Synthetic Aperture Radar (InSAR) airborne or satellite monitoring. This method is based on the use of synthetic aperture radar to map the surface of the storage area through the time identifying the displacements. The injection of 3 Mt CO₂ in the In Salah Gas Field (Algeria) caused a lifting of 5 mm/y which was detected by InSAR [15].

Geochemical sampling

It is possible to collect samples of fluids from boreholes inside the storage area and observe the chemical variation induced by the injection of CO₂. The most evident effect is a drop in pH and changes in the concentration of minerals, such as carbonates and some silicates, due to the acidification. Measuring the pH drop in groundwater allows the identification of CO₂ leakages of the order of 10³ t/year [15].

Atmospheric monitoring

CO₂ could seep from the reservoir and reach the surface, leaking into the atmosphere. Monitoring the atmospheric concentration of CO₂ in the storage area can be used to identify anomalies above the natural baseline. Large natural variation in CO₂ values due to soil respiration, organic matter decomposition or peculiar climatic condition may affect the reliability of these techniques

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.

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

Conclusions

In order to meet GHG emissions reduction target, a complimentary 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. 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.

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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