FOSSIL FUELS. CARBON CAPTURE and STORAGE

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1. Fossil Fuels 1.1. Features and reserves

From the 19th century until today, fossil fuels provided the main share of the global energy consumption (fig.1). This class of energy sources include many species like coal, oil and natural gas. During the time, the dominant fuel on the energy market was: coal in the 19th century and the first half of the 20th, oil from the second half of the 20th century until today and natural gas from now and further.



Fig.1 – Energy sources participation to the global consumption

The dominant position of the fossil fuels in the global energy survey relies on some features like:

- Large quantites in on-shore and off-shore deposits;
- High concentration of energy defined by the low calorific value;
- Easy acces and high rate of operation;
- Versatil utilization for all end energy comsumption domains;

• Wide available technologies for extraction, transport, storage and conversion;

However, these favourable issues may be lost because of a great drawbeck: the exhaust gases from the fuel combustion like CO_2 , SO_x and NO_x .

The fossil fuels reserves and the annual extraction rates change during time as result of consumption and new discovered deposits. The last global survey of the WEC (World Energy Council) isued in year 2013 presents the situation at the end of 2011.

Year	Coal (10 ⁹ tec)		C (10 ⁹	vil toe)	Natural gas (10 ¹² m ³)	
	Reserves	Annual extraction	Reserves	Annual extraction	Reserves	Annual extraction
2011	891.53	7.52	176.682	3.796	209.742	3.518
1978	636	2.55	88.34	2.68	63.6	1.37
2011/1978 (p.u.)	1.402	2.95	2.00	1.416	3.298	2.568

For comparison, in the table, are shown the similar amounts for the end of the year 1978, and the corresponding ratios, too.

The main aspect is that despite the growing extraction, the proved deposits are larger over 33 years owing to the huge exploration effort.

1.2 Exhausting time

Although the known reserves are important and seem to be available many years in the future, its are not renewable, so that at some time or other will be exhausted. Knowing this moment is of great importance for the planning of the energy supplying.

There are some methods to evaluate the exhaust time.

a) *The fictitious exhaust time*: both the amounts of reserve (R) and the annual extraction (C) are considered constant from an year to the next, so that

$$t_f = \frac{R}{C}.$$

b) The shortest exhausting time: the reserve extent (\mathbf{R}) is constant and the annual extraction amount changes steadily with an constant rate (q). So, the extracted amount changes as follows:

Year	1	2	3		i	
Annual	C.	aC.	a^2C		a ⁱ⁻¹ C	
consumtion	c_{θ}	Y€0	ΥCO	••••	Υ Cθ	

After a period of t_m years, the sum of the extracted amounts becomes equal to the reserve size:

$$R = \sum_{i=1}^{t_m} C_0 q^{t_m - 1} = C_0 \frac{q^{t_m} - 1}{q - 1} \text{ and}$$
$$t_m = \frac{\ln \left[\frac{R}{C_0}(q - 1) + 1\right]}{\ln q}.$$

c) *The real exhausting time*: both the reserve and the annual extraction changes steadily with constant rates, respectively (q) and (p).

Year	1	2	3		i	
Reserve	R	pR			$p^{i-1}R$	
Annual consumption	C_{θ}	qC_{θ}	$q^2 C_{\theta}$	••••	$q^{i-1}C_{ heta}$	••••

After t_r years, the whole reserve becomes equal to the cumulated extraction:

$$p^{t_r-l}R = \sum_{i=1}^{t_r} C_0 q^{t_m-l}$$

This equation can not be solved analitically, only by numerically methods.

2. CO₂ capture and storage

There is new and stronger evidence that most of the global warming observed over the past 50 years is attributable to human activities. Human influences are expected to continue to change atmospheric composition throughout the 21^{st} century.

The greenhouse gas making the largest contribution from human activities is carbon dioxide (CO_2). It is released by burning fossil fuels and biomass and by certain industrial and resource extraction processes.

Emissions of CO_2 due to fossil fuel burning are virtually certain to be the dominant influence on the trends in atmospheric CO_2 concentration during the 21st century. Global average temperatures and sea level are projected to rise under all scenarios.

The ultimate objective of the UN Framework Convention on Climate Change, which has been accepted by 189 nations, is to achieve: "stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system", although a specific level has yet to be agreed.

Technological options for reducing net CO₂ emissions to the atmosphere include:

- reducing energy consumption, for example by increasing the efficiency of energy conversion and/or utilization (including enhancing less energy-intensive economic activities);
- switching to less carbon intensive fuels, for example natural gas instead of coal;
- increasing the use of renewable energy sources or nuclear energy, each of which emits little or no net CO₂;
- sequestering CO₂ by enhancing biological absorption capacity in forests and soils;
- capturing and storing CO₂ chemically or physically.

Carbon dioxide Capture and Storage (CCS) means that CO_2 arising from the combustion of fossil and/or renewable fuels and from processing industries would be captured and stored away from the atmosphere for a very long period of time.

There are three main components of the process:

- capturing CO₂, for example by separating it from the flue gas stream of a fuel combustion system and compressing it to a high pressure;
- transporting it to the storage site;
- storing it.

There are many factors that must be considered when deciding what role CO_2 capture and storage could play in mitigating climate change. These include the cost and capacity of emission reduction relative to, or in combination with, other options, the resulting increase in demand for primary energy sources, the range of applicability, and the technical risk. Other important factors are the social and environmental consequences, the safety of the technology, the security of storage and ease of monitoring and verification, and the extent of opportunities to transfer the technology to developing countries.

To reduce the CO_2 emissions from the power and industry sectors through the use of CO_2 capture and storage, it is important to understand where these emissions arise and what their geographical relationship is with respect to potential storage opportunities. If there is a good geographical relationship between the large stationary emission sources and potential geological storage sites then it is possible that a significant proportion of the emissions from these sources can be reduced using CO_2 capture and storage. If, however, they are not well matched geographically, then there will be implications for the length and size of the transmission infrastructure that is required, and this could impact significantly on the cost of CO_2 capture and storage, and on the potential to achieve deep reductions in global CO_2 emissions. It may be the case that there are regions of the world that have greater potential for the application of CO_2 capture and storage than others given their source/storage opportunity relationship. Understanding the regional differences will be an important factor in assessing how much of an impact CO_2 capture and storage can have on global emissions reduction and which of the portfolio of mitigation options is most important in a regional context.

2.1 Sources of CO₂

Power and industry sectors combined dominate current global CO_2 emissions, accounting for about 60% of total CO_2 emissions. Future projections indicate that the share of these emissions will decline to around 50% of global CO_2 emissions by 2050. The CO_2 emissions in these sectors are generated by boilers and furnaces burning fossil fuels and are typically emitted from large exhaust stacks. These stacks can be described as large stationary sources, to distinguish them from mobile sources such as those in the transport sector and from smaller stationary sources represent potential opportunities for the addition of CO_2 capture plants.

Other sectors of the economy, such as the residential and transport sectors, contribute around 30% of global CO_2 emissions and also produce a large number of point source emissions. However, the emission volumes from the individual sources in these sectors tend to be small in comparison to those from the power and industry sectors and are much more widely distributed, or even mobile rather than stationary. It is currently not considered to be technically possible to capture emissions from these other small stationary sources, because there are still substantial technical and economic issues that need to be resolved.

However, in the future, the use of low-carbon energy carriers, such as electricity or hydrogen produced from fossil fuels, may allow CO_2 emissions to be captured from the residential and transport sectors as well. Such fuels would most probably be produced in large centralized plants and would be accompanied by capture and storage of the CO_2 co-product. The distributed fuels could then be used for distributed generation in either heaters or fuels cells and in vehicles in the transport sector. In this scenario, power generation and industrial sources would be unaffected but additional point sources would be generated that would also require storage. In the medium to long term therefore, the development and commercial deployment of such technology, combined with an accelerated shift to low- or zero carbon fuels in the transport sector, could lead to a significant change in the geographical pattern of CO_2 emissions compared to that currently observed.

Source types

These sources are present in three main areas:

- fuel combustion activities,
- industrial processes and
- natural gas processing.

The largest CO_2 emissions by far result from the oxidation of carbon when fossil fuels are burned. These emissions are associated with fossil fuel combustion in power plants, oil refineries and large industrial facilities.

Such processes include:

- the use of fuels as feedstocks in petrochemical processes;
- the use of carbon as a reducing agent in the commercial production of metals from ores;
- the thermal decomposition (calcination) of limestone and dolomite in cement or lime production;
- the fermentation of biomass (e.g., to convert sugar to alcohol).

In some instances these industrial-process emissions are produced in combination with fuel combustion emissions, a typical example being aluminium production.

A third type of source occurs in natural-gas processing installations. CO_2 is a common impurity in natural gas, and it must be removed to improve the heating value of the gas or to meet pipeline specifications.

CO₂ content

In CO₂ capture, the CO₂ partial pressure of the gas stream to be treated is important as well as the concentration of the stream. For practical purposes, this partial pressure can be defined as the product of the total pressure of the gas stream times the CO₂ mole fraction. It can be said that the lower the CO₂ partial pressure of a gas stream, the more stringent the conditions for the separation process. Typical CO₂ concentrations and their corresponding partial pressures for large stationary combustion sources are shown in Table 1, which also includes the newer Integrated Gasification Combined Cycle technology (IGCC).

Source	CO2 concentration % vol (dry)	Pressure of gas stream MPa ^{(a}	CO2 partial pressure MPa
CO ₂ from fuel combustion			
Power station flue gas:			
Natural gas fired boilers	7 - 10	0.1	0.007 - 0.010
Gas turbines	3 - 4	0.1	0.003 - 0.004
Oil fired boilers	11 - 13	0.1	0.011 - 0.013
Coal fired boilers	12 - 14	0.1	0.012 - 0.014
IGCC ^{(b} : after combustion	12 - 14	0.1	0.012 - 0.014
Oil refinery and petrochemical plant fired heaters	8	0.1	0.008
CO ₂ from chemical transformations + fuel			
combustion			
• Blast furnace gas ^{(c} :			
Before combustion _c	20	0.2 - 0.3	0.040 - 0.060
After combustion	27	0.1	0.027
Cement kiln off-gas	14 - 33	0.1	0.014 - 0.033
CO ₂ from chemical transformations before	8 - 20	2 - 7	0.16 - 1.4
combustion			
 IGCC: synthesis gas after gasification 			
a = 1 har			

Table 1 Properties of candidate gas streams that can be inputted to a capture process

a) 0.1 MPa = 1 bar.

b)IGCC: Integrated gasification combined cycle.

c)Blast furnace gas also contains significant amounts of carbon monoxide that could be converted to CO2 using the so-called shift reaction

Typically, the majority of emission sources from the power sector and from industrial processes have low CO_2 partial pressures; hence the focus of the discussion in this section. Where emission sources with high partial pressure are generated, for example in ammonia or hydrogen production, these sources require only dehydration and some compression, and therefore they have lower capture costs.

Source	CO2 concentration % vol	Pressure of gas stream MPa	CO2 partial pressure MPa	
Chemical reaction(s)				
 Ammonia production^{(a}) 	18	2.8	0.5	
Ethylene oxide	8	2.5	0.2	
 Hydrogen production^(a) 	15 - 20	2.2 - 2.7	0.3 - 0.5	
• Methanol production ^{(a}	10	2.7	0.27	
Other processes				
 Natural gas processing 	2 - 65	0.9 - 8	0.05 - 4.4	

Fable 2	Typical	properties of	gas streams	that are already	input to a	capture process
abic 4	rypical	properties of	gas streams	that are arready	mput to a	capture process

(a The concentration corresponds to high operating pressure for the steam methane reformer.

2.2 CO₂ capture Basic systems

There are four basic systems for capturing CO_2 from use of fossil fuels and/or biomass:

- Capture from industrial process streams;
- Post-combustion capture;
- Oxy-fuel combustion capture;
- Pre-combustion capture).

These systems are shown in simplified form in Figure 1.

Post-combustion capture

Capture of CO_2 from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO_2 . The CO_2 is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. A chemical sorbent process would normally be used for CO_2 separation. Other techniques are also being considered but these are not at such an advanced stage of development. Besides industrial applications, the main systems of reference for post-combustion capture are the current installed capacity of oil, coal and natural gas power plants and in particular, of supercritical pulverized coal fired plants and of natural gas combined cycle (NGCC) plants, both representing the types of high efficiency power plant technology where CO_2 capture can be best applied.

Pre-combustion capture

Pre-combustion capture involves reacting a fuel with oxygen or air and/or steam to give mainly a "synthesis gas (syngas)" or "fuel gas" composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to give CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells. These systems are considered to be strategically important.



Fig. 1 CO₂ capture systems

Oxy-fuel combustion capture

In oxy-fuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that is mainly CO_2 and H_2O . If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO_2 and/or H_2O -rich flue gas can be recycled to the combustor to moderate this. Oxygen is usually produced by low temperature (cryogenic) air separation and novel techniques to supply oxygen to the fuel, such as membranes and chemical looping cycles are being developed.

Capture from industrial process streams

 CO_2 has been captured from industrial process streams for 80 years, although most of the CO_2 that is captured is vented to the atmosphere because there is no incentive or requirement to store it. Current examples of CO_2 capture from process streams are purification of natural gas and production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels. Most of the techniques employed for CO_2 capture in the examples mentioned are also similar to those used in precombustion capture. Other industrial process streams which are a source of CO_2 that is not captured include cement and steel production, and fermentation processes for food and drink production. CO_2 could be captured from these streams using techniques that are common to post-combustion capture, oxyfuel combustion capture and pre-combustion capture.

CO₂ capture technologies

Separation with sorbents/solvents

The separation is achieved by passing the CO_2 -containing gas in intimate contact with a liquid absorbent or solid sorbent that is capable of capturing the CO_2 . In the general scheme

of

Figure 2a, the sorbent loaded with the captured CO_2 is transported to a different vessel, where it releases the CO_2 (regeneration) after being heated, after a pressure decrease or after any

other change in the conditions around the sorbent. The sorbent resulting after the regeneration step is sent back to capture more CO_2 in a cyclic process.



Figure 2 General schemes of the main separation processes relevant for CO2 capture

In some variants of this scheme the sorbent is a solid and does not circulate between vessels because the sorption and regeneration are achieved by cyclic changes (in pressure or temperature) in the vessel where the sorbent is contained. A make-up flow of fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses. In some situations, the sorbent may be a solid oxide which reacts in a vessel with fossil fuel or biomass producing heat and mainly CO_2 . The spent sorbent is then circulated to a second vessel where it is re-oxidized in air for reuse with some loss and make up of fresh sorbent.

One common problem of these CO_2 capture systems is that the flow of sorbent between the vessels of Figure 2a) is large because it has to match the huge flow of CO_2 being processed in the power plant. Therefore, equipment sizes and the energy required for sorbent regeneration are large and tend to translate into an important efficiency penalty and added cost. Good sorbent performance under high CO_2 loading in many repetitive cycles is obviously a necessary condition in these CO_2 capture systems.

Separation with membranes

Membranes (Figure 2b) are specially manufactured materials that allow the selective permeation of a gas through them. The selectivity of the membrane to different gases is intimately related to the nature of the material, but the flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high-pressure streams are usually preferred for membrane separation. There are many different types of membrane materials (polymeric, metallic, ceramic) that may find application in CO_2 capture systems to preferentially separate H_2 from a fuel gas stream, CO_2 from a range of process streams or O_2 from air. Although membrane separation finds many current commercial

applications in industry (some of a large scale, like CO_2 separation from natural gas) they have not yet been applied for the large scale and demanding conditions in terms of reliability and low-cost required for CO_2 capture systems.

Distillation of a liquefied gas stream and refrigerated separation

A gas can be made liquid by a series of compression, cooling and expansion steps. Once in liquid form, the components of the gas can be separated in a distillation column. In the case of air, this operation is currently carried out commercially on a large scale. Oxygen can be separated from air following the scheme of Figure 5 c and be used in a range of CO_2 capture systems (oxy-fuel combustion and pre-combustion capture). The key issue for these systems is the large flow of oxygen required. Refrigerated separation can also be used to separate CO_2 from other gases. It can be used to separate impurities from relatively high purity CO_2 streams, for example, from oxy-fuel combustion and for CO_2 removal from natural gas or synthesis gas that has undergone a shift conversion of CO to CO_2 .

2.3 Transport of CO₂

 CO_2 can be transported in three states: gas, liquid and solid. Commercial-scale transport uses tanks, pipelines and ships for gaseous and liquid carbon dioxide. Gas transported at close to atmospheric pressure occupies such a large volume that very large facilities are needed. Gas occupies less volume if it is compressed, and compressed gas is transported by pipeline where operating pressures are between 10 and 80 MPa. Volume can be further reduced by liquefaction, solidification or hydration. Liquefaction is an established technology for gas transport by ship as LPG (liquefied petroleum gas) and LNG (liquefied natural gas). This existing technology and experience can be transferred to liquid CO_2 transport. Solidification needs much more energy compared with other options, and is inferior from a cost and energy viewpoint. Each of the commercially viable technologies is currently used to transport carbon dioxide.

Pipeline systems

A transportation infrastructure that carries carbon dioxide in large enough quantities to make a significant contribution to climate change mitigation will require a large network of pipelines. As growth continues it may become more difficult to secure rights-of-way for the pipelines, particularly in highly populated zones that produce large amounts of carbon dioxide.

CO₂ pipeline operators have established minimum specifications for composition:

- (a) **Carbon Dioxide**. Product shall contain at least 95% of Carbon Dioxide as measured at the delivery meter.
- (b) Water. Product shall contain no free water, or in the vapour phase.
- (c) **Hydrogen Sulphide.** Product shall not contain more than 1500 ppm, by weight, of hydrogen sulphide.
- (d) **Total Sulphur.** Product shall not contain more than 1450 ppm, by weight, of total sulphur.
- (e) **Temperature.** Product shall not exceed a temperature of 48.9°C.
- (f) **Nitrogen.** Product shall not contain more than 4% of nitrogen.
- (g) **Hydrocarbons.** Product shall not contain more than 5% of hydrocarbons and the dew point of Product (with respect to such hydrocarbons) shall not exceed -28.9 oC.
- (h) **Oxygen.** Product shall not contain more than ten 10 pps, by weight, of oxygen.

(i) **Glycol.** Product shall not contain more than $4 \ge 10^{-5}$ Lm⁻³ of glycol and at no time shall such glycol be present in a liquid state at the pressure and temperature conditions of the pipeline.

This specification is for gas for an enhanced oil recovery (EOR) project, and parts of it would not necessarily apply to a CO_2 storage project. A low nitrogen content is important for EOR, but would not be so significant for CCS. A CO_2 pipeline through populated areas might have a lower specified maximum H₂S content.

Dry carbon dioxide does not corrode the carbon-manganese steels generally used for pipelines, as long as the relative humidity is less than 60%; this conclusion continues to apply in the presence of N_2 , NOx and SOx contaminants.

The water solubility limit in high-pressure CO_2 (500 bar) is 5000 ppm at 75°C and 2000 ppm at 30°C. Methane lowers the solubility limit, and H₂S, O₂ and N₂ may have the same effect. Corrosion rates are much higher if free water is present; hydrates might also form. It is unlikely to be practicable to transport wet CO_2 in low-alloy carbon steel pipelines because of this high corrosion rate. If the CO_2 cannot be dried, it may be necessary to build the pipeline of a corrosion-resistant alloy ('stainless steel'). However the cost of steel has greatly increased recently and this may not be economical.

Once the CO_2 has been dried and meets the transportation criteria, the CO_2 is measured and transported to the final use site. All the pipelines have state-of-the-art metering systems that accurately account for sales and deliveries on to and out of each line, and SCADA (Supervisory Control and Data Acquisition) systems for measuring pressure drops, and redundancies built in to allow for emergencies. In the USA, these pipelines are governed by Department of Transportation regulations.

Pipeline	Location	Operator	Capacity	Length	Year finished
			$(MtCO_2 yr^{-1})$	(km)	
Cortez	USA	Kinder Morgan	19.3	808	1984
Sheep Mountain	USA	BP Amoco	9.5	660	-
Bravo	USA	BP Amoco	7.3	350	1984
Canyon Reef Carriers	USA	Kinder Morgan	5.2	225	1972
Val Verde	USA	Petrosource	2.5	130	1998
Bati Raman	Turkey	Turkish Petroleum	1.1	90	1983
Weyburn USA & Gasif		Gasification Co.	5	328	2000
	Canada				
Total			49.9	2591	

 Table 1 Existing long-distance CO2 pipelines

Operations

Operational aspects of pipelines are divided into three areas: daily operations, maintenance, and health, safety and environment.

Operations include daily maintenance, scheduled planning and policies for inspecting, maintaining and repairing all equipment on the line and the pipeline itself, as well as supporting the line and pipeline. This equipment and support includes valves, compressors, pumps, tanks, rights of way, public signs and line markers as well as periodic pipeline flyovers.

Long-distance pipelines are instrumented at intervals so that the flow can be monitored. The monitoring points, compressor stations and block valves are tied back to a central operations centre. Computers control much of the operation, and manual intervention is necessary only in unusual upsets or emergency conditions. The system has inbuilt redundancies to prevent loss of operational capability if a component fails. Pipelines are cleaned and inspected by "pigs", piston-like devices driven along the line by the gas pressure. Pigs have reached a high level of sophistication, and can measure internal corrosion, mechanical deformation, external corrosion, the precise position of the line, and the development of spans in underwater lines. Further functionality will develop as pig technology evolves, and there is no reason why pigs used for hydrocarbon pipelines should not be used for carbon dioxide.

Pipelines are also monitored externally. Land pipelines are inspected from the air, at intervals agreed between the operator and the regulatory authorities. Inspection from the air detects unauthorized excavation or construction before damage occurs. Currently, underwater pipelines are monitored by remotely operated vehicles, small unmanned submersibles that move along the line and make video records, and in the future, by autonomous underwater vehicles that do not need to be connected to a mother ship by a cable. Some pipelines have independent leak detection systems that find leaks acoustically or by measuring chemical releases, or by picking up pressure changes or small changes in mass balance. This technology is available and routine.

Marine transportation system

Carbon dioxide is continuously captured at the plant on land, but the cycle of ship transport is discrete, and so a marine transportation system includes temporary storage on land and a loading facility. The capacity, service speed, number of ships and shipping schedule will be planned, taking into consideration, the capture rate of CO_2 , transport distance, and social and technical restrictions. This issue is, of course, not specific to the case of CO_2 transport; CO_2 transportation by ship has a number of similarities to liquefied petroleum gas (LPG) transportation by ship.

What happens at the delivery point depends on the CO_2 storage system. If the delivery point is onshore, the CO_2 is unloaded from the ships into temporary storage tanks. If the delivery point is offshore – as in the ocean storage option – ships might unload to a platform, to a floating storage facility (similar to a floating production and storage facility routinely applied to offshore petroleum production), or directly to a storage system.

Risk, safety and monitoring

Pipelines and marine transportation systems have an established and good safety record. Comparison of CO_2 systems with these existing systems for long-distance pipeline transportation of gas and oil or with marine transportation of oil, yields that risks should be comparable in terms of failure and accident rates.

The incidence of failure is relatively small, between $(1..3)10^{-4}$ /km.yr. Most of the incidents refer to very small pipelines, less than 100 mm in diameter, principally applied to gas distribution systems. The failure incidence for 500 mm and larger pipelines is very much lower, below 5.10^{-5} / km.year. These figures cover many kinds of incidents, not all of them serious, and there is substantial variation between pipelines, reflecting factors such as system age and inspection frequency.

For western European oil pipelines, the incident frequency was 0.0003 km⁻¹yr⁻¹. The corresponding figure for US onshore gas pipelines was 0.00011 km⁻¹yr⁻¹ for the 1986-2002 period, defining an incident as an event that released gas and caused death, inpatient hospitalization or property loss of 50.000 USD: this difference in reporting threshold is thought to account for the difference between European and US statistics.

However, unlike oil and gas, CO_2 does not form flammable or explosive mixtures with air. Existing CO_2 pipelines are mainly in areas of low population density, which would also tend to result in lower average impacts. Preventative measures such as increasing the depth of cover and use of concrete barriers above a pipeline and warning tape can greatly reduce the risk. For example, increasing cover from 1 m to 2 m reduces the damage frequency by a factor of 10 in rural areas and by 3,5 in suburban areas.

Carbon dioxide leaking from a pipeline forms a potential physiological hazard for humans and animals. The consequences of CO_2 incidents can be modeled and assessed on a site-specific basis using standard industrial methods, taking into account local topography, meteorological conditions, population density and other local conditions.

A property of CO_2 that needs to be considered when selecting a pipeline route is the fact that CO_2 is denser than air and can therefore accumulate to potentially dangerous concentrations in low lying areas. Any leak transfers CO_2 to the atmosphere. If substantial quantities of impurities, particularly H_2S , are included in the CO_2 , this could affect the potential impacts of a pipeline leak or rupture. The exposure threshold at which H_2S is immediately dangerous to life or health is 100 ppm, compared to 40.000 ppm for CO_2 .

If CO_2 is transported for significant distances in densely populated regions, the number of people potentially exposed to risks from CO_2 transportation facilities may be greater than the number exposed to potential risks from CO_2 capture and storage facilities. Public concerns about CO_2 transportation may form a significant barrier to large-scale use of CCS. A gathering system would be needed if CO_2 were brought from distributed sources to a trunk pipeline, and for some storage options a distribution system would also be needed: these systems would need to be planned and executed with the same regard for risk outlined here.

2.4 CO₂ Storage

The subsurface is the Earth's largest carbon reservoir, where the vast majority of the world's carbon is held in coals, oil, gas organic-rich shale and carbonate rocks. Geological storage of CO_2 has been a natural process in the Earth's upper crust for hundreds of millions of years. Carbon dioxide derived from biological activity, igneous activity and chemical reactions between rocks and fluids accumulates in the natural subsurface environment as carbonate minerals, in solution or in a gaseous or supercritical form, either as a gas mixture or as pure CO_2 .

2.4.1 Underground geological storage

CO₂ storage mechanisms in geological formations

The effectiveness of geological storage depends on a combination of physical and geochemical trapping mechanisms. The most effective storage sites are those where CO_2 is immobile because it is trapped permanently under a thick, low-permeability seal or is converted to solid minerals or is adsorbed on the surfaces of coal micro pores or through a combination of physical and chemical trapping mechanisms.

Physical trapping: stratigraphic and structural

Initially, physical trapping of CO_2 below low-permeability seals (caprocks), such as very-low-permeability shale or salt beds, is the principal means to store CO_2 in geological formations. In some high latitude areas, shallow gas hydrates may conceivably act as a seal. Sedimentary basins have such closed, physically bound traps or structures, which are occupied mainly by saline water, oil and gas. Structural traps include those formed by folded or fractured rocks. Faults can act as permeability barriers in some circumstances and as preferential pathways for fluid flow in other circumstances.

Stratigraphic traps are formed by changes in rock type caused by variation in the setting where the rocks were deposited. Both of these types of traps are suitable for CO_2 storage, although, care must be taken not to exceed the allowable overpressure to avoid fracturing the caprock or re-activating faults.



Fig. 3 Underground geological storage

Physical trapping: hydrodynamic

Hydrodynamic trapping can occur in saline formations that do not have a closed trap, but where fluids migrate very slowly over long distances. When CO_2 is injected into a formation, it displaces saline formation water and then migrates buoyantly upwards, because it is less dense than the water. When it reaches the top of the formation, it continues to migrate as a separate phase until it is trapped as residual CO_2 saturation or in local structural or stratigraphic traps within the sealing formation. In the longer term, significant quantities of CO_2 dissolve in the formation water and then migrate with the groundwater.

Where the distance from the deep injection site to the end of the overlying impermeable formation is hundreds of kilometres, the time scale for fluid to reach the surface from the deep basin can be millions of years.

Geochemical trapping

Carbon dioxide in the subsurface can undergo a sequence of geochemical interactions with the rock and formation water that will further increase storage capacity and effectiveness. First, when CO_2 dissolves in formation water, a process commonly called solubility trapping occurs. The primary benefit of solubility trapping is that once CO_2 is dissolved, it no longer exists as a separate phase, thereby eliminating the buoyant forces that drive it upwards. Next, it will form ionic species as the rock dissolves, accompanied by a rise in the pH. Finally, some fraction may be converted to stable carbonate minerals (mineral trapping), the most permanent form of geological storage. Mineral trapping is believed to be comparatively slow, potentially taking a thousand years or longer. Nevertheless, the permanence of mineral storage, combined with the potentially large storage capacity present in some geological settings, makes this a desirable feature of long term storage. Dissolution of CO_2 in formation waters can be represented by the chemical reaction:

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO3^{2-} + 2H^+.$$

The CO_2 solubility in formation water decreases as temperature and salinity increase. Dissolution is rapid when formation water and CO_2 share the same pore space, but once the formation fluid is saturated with CO_2 , the rate slows and is controlled by diffusion and convection rates. CO_2 dissolved in water produces a weak acid, which reacts with the sodium and potassium basic silicate or calcium, magnesium and iron carbonate or silicate minerals in the reservoir or formation to form bicarbonate ions by chemical reactions approximating to:

3 K-feldspar + $2H_2O$ + $2CO_2 \leftrightarrow$ Muscovite + 6 Quartz + 2K++ $2HCO_3$

Reaction of the dissolved CO2 with minerals can be rapid (days) in the case of some carbonate minerals, but slow (hundreds to thousands of years) in the case of silicate minerals. Formation of carbonate minerals occurs from continued reaction of the bicarbonate ions with calcium, magnesium and iron from silicate minerals such as clays, micas, chlorites and feldspars present in the rock matrix.

Was estimate that over 5000 years, all the CO_2 injected into the Weyburn Oil Field will dissolve or be converted to carbonate minerals within the storage formation. Equally importantly, they show that the caprock and overlying rock formations have an even greater capacity for mineralization. This is significant for leakage risk assessment because once CO_2 is dissolved, it is unavailable for leakage as a discrete phase. Some modeling suggests more than 60% of CO_2 is trapped by residual CO_2 trapping by the end of the injection phase (100% after 1000 years), although laboratory experiments suggest somewhat lower percentages. When CO_2 is trapped at residual saturation, it is effectively immobile. However, should there be leakage through the caprock, then saturated brine may degas as it is depressurized, although the tendency of saturated brine is to sink rather than to rise.

Reaction of the CO_2 with formation water and rocks may result in reaction products that affect the porosity of the rock and the flow of solution through the pores. This possibility has not, however, been observed experimentally and its possible effects cannot be quantified.

Yet another type of fixation occurs when CO_2 is preferentially adsorbed onto coal or organic-rich shales. This has been observed in batch and column experiments in the laboratory, as well as in field experiments at the Fenn Big Valley, Canada and the San Juan Basin, USA. A rather different form of fixation can occur when CO_2 hydrate is formed in the deep ocean seafloor and onshore in permafrost regions.

Coal seams

Coal contains fractures (cleats) that impart some permeability to the system. Between cleats, solid coal has a very large number of micro pores into which gas molecules from the cleats can diffuse and be tightly adsorbed. Coal can physically adsorb many gases and may contain up to 25 normal m³ (m³ at 1 atm and 0°C) methane per tonne of coal at coal seam pressures. It has a higher affinity to adsorb gaseous CO_2 than methane. The volumetric ratio of adsorbable CO_2 :CH₄ ranges from as low as one for mature coals such as anthracite, to ten or more for younger, immature coals such as lignite. Gaseous CO_2 injected through wells will flow through the cleat system of the coal, diffuse into the coal matrix and be adsorbed onto the coal micro pore surfaces, freeing up gases with lower affinity to coal (i.e., methane).

The process of CO_2 trapping in coals for temperatures and pressures above the critical point is not well understood. It seems that adsorption is gradually replaced by absorption and the CO_2 diffuses or 'dissolves' in coal. Carbon dioxide is a 'plasticizer' for coal, lowering the temperature required to cause the transition from a glassy, brittle structure to a rubbery, plastic structure (coal softening). In one case, the transition temperature was interpreted to drop from about 400°C at 3 MPa to <30°C at 5.5 MPa CO_2 pressure. The transition

temperature is dependent on the maturity of the coal, the maceral content, the ash content and the confining stress and is not easily extrapolated to the field. Coal plasticization or softening, may adversely affect the permeability that would allow CO_2 injection. Furthermore, coal swells as CO_2 is adsorbed and/or absorbed, which reduces permeability and injectivity by orders of magnitude or more and which may be counteracted by increasing the injection pressures. Some studies suggest that the injected CO_2 may react with coal, further highlighting the difficulty in injecting CO_2 into low permeability coal.

If CO_2 is injected into coal seams, it can displace methane, thereby enhancing CBM recovery. Carbon dioxide has been injected successfully at the Allison Project and in the Alberta Basin, Canada, at depths greater than that corresponding to the CO_2 critical point. Carbon dioxide-ECBM has the potential to increase the amount of produced methane to nearly 90% of the gas, compared to conventional recovery of only 50% by reservoir-pressure depletion alone.

Coal permeability is one of several determining factors in selection of a storage site. Coal permeability varies widely and generally decreases with increasing depth as a result of cleat closure with increasing effective stress. Most CBM-producing wells in the world are less than 1000 m deep. Original screening criteria proposed in selecting favorable areas for CO_2 ECBM include:

• Adequate permeability (minimum values have not yet been determined);

• Suitable coal geometry (a few, thick seams rather than multiple, thin seams);

• Simple structure (minimal faulting and folding);

• Homogeneous and confined coal seam(s) that are laterally continuous and vertically isolated;

• Adequate depth (down to 1500 m, greater depths have not yet been studied);

• Suitable gas saturation conditions (high gas saturation for ECBM);

• Ability to dewater the formation.

However, more recent studies have indicated that coal rank may play a more significant role than previously thought, owing to the dependence on coal rank of the relative adsorptive capacities of methane and CO_2 .

If the coal is never mined or depressurized, it is likely CO_2 will be stored for geological time, but, as with any geological storage option, disturbance of the formation could void any storage. The likely future fate of a coal seam is, therefore, a key determinant of its suitability for storage and in storage site selection. Conflicts between mining and CO_2 storage are possible, particularly for shallow coals.

2.4.2 Ocean storage

Basic approach

The basic concept of intentional CO_2 storage in the ocean is to take a stream of CO_2 that has been captured and compressed and transport it to the deep ocean for release at or above the sea floor. Once released, the CO_2 would dissolve into the surrounding sea water, disperse and become part of the ocean carbon cycle.

In 1977 was proposed to inject liquefied CO_2 into the waters flowing over the Mediterranean sill into the middepth North Atlantic, where the CO_2 would be isolated from the atmosphere for centuries. This concept relies on the slow exchange of deep ocean waters with the surface to isolate CO_2 from the atmosphere. The effectiveness of ocean storage will depend on how long CO_2 remains isolated from the atmosphere.

Over the centuries and millennia, CO_2 released to the deep ocean will mix throughout the oceans and affect atmospheric CO_2 concentration. The object is to transfer the CO_2 to deep waters because the degree of isolation from the atmosphere generally increases with depth in the ocean. Proposed methods would inject the CO_2 below the thermocline for more effective storage.



Fig. 4 Ocean storage

The thermocline is the layer of the ocean between about 100 and 1000 m depth that is stably stratified by large temperature and density gradients, thus inhibiting vertical mixing. Vertical mixing rates in the thermocline can be about 1000 times less than those in the deep sea. This zone of slow mixing would act as a barrier to slow degassing of CO2 released in the deep ocean to the atmosphere.

Depending on the details of the release and local sea floor topography, the CO_2 stream could be engineered to dissolve in the ocean or sink to form a lake on the sea floor. CO_2 , dissolved in sea water at high concentrations can form a dense plume or sinking current along an inclined sea floor. If release is at a great enough depth, CO_2 liquid will sink and could accumulate on the sea floor as a pool containing a mixture of liquid and hydrate.

In the short-term, fixed or towed pipes appear to be the most viable methods for oceanic CO_2 release, relying on technology that is already largely commercially available.

Status of development

To date, injection of CO_2 into sea water has only been investigated in the laboratory, in small-scale *in-situ* experiments, and in models. Larger-scale *in-situ* experiments have not yet been carried out.

An international consortium involving engineers, oceanographers and ecologists from 15 institutions in the United States, Norway, Japan and Canada proposed an *in-situ* experiment to help evaluate the feasibility of ocean carbon storage as a means of mitigating atmospheric increases. This was to be a collaborative study of the physical, chemical, and biological changes associated with direct injection of CO_2 into the ocean. The proposed CO_2 Ocean Sequestration Field Experiment was to inject less than 60 tonnes of pure liquid carbon dioxide (CO_2) into the deep ocean near Keahole Point on the Kona coast of the Island of Hawaii. This would have been the largest intentional CO_2 release into the ocean water

column. The test was to have taken place in water about 800 m deep, over a period of about two weeks. A small steel pipeline, about 4 cm in diameter, was to have been deployed from a ship down to the injection depth, with a short section of pipeline resting on the sea floor to facilitate data collection. The liquid CO_2 was to have been dispersed through a nozzle, with CO_2 droplets briefly ascending from the injection point while dissolving into the sea water. However, the project met with opposition from environmental organizations and was never able to acquire all of the necessary permits within the prescribed budget and schedule.

Following this experience, the group developed a plan to release 5,4 tonnes of liquefied CO_2 at a depth of 800 metres off the coast of Norway, and monitor its dispersion in the Norwegian Sea. Initially, the Norwegian Pollution Control Authority granted a permit for the experiment after the public hearing procedure, but he Norwegian Environment ministry subsequently announced that the project would not go ahead.

Several smaller scale scientific experiments (less than 100 litres of CO_2) have however been executed and the necessary permits have also been issued for experiments within a marine sanctuary.

Basic behavior of CO₂ released in different forms

The near-field behavior of CO_2 released into the ocean depends on the physical properties of CO_2 and the method for CO_2 release.

The near field may be defined as that region in which it is important to take effects of CO_2 -induced density changes on the fluid dynamics of the ocean into consideration. The size of this region depends on the scale and design of CO_2 release.

Dissolved CO₂ increases the density of sea water and this affects transport and mixing.

 CO_2 plume dynamics depend on the way in which CO_2 is released into the ocean water column. CO_2 can be initially in the form of a gas, liquid, solid or solid hydrate. All of these forms of CO_2 would dissolve in sea water, given enough time.

The dissolution rate of CO_2 in sea water is quite variable and depends on the form (gas, liquid, solid, or hydrate), the depth and temperature of disposal, and the local water velocities. Higher flow rates increase the dissolution rate.

Gas. CO_2 could potentially be released as a gas above roughly 500 m depth. Below this depth, pressures are too great for CO_2 to exist as a gas. The gas bubbles would be less dense than the surrounding sea water so tend to rise towards the surface, dissolving at a radial speed of about 0.1 cm/h. In waters colder than about 9°C, a CO_2 hydrate film could form on the bubble wall. CO_2 diffusers could produce gaseous CO_2 bubbles that are small enough to dissolve completely before reaching the surface.

Liquid. Below roughly 500 m depth, CO_2 can exist in the ocean as a liquid. Above roughly 2500 m depth CO_2 is less dense than sea water, so liquid CO_2 released shallower than 2500 m would tend to rise towards the surface. Because most ocean water in this depth range is colder than 9°C, CO_2 hydrate would tend to form on the droplet wall. Under these conditions, the radius of the droplet would diminish at a speed of about 0.5 cm/h. Under these conditions a 0.9 cm diameter droplet would rise about 400 m in an hour before dissolving completely; 90% of its mass would be lost in the first 200 m. Thus, CO_2 diffusers could be designed to produce droplets that will dissolve within roughly 100 m of the depth of release. If the droplet reached approximately 500 m depth, it would become a gas bubble.

 CO_2 nozzles could be engineered to produce large droplets that would sink to the sea floor or small droplets that would dissolve in the sea water before contacting the sea floor. Natural ocean mixing and droplet motion are expected to prevent concentrations of dissolved CO_2 from approaching saturation, except near liquid CO_2 that has been intentionally placed in topographic depressions on the sea floor. *Solid.* Solid CO_2 is denser than sea water and thus would tend to sink. Solid CO_2 surfaces would dissolve in sea water at a speed of about 0.2 cm/h. Thus small quantities of solid CO_2 would dissolve completely before reaching the sea floor; large masses could potentially reach the sea floor before complete dissolution.

Hydrate. CO_2 hydrate is a form of CO_2 in which a cage of water molecules surrounds each molecule of CO_2 . It can form in average ocean waters below about 400 m depth. A fully formed crystalline CO_2 hydrate is denser than sea water and will sink. The surface of this mass would dissolve at a speed similar to that of solid CO_2 , about 0.2 cm/h and thus droplets could be produced that either dissolve completely in the sea water or sink to the sea floor. Pure CO_2 hydrate is a hard crystalline solid and will not flow through a pipe; however a paste-like composite of hydrate and sea water may be extruded, and this will have a dissolution rate intermediate between those of CO_2 droplets and a pure CO_2 hydrate.

Behavior of injected CO_2 in the near field: CO_2 -rich plumes

As it leaves the near field, CO_2 enriched water will reside at a depth determined by its density. The oceans are generally stably stratified with density increasing with depth. Parcels of water tend to move upward or downward until they reach water of the same density, and then there are no buoyancy forces to induce further motion.

The dynamics of CO_2 -rich plumes determine both the depth at which the CO_2 leaves the near-field environment and the amount of initial dilution (and consequently the amount of *p*H change).

When CO_2 is released in any form into seawater, the CO_2 can move upward or downward depending on whether the CO_2 is less or more dense than the surrounding seawater. Drag forces transfer momentum from the CO_2 droplets to the surrounding water column producing motion in the adjacent water, initially in the direction of droplet motion. Simultaneously, the CO_2 dissolves into the surrounding water, making the surrounding water denser and more likely to sink. As the CO_2 -enriched water moves, it mixes with surrounding water that is less enriched in CO_2 , leading to additional dilution and diminishing the density contrast between the CO_2 -enriched water and the surrounding water.

 CO_2 releases could be engineered to produce CO_2 plumes with different characteristics. Modeling studies indicate that releases of small droplets at slow rates produce smaller plumes than release of large droplets at rapid rates. Where CO_2 is denser than seawater, larger droplet sizes would allow the CO_2 to sink more deeply. CO_2 injected at intermediate depths could increase the density of CO_2 -enriched sea water sufficiently to generate a sinking plume that would carry the CO_2 into the deep ocean. Apparent coriolis forces would operate on such a plume, turning it towards the right in the Northern Hemisphere and towards the left in the Southern Hemisphere. The channeling effects of submarine canyons or other topographic features could help steer dense plumes to greater depth with minimal dilution

Behavior of injected CO_2 in the far field

The far field is defined as the region in which the concentration of added CO_2 is low enough such that the resulting density increase does not significantly affect transport, and thus CO_2 may be considered a passive tracer in the ocean. Typically, this would apply within a few kilometres of an injection point in midwater, but if CO_2 is released at the sea floor and guided along topography, concentration may remain high and influence transport for several tens of kilometres. CO_2 is transported by ocean currents and undergoes further mixing and dilution with other water masses. Most of this mixing and transport occurs along surfaces of nearly constant density, because buoyancy forces inhibit vertical mixing in a stratified fluid. Over time, a release of CO_2 becomes increasingly diluted but affects ever greater volumes of water. The concept of ocean injection from a moving ship towing a trailing pipe was developed in order to minimize the local environmental impacts by accelerating the dissolution and dispersion of injected liquid CO_2 . A moving ship could be used to produce a sea water plume with relatively dilute initial CO_2 concentrations. In the upper ocean where CO_2 is less dense than seawater, nozzles engineered to produce mm-scale droplets would generate CO_2 plumes that would rise less than 100 m.

Ocean general circulation models have been used to predict changes in ocean chemistry resulting from the dispersion of injected CO₂ for hypothetical examples of ocean storage estimated that injection into the deep ocean at a rate of 0,37 GtCO₂/yr for 100 years would produce a $\Delta pH < -0.3$ over a volume of sea water equivalent to 0.01% or less of total ocean volume. In this example, for each GtCO₂ released to the deep ocean, less than about 0.0001%, 0.001% and 0.01% of the ocean volume has ΔpH of less than -0.3, -0.2, and -0.1 *p*H units respectively. Simulations, in which ocean injection provided 10% of the total mitigation effort, resulted in significant changes in ocean *p*H in year 2100 over roughly 1% of the ocean volume. By year 2300, injection rates have slowed but previously injected carbon has spread through much of the ocean resulting in an additional 0.1 *p*H unit reduction in ocean *p*H over most of the ocean.

Behavior of CO₂ lakes on the sea floor

Long-term storage of carbon dioxide might be more effective if CO_2 were stored on the sea floor in liquid or hydrate form below 3000 meters, where CO_2 is denser than sea water. Liquid carbon dioxide could be introduced at depth to form a lake of CO_2 on the sea floor. Alternatively, CO_2 hydrate could be created in an apparatus designed to produce a hydrate pile or pool on the sea floor. To date, the concept of CO_2 lakes on the sea floor has been investigated only in the laboratory, in small-scale (tens of liters) *in-situ* experiments and in numerical models. Larger-scale *in-situ* experiments have not yet been carried out.

Liquid or hydrate deposition of CO_2 on the sea floor could increase isolation, however in the absence of a physical barrier the CO_2 would dissolve into the overlying water. In this aspect, most sea floor deposition proposals can be viewed as a means of 'time-delayed release' of CO_2 into the ocean. Thus, many issues relevant to sea floor options, especially the far-field behavior, are discussed in sections relating to CO_2 release into the water column.

 CO_2 released onto the sea floor deeper than 3 km is denser than surrounding sea water and is expected to fill topographic depressions, accumulating as a lake of CO_2 over which a thin hydrate layer would form. This hydrate layer would retard dissolution, but it would not insulate the lake from the overlying water. The hydrate would dissolve into the overlying water (or sink to the bottom of the CO_2 lake), but the hydrate layer would be continuously renewed through the formation of new crystals. Laboratory experiments and small deep ocean experiments show that deep-sea storage of CO_2 would lead to CO_2 hydrate formation (and subsequent dissolution).

Predictions of the fate of large-scale CO_2 lakes rely on numerical simulations because no large-scale field experiments have yet been performed. For a CO_2 lake with an initial depth of 50 m, the time of complete dissolution varies from 30 to 400 years depending on the local ocean and sea floor environment.

The time to dissolve a CO_2 lake depends on its depth, complex dynamics of the ocean bottom boundary layer and its turbulence characteristics, mechanism of CO_2 hydrate dissolution, and properties of CO_2 in solution. The lifetime of a CO_2 lake would be longest in relatively confined environments, such as might be found in some trenches or depressions with restricted flow.

Strong flows have been observed in trenches. Nevertheless, simulation of CO_2 storage in a deep trench indicates that the bottom topography can weaken vertical momentum and mass transfer, slowing the CO_2 dissolution rate. In a quiescent environment, transport would

be dominated by diffusion. Double-diffusion in the presence of strong stratification may produce long lake lifetimes. In contrast, the flow of sea water across the lake surface would increase mass transfer and dissolution. For example, CO_2 lake lifetimes of >10.000 yr for a 50 m thick lake can be estimated from the dissolution rate of 0.44 cm/yr for a quiescent, purely diffusive system. A mean horizontal velocity of 0,05 m/s would cause the CO_2 lake to dissolve >25 times more rapidly.

Biological impacts and risk

Overall, there is limited knowledge of deep-sea population and community structure and of deep-sea ecological interactions. Thus the sensitivities of deep ocean ecosystems to intentional carbon storage and the effects on possibly unidentified goods and services that they may provide remain largely unknown.

Most ocean storage proposals seek to minimize the volume of water with high CO_2 concentrations either by diluting the CO_2 in a large volume of water or by isolating the CO_2 in a small volume (e.g., in CO_2 lakes). Nevertheless, if deployed widely, CO_2 injection strategies ultimately will produce large volumes of water with somewhat elevated CO_2 concentrations. Because large amounts of relatively pure CO_2 have never been introduced to the deep ocean in a controlled experiment, conclusions about environmental risk must be based primarily on laboratory and small-scale *in-situ* experiments and extrapolation from these experiments using conceptual and mathematical models. Natural analogues can be relevant, but differ significantly from proposed ocean engineering projects.

Compared to the surface, most of the deep sea is stable and varies little in its physiochemical factors over time. The process of evolutionary selection has probably eliminated individuals apt to endure environmental perturbation. As a result, deep-sea organisms may be more sensitive to environmental disturbance than their shallow water cousins.

Ocean storage would occur deep in the ocean where there is virtually no light and photosynthesizing organisms are lacking, thus the following discussion primarily addresses CO_2 effects on heterotrophic organisms, mostly animals. The diverse fauna that lives in the waters and sediments of the deep ocean can be affected by ocean CO_2 storage, leading to change in ecosystem composition and functioning. Thus, the effects of CO_2 need to be identified at the level of both the individual (physiological) and the ecosystem.

As already described, introduction of CO_2 into the ocean either directly into sea water or as a lake on the sea floor would result in changes in dissolved CO_2 near to and down current from a discharge point. Dissolving CO_2 in sea water increases the partial pressure of CO_2 (pCO_2 , expressed as a ppm fraction of atmospheric pressure, equivalent to µatm), causes decreased pH (more acidic) and decreased CO_3^{2-} concentrations (less saturated). This can lead to dissolution of CaCO₃ in sediments or in shells of organisms.

Bicarbonate (HCO₃⁻) is then produced from carbonate (CO₃^{2–}). The spatial extent of the waters with increased CO₂ content and decreased *p*H will depend on the amount of CO₂ released and the technology and approach used to introduce that CO₂ into the ocean.

On evolutionary time scales most extant animal life has adapted to, on average, low ambient CO_2 levels. Accordingly, extant animal life may rely on these low pCO_2 values and it is unclear to what extent species would be able to adapt to permanently elevated CO_2 levels. Exposure to high CO_2 levels and extremely acidic water can cause acute mortality, but more limited shifts in CO_2 , pH, and carbonate levels can be tolerated at least temporarily. Studies of shallow water organisms have identified a variety of physiological mechanisms by which changes in the chemical environment can affect fauna. These mechanisms should also apply to organisms living in the deep ocean. However, knowing physiological mechanisms alone does not enable full assessment of impacts at ecosystem levels. Long-term effects, for intervals greater than the duration of the reproduction cycle or the lifespan of an individual, may be overlooked, yet may still drastically change an ecosystem. Species living in the open ocean are exposed to low and relatively constant CO_2 levels, and thus may be sensitive to CO_2 exposure. In contrast, species dwelling in marine sediments, especially in the intertidal zone, are regularly exposed to CO_2 fluctuations and thus may be better adapted to high and variable CO_2 concentrations. Physiological mechanisms associated with CO_2 adaptation have been studied mostly in these organisms.

They respond to elevated CO_2 concentrations by transiently diminishing energy turnover. However, such responses are likely become detrimental during long-term exposure, as reduced metabolism involves a reduction in physical activity, growth, and reproduction. Overall, marine invertebrates appear more sensitive than fish.