CO$_2$ storage in geological media: Role, means, status and barriers to deployment

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Abstract

Carbon dioxide capture and geological storage is an enabling technology that will allow the continued use well into this century of fossil fuels, mainly coal, for power generation and combustion in industrial processes because they are relatively abundant, cheap, available and globally distributed, thus enhancing the security and stability of energy systems. Geological media suitable for CO$_2$ storage through various physical and chemical trapping mechanisms must have the necessary capacity and injectivity, and must confine the CO$_2$ and impede its lateral migration and/or vertical leakage to other strata, shallow potable groundwater, soils and/or atmosphere. Such geological media are mainly oil and gas reservoirs and deep saline aquifers that are found in sedimentary basins. Storage of gases, including CO$_2$, in these media has been demonstrated on a commercial scale by enhanced oil recovery operations, natural gas storage and acid gas disposal. Some of the risks associated with CO$_2$ capture and geological storage are similar to, and comparable with, any other industrial activity for which extensive safety and regulatory frameworks are in place. Specific risks associated with CO$_2$ storage relate to the operational (injection) phase and to the post-operational phase, of which the risks of most concern are those posed by the potential for acute or chronic CO$_2$ leakage from the storage site. Notwithstanding the global climate effect of CO$_2$ returning to the atmosphere, the local risks to health and safety, environment and equity need to be properly assessed and managed. Currently there are very few operations in the world where CO$_2$ is injected and stored in the ground, mostly if not exclusively as a by-product of an operation driven by other considerations than climate change, such as oil production or regulatory requirements regarding H$_2$S. These operations show that there are no major technological barriers to CO$_2$ geological storage, and that challenges and barriers lie elsewhere. A major challenge in the implementation of CO$_2$ geological storage is the high cost of CO$_2$ capture, particularly for dilute streams like those from power plants and industrial combustion processes. There are concerns that public opinion and public's acceptance or rejection of this technology will likely affect the large-scale implementation of CO$_2$ geological storage. The current paucity of policy, legislation and a proper regulatory framework in most jurisdictions is presently the most significant barrier. The resolution of these challenges will affect the economics and financial risk of CO$_2$ geological storage and will accelerate or delay the deployment of this technology for reducing anthropogenic CO$_2$ emissions into the atmosphere.

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1. Introduction

Interpretation of the temperature record on a scale of centuries to millennia indicates a slight increase in global average annual temperatures in the last 150 years, in the order of 0.76 °C [1], and predictions are that, if continuing in a business-as-usual scenario, humankind is facing significant climate change by the end of this century as a result of continuing warming forecast to be in the range of 1.1–6.3 °C depending on emissions scenario [1]. It is very likely (>90% likelihood) and generally accepted that the main cause of the observed global warming is the increase in atmospheric concentrations of greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) [1]. This increase, noticeable since the beginning of the industrial revolution, is due to human activity in land use (agriculture and deforestation), which is the major factor in CH_4 and N_2O concentration increases, and ever increasing consumption of fossil energy resources, which is the main factor (>80%) in the increase in CO_2 concentration [1]. Of all the greenhouse gases, CO_2, whose atmospheric concentrations have risen from pre-industrial levels of 280 ppm to 380 ppm in 2005 [1], is the most important greenhouse gas, being responsible for about two-thirds of the enhanced 'greenhouse effect' [1,2]. The detailed response of the climate system to increasing CO_2 concentration in the atmosphere is uncertain because of its inherent complexity and natural variability; however, the close coupling between the carbon cycle, including CO_2 and CH_4, and climate suggests that changes in the former will be accompanied by changes in the latter [3]. Although a direct causal link between the rise in greenhouse gas concentrations in the atmosphere and global warming has not been demonstrated, significant circumstantial evidence points toward this link, which has been generally accepted by a broad segment of the scientific community (e.g., [1,4]) and by policy makers. There is also almost general acceptance that the world cannot wait for definitive answers on this subject and that preventive and mitigating actions have to take place concurrently (e.g., [3]). Thus, a major challenge in mitigating climate change effects is the reduction of CO_2 emissions to the atmosphere, which hopefully will lead to a stabilization of CO_2 concentration to no more than double the pre-industrial level at around 550 ppm (i.e., double of the pre-industrial level), for which a corresponding warming of between 2 and 4.5 °C is likely [1]. A broad portfolio of measures and actions are envisaged for reducing anthropogenic CO_2 emissions into the atmosphere. Among these CO_2 capture and storage, which entails CO_2 capture from large industrial processes, mainly power generation based on fossil fuels, and injection into deep geological formations, plays an important role [5,6]. This paper reviews the role and place of CO_2 storage in geological media, its status, and what are current challenges and barriers to implementation.

2. Role of CO_2 geological storage

There is a direct link between net CO_2 emissions (indicated by carbon C) and human population, P, economic development (indicated by the gross domestic product, GDP), energy production, E, carbon-based fuels used for energy production, C, and CO_2 sinks, S_{CO_2}, as expressed by Kaya's identity [7] modified to include CO_2 sinks [8]:

$$C = P \frac{GDP}{P} \frac{E}{GDP} \frac{C}{E} - S_{CO_2}. \tag{1}$$

The above relationship shows that the forces that drive the increase in anthropogenic CO_2 emissions are population increase, per capita GDP (also known as "affluence level"), the energy intensity of the economy (E/GDP) and the carbon intensity of the energy system (C/E). The term E/GDP reflects the sectorial make-up of the economy (i.e., how much energy-intensive industry is present), climate effects (i.e., how much heating and/or cooling is needed) and the energy efficiency of the economy. Examination of relation (1) indicates that, in principle, there are five ways to reduce atmospheric emissions of anthropogenic CO_2, of which the first two, a reduction in population and/or decline in economic output and standards of living, are unacceptable as policy instruments. The next two terms show that increasing energy efficiency and conservation (i.e., reducing the third term) and switching from fossil fuels to other forms of energy (e.g., nuclear and renewables such as solar, wind and hydro), or from fuels heavy in carbon, such as coal, to fuels light in carbon, such as gas (i.e., reducing the fourth term), are means for reducing anthropogenic CO_2 emissions that depend mainly on technology and economics. The fifth term, increasing the capacity and uptake rate of CO_2 sinks, depends significantly on technology, policy, economics and public support.

Historical evidence shows that: (1) population decrease and/or economic decline, like after the two world wars or in Russia after the collapse and breakdown of the Soviet Union, are geographically localized and temporally limited, and (2) generally, although the CO_2 emission intensity of the economy (C/GDP) decreased in the last 150 years, overall CO_2 emissions increased as a result of population and economy growth at a relatively higher rate (for example, in North America the first two terms in relation (1) increased on aggregate at an annualized rate of 3% while the next two terms decreased at a combined annualized rate of only 1.5%). If the trend of the past

100 years of 1% annual improvement in global energy efficiency (*GWP/E*, where *GWP* is Gross World Product) is maintained, then anthropogenic CO_2 emissions will increase as a result of population increase, economic development and increase in living standards (affluence), particularly in developing economies, foremost in China and India, which, in terms of CO_2 emissions, are over-taking USA, currently the largest CO_2 emitter in the world. The potential for improving the efficiency of converting primary energy (e.g., fossil fuels, nuclear) into useful energy (e.g., heat, electricity) is thermodynamically limited [9], thus the efficiency of energy end-use has to be increased significantly. However, even with aggressive research and development, widespread technology diffusion and re-moval of market imperfections, possible large improve-ments ($\geqslant$ 5-fold) in energy efficiency this century will be more than dwarfed by the 12- to 26-fold increase in global world economy (GWP) [10].

Reducing the carbon intensity of the energy system (*C/E*) can be achieved by four means [11]: (a) switching from carbon-rich fossil fuels such as coal to hydrogen-rich ones such as natural gas; (b) decarbonizing fossil fuels to generate hydrogen, a carbon-free energy carrier (but this option works only if the CO_2 is captured and stored); (c) switching to renewable solar energy sources (biomass, wind, hydroelectric, solar-heating, solar–thermal and solar–photovoltaic); and (d) switching to nuclear energy generation. However, a major switch from coal-fired power generation to natural gas, like in the UK in the 1990s, has a limited temporal impact and it will be short-lived because of limited supply of natural gas. Furthermore, the need for energy security is pushing countries rich in coal, such as China, USA, India and South Africa, towards increased rather than reduced use of coal beyond power generation, to coal-to-liquids and coal gasification to produce synthetic oil and gas. Similarly, production of synthetic oil from tar sands and oil shales in Canada and the USA will increase. In all these cases of partial or total decarbonization (synthetic oil and gas, and hydrogen), CO_2 is generated as a byproduct and has to be dealt with through the sink term of relation (1).

The theoretical potential of renewable energy sources exceeds by one order of magnitude the current worldwide energy consumption [10], but the barriers to rapid transition from fossil fuels to renewables are economic (much higher cost than fossil fuels) and political. In addition, significant and unavoidable negative environ-mental impacts will be associated with the use of renew-ables on the scale needed to satisfy the growing energy demand [11,12]. This is because many of the solar-based energy flows and stocks play crucial roles in shaping the environment and a large-scale intervention and diversion of a significant fraction of these will have adverse effects [13], although maybe not as obvious as those caused by climate change. In addition, expansion of biomass produc-tion will lead to conflicts with other land and water uses, food production and forestation [14,15], the expansion for

hydroelectric power generation is rather limited, and public resistance to wind energy is increasing [11]. Furthermore, given the intermittent and unpredictable nature of most forms of solar energy and the great difficulty in storing the energy thus generated, back-up base systems based on either fossil fuels or nuclear will have to be installed, raising significantly the cost of energy production from renewables.

Nuclear energy alone cannot be a long-term solution to global climate change because of (1) concerns about nuclear waste disposal, high cost, security concerns relating to weapons proliferation if fissionable plutonium and/or uranium are produced in breeder reactors, (2) public opposition, and (3) limited proven and recoverable reserves of uranium [11,15]. In addition, nuclear energy cannot be stored, and currently cannot be used in transportation unless it is converted into fuel, electricity or heat. As a result of all these limitations in alternative energy produc-tion, forecasts indicate that fossil fuels, which currently provide ~80% of the world's energy, will increase their share to ~85% by the middle of this century [5,6] due to their relative low cost compared with other forms of energy, versatility and ease of storage.

The forecast emissions gap created by the increase in population (*P*), global standard of living (*GWP/P*), and carbon intensity of the energy system (*C/E*) on one side, and the increase in energy efficiency and conservation (*GWP/E*) on the other side can be partially or totally covered by the artificial increase in the capacity and uptake rate of CO_2 sinks S_{CO_2}. Carbon sequestration involves either the diffuse removal of CO_2 from the atmosphere, *after* its release, by terrestrial or marine photosynthesis and subsequent long-term storage of the carbon-rich biomass, or the capture of CO_2 emissions at source *prior* to potential release, and storage in deep oceans or geological media, or through surface mineral carbonation (known collectively as carbon capture and storage, CCS).

Terrestrial CO_2 sequestration involves the photosyn-thetic fixation of CO_2 by plants and soils, and its capacity and uptake rate *might* be increased by reforestation and aforestation, and changing soil and land management practices. However, this would be in direct conflict with population increase and agricultural land use, notwith-standing that it has limited CO_2 mitigation potential because of its relatively small *capacity* of 200 Gt C [10,11]. Recent research has shown that increasing forestation may decrease the CO_2 uptake rate by soils, leading to an approximately neutral outcome [16], and that forests have much smaller storage capacity than previously thought because only the tropical forests, and not the temperate and boreal ones, are taking up CO_2 [17]. In addition, the retention time of terrestrial systems is in the order of decades—basically their use amounts to "buying time" to develop other sequestration technologies or make the transition to zero-emissions economy. Ocean fertilization involves the addition of micronutrients to stimulate the growth of phytoplankton, a fraction of which will sink to

the ocean floor when dead and will be incorporated into deep-sea sediments. Sequestration of significant CO_2 emissions would require extremely large ocean areas and would likely have detrimental consequences to marine ecosystems and biogeochemical cycles [18,19]. Furthermore, deep ocean circulation would bring the CO_2 back to the atmosphere on a time-scale of several centuries [20].

In contrast to natural sinks that capture CO_2 after its release into the atmosphere, CCS is a process that consists of separating and capturing CO_2 from large stationary sources (e.g., power plants, refineries, etc.), transporting it to a storage site, and isolating it from the atmosphere for long periods of time, in the order of centuries to millennia and up to millions of years. Three means of CCS have been considered to date: geological storage, ocean storage and surface mineral carbonation [21]. The later involves converting CO_2 to solid inorganic carbonates using chemical reactions, in an accelerated process similar to natural weathering. It depends on the existence and availability of certain minerals like serpentine and olivine, requires mining on a large-scale (with all the associated environmental impacts) and large amounts of energy for crushing and milling the mineral and heating for speeding up the chemical process. It then requires transportation and storage of the large amounts of carbonate rocks that result from this process. This process would require 1.6–3.7 t of mineral and produce 2.6–4.7 t of carbonate rock to be disposed for each tonne of stored CO_2 [21]. The availability of rocks for mineral carbonation, the high energy penalty and environmental impact, and the high cost involved with this technology exclude it from consideration for large-scale implementation at least for the near to medium term.

Ocean storage of CO_2 consists of injecting CO_2 at great depths where it will dissolve or will form hydrates or heavier-than-water plumes that will sink at the bottom of the ocean (e.g., [22]), thus removing the injected CO_2 from the atmosphere for several hundred years [21]. The rationale is to accelerate the transfer of CO_2 from the atmosphere to the deep ocean, a process that occurs naturally at an estimated rate of 2 Gt C/yr and that will lead anyway to the transfer of CO_2 to the oceans over a 1000-year period [23]. However, ocean disposal involves issues of poorly understood physical and chemical processes, storage efficiency, cost, technical feasibility and environmental impact, while the technology of disposing of CO_2 from either ships or deep pipelines is only in the development stage. Injection of only a few Gt CO_2 would produce a measurable change in ocean chemistry (pH) in the injection region, whereas injection of hundreds of Gt CO_2 would eventually produce measurable changes over the entire ocean volume, with corresponding consequences on marine life [21,24]. In addition, ocean circulation and processes may bring to the fore legal, political and international limitations to large-scale ocean disposal of CO_2, notwithstanding strong opposition from the public and from environmental non-governmental organizations

(E-NGOs). Thus, CO_2 ocean storage is an option, that, although still pursued scientifically and experimentally in a few countries, is not seriously considered from economic and policy points of view.

In contrast to surface mineral carbonation and ocean storage, the geological storage of CO_2 currently represents the best and likely the only short-to-medium term option for significantly enhancing CO_2 sinks, thus reducing net carbon emissions into the atmosphere. This option is indeed the only option for landlocked regions that are major energy and power producers, such as the provinces of Alberta and Saskatchewan in Canada and the Ohio valley in the USA. In this context, the meaning of *carbon capture and geological storage (CCGS)* is the *removal of CO_2 directly from anthropogenic sources (capture) and its disposal in geological media, either permanently (sequestration) or for significant time periods (storage)*. This technology could be applied immediately as a result of the experience gained in other industries, particularly in oil and gas exploration and production, natural gas storage and deep disposal of liquid wastes and acid gas. Furthermore, the capacity for CO_2 storage in geological media is significant, although unevenly distributed around the globe, and the likely retention time is more than adequate, being in the order of millennia to millions of years [21]. As a result of these inherent advantages, CO_2 geological storage is currently being actively pursued in North America, northern Europe and Australia. By making possible the continued use of coal as a fuel for power generation and the production of synthetic fuels and hydrogen, CCGS is a technology that contributes to the stability and security of energy systems in North America and elsewhere, and *could* provide a bridge from the current fossil-fuel-based energy systems to a hydrogen-based economy envisaged for late this century [5,25].

The storage of CO_2 in geological media shares many similar features with oil and gas accumulations in hydrocarbon reservoirs and with methane in coal beds [26]. From a technological point of view there is extensive experience, especially in the oil and gas industry, with various CCGS components. Capture and separation, mainly amine-based, is practiced at oil and gas processing facilities, as well as at selected chemical processing facilities. Large-scale CO_2 transportation systems have been developed in the USA for CO_2 enhanced oil recovery (EOR) operations, and injection of natural gas, CO_2 and/or acid gases is extensively practiced in North America and Europe. Geophysical surveying for the detection in the subsurface of fluids other than water (i.e., oil and gas) has been long-practiced in oil and gas exploration. However, although the individual components of this emerging technology all exist separately, they have not been implemented in an integrated CCGS system, and certainly not on the scale needed to reduce significantly CO_2 emissions in the atmosphere.

Although various climate change mitigation options have different spatial and temporal ranges of applicability, relation (1) and the previous discussion show that a

reduction of anthropogenic CO_2 emissions into the atmosphere can be achieved only through the broad and deep application, in developed and developing countries alike, of a portfolio of measures that includes significant technological breakthroughs to increase energy efficiency, increasing as much as possible the share of non-fossil forms of energy production, and increasing the size and intake rate of CO_2 sinks, particularly carbon capture and storage in geological media [5,27–29]. In this context, the focus of this review is the geological storage component of the emerging CCGS technology.

3. Trapping mechanisms and means of CO_2 geological storage

Geological media suitable for CO_2 storage must have the following characteristics:

- capacity, to accept the intended volume of CO_2;
- injectivity, to take in CO_2 at the rate that it is supplied from the CO_2 emitter(s); and
- confinement, to prevent the migration and leakage of the buoyant and mobile CO_2 from the storage space to other places in the subsurface, to shallow potable groundwater and/or to the surface.

Geological media found in sedimentary basins can posses these characteristics, because generally only sandstone and carbonate rocks have the porosity needed to provide storage capacity and the permeability required for injectivity, while confining low-permeability shales and evaporites (known also as caprock in the petroleum industry), such as salt beds and anhydrites, provide a primary physical barrier to CO_2 migration and/or leakage out of the intended storage unit (in this context, migration is defined as lateral movement within the injection stratum, while leakage is defined as upward flow across strata). Coals, which can also be used for CO_2 storage due to their adsorption properties (see below), are found in sedimentary basins too. Crystalline, metamorphic and volcanic rocks, such as granite and basalts, are not suitable for CO_2 storage because they generally do not meet the above requirements. Some research is focusing on the possibility of using basalts for CO_2 storage [30], but this work is only in early stages of proof-of-concept.

Carbon dioxide can be stored in geological media by various means through a variety of physical and chemical trapping mechanisms [31] as a result of its properties at the pressure and temperature conditions found in Earth's subsurface. At normal standard conditions CO_2 is a gas with a density of $1.872 \, \text{kg/m}^3$ (slightly heavier than air). The critical point for CO_2 is $T_c = 31.1 \, °C$ and $P_c = 7.38 \, \text{MPa}$ (equivalent to 738 m hydrostatic column of water), where T and P are temperature and pressure, respectively, and the subscript c denotes the critical point. For $T < T_c$ and pressures above the vaporization curve, CO_2 is a liquid, while for temperatures and pressures above

the critical point CO_2 is a supercritical fluid (Fig. 1a). At supercritical conditions, a fluid has different properties than in either the liquid or gaseous phase, but the most notable and relevant in this case are the high-density characteristic of liquids, and occupying the entire available volume, like a gas. Since both temperature and pressure increase with depth in the subsurface, but have opposite effects on CO_2 density (Fig. 2a), the latter increases rapidly with depth and then stabilizes or even decreases, depending on the geothermal regime (Fig. 2b) [35]. Fig. 2 shows that in most cases CO_2 injected deep in the subsurface will be a buoyant fluid lighter than water. Only in the case of overpressured conditions approaching lithostatic could CO_2 reach densities greater than water [35]. Other relevant CO_2 characteristics are its affinity to coal (Fig. 1b), which is greater than that of nitrogen (N_2) and CH_4 but less than that of hydrogen sulphide (H_2S) and sulphur dioxide (SO_2), and its solubility in water (Fig. 1c), which increases with increasing pressure and decreases with increasing temperature and water salinity (Fig. 1d).

In regard to oil, relevant important properties of CO_2 are its solubility in oil (approximately 10 times greater than that in water) and its miscibility with oil under certain conditions of temperature, pressure and oil type (usually light to medium oils, with API gravity greater than 25) [36,37]. If injected in an oil reservoir that meets the miscibility criteria, the miscible mixing of oil and CO_2 leads to oil swelling and also lowers oil's viscosity, allowing it to flow to producing wells. This property of the CO_2 is used in CO_2 EOR. Some of the injected CO_2 is produced together with the oil and, after separation, is re-circulated back in the system, but a significant portion of the injected CO_2, in the 40–50% range, remains in the reservoir [38,39], being permanently stored.

Physical trapping of CO_2 occurs when CO_2 is immobilized as a free gas or supercritical fluid and as a process it depends on the available storage volume. There are two types of physical trapping:

(1) static trapping of mobile CO_2 in stratigraphic and structural traps,[1] or in man-made caverns (mobile in this context means that the flow of CO_2 is impeded by a physical low-permeability barrier, and that, if a pathway is found, CO_2 will flow driven by its own buoyancy and other forces); and
(2) residual-gas trapping in the pore space at irreducible gas saturation, in which case CO_2 is immobile because of the interfacial tension between CO_2 and formation water, and flow is not possible even if a pathway is available.

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[1]Structural and stratigraphic traps refer to permeable geological media overlain and surrounded by low-permeability rock, whose shape precludes the upward and lateral movement of a buoyant fluid such as oil and gas (and in this case, CO_2). Structural traps are the result of crust movement (faults and folds), while stratigraphic traps are the result of depositional and/or diagenetic processes.
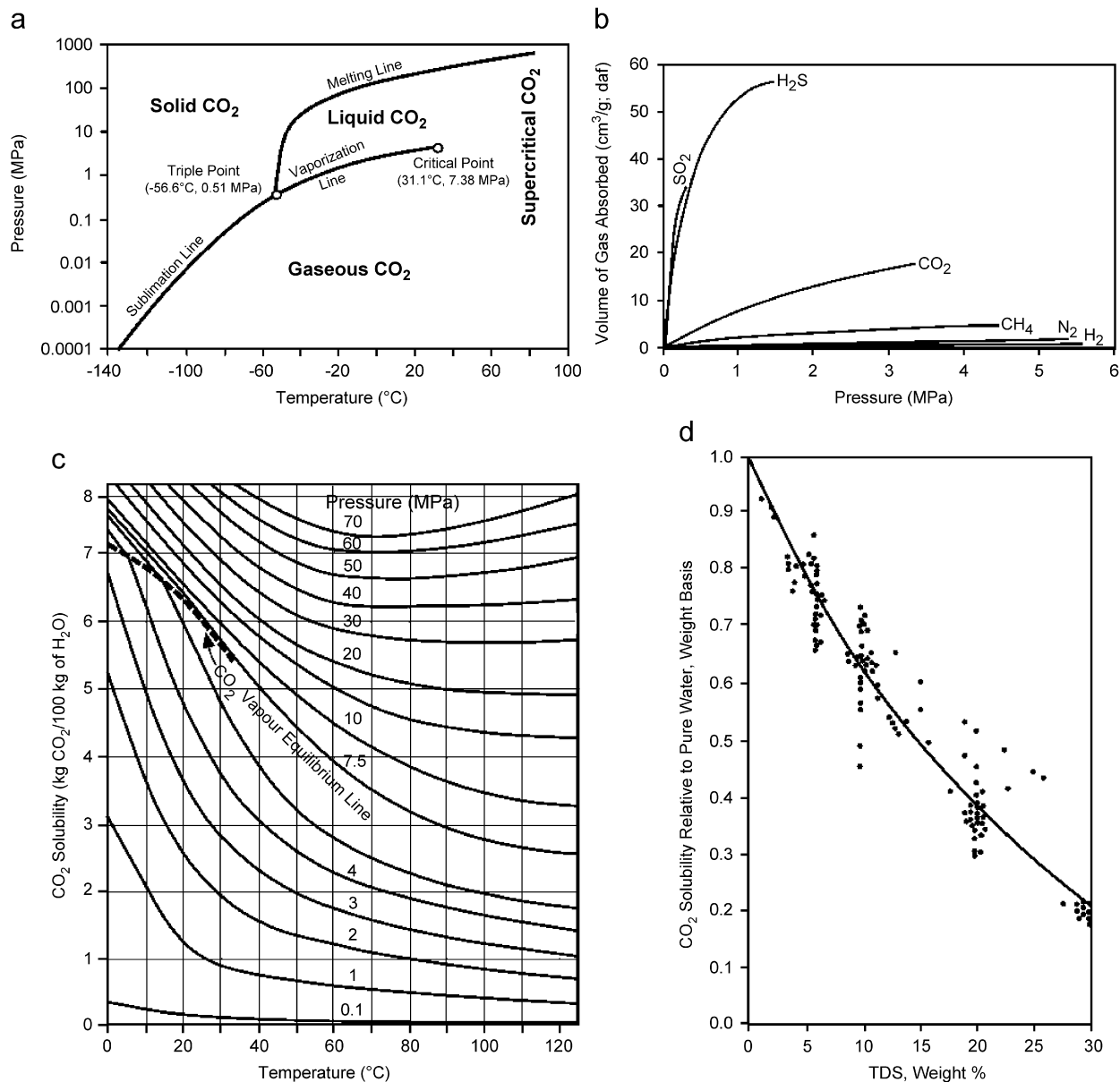
Fig. 1. Relevant characteristics of CO_2: (a) phase diagram; (b) adsorption on coal (from [32]); (c) solubility in fresh water (from [33]); and (d) decrease in solubility with increasing water salinity (from [34]).

Residual-gas trapping is based on disconnected gas bubbles (Fig. 3a) being left in the wake of a migrating stream or plume of CO_2 (non-wetting phase) when water (wetting phase) moves back into the pore space during an imbibition cycle, after it was expelled from the pore space during the drainage cycle by the injected and/or migrating CO_2, and is due to the hysteretic properties of relative permeability[2] (Fig. 3b). During injection, CO_2 saturation increases in a drainage-like process, and vertical and lateral flow paths are created as CO_2 migrates laterally away from the injection wells and to the top of the injection aquifer due to buoyancy forces. Once injection stops, CO_2 continues to migrate upward and displace water at the leading edge of the plume, while at the trailing edge water displaces CO_2 in an imbibition-like process. A trail of residual, immobile CO_2 is left behind the plume as it migrates laterally and upward [41,42]. Thus, residual-gas

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[2]When a non-wetting fluid, like oil or CO_2, moves into, or invades a porous medium saturated with a wetting fluid (most commonly water), the latter is displaced from some of the pore space (a process referred to as drainage, hence the term "drainage cycle"), but it returns when the non-wetting fluid retreats or moves out (a process referred to as imbibition, hence the term "imbibition cycle). Some residual, discontinuous water is left in the pore space when the non-wetting phase attains maximum saturation during the drainage cycle, and vice versa, some residual,

(footnote continued)

discontinuous and immobile non-wetting fluid remains in the pore space when the wetting fluid reaches maximum saturation during the imbibition cycle. Hysteresis refers to irreversibility, or path-dependence of relative permeability and capillary pressures on the saturation path and history.
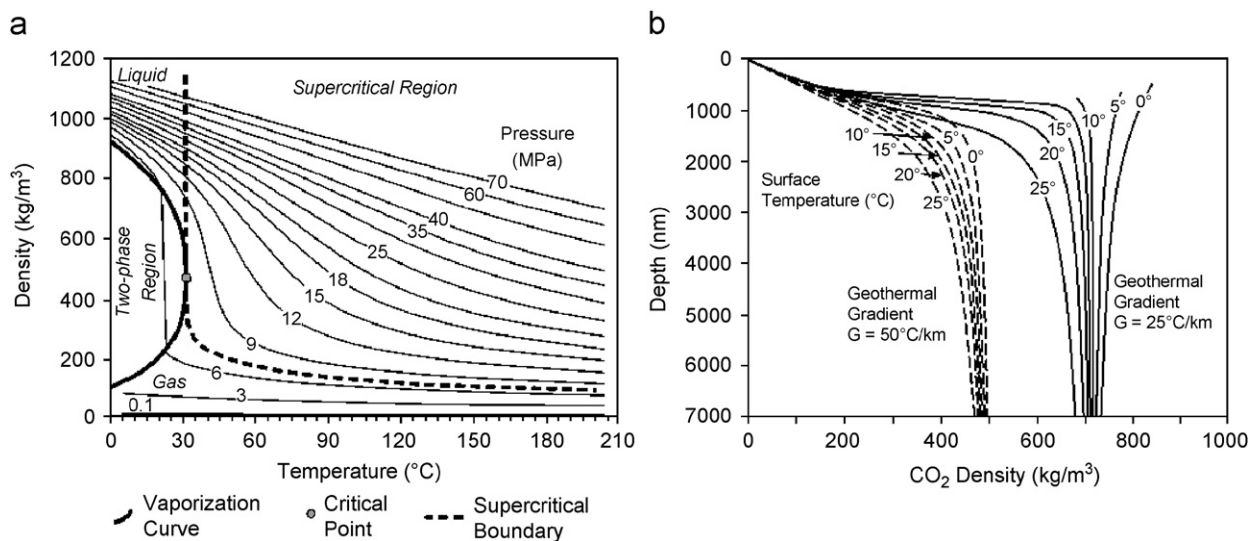
Fig. 2. Variation of CO_2 density: (a) as a function pr pressure and temperature, and (b) in the subsurface as a function of depth assuming hydrostatic conditions and various geothermal regimes defined by geothermal gradients and surface temperatures (from [35], with permission from Springer Science and Business Media).
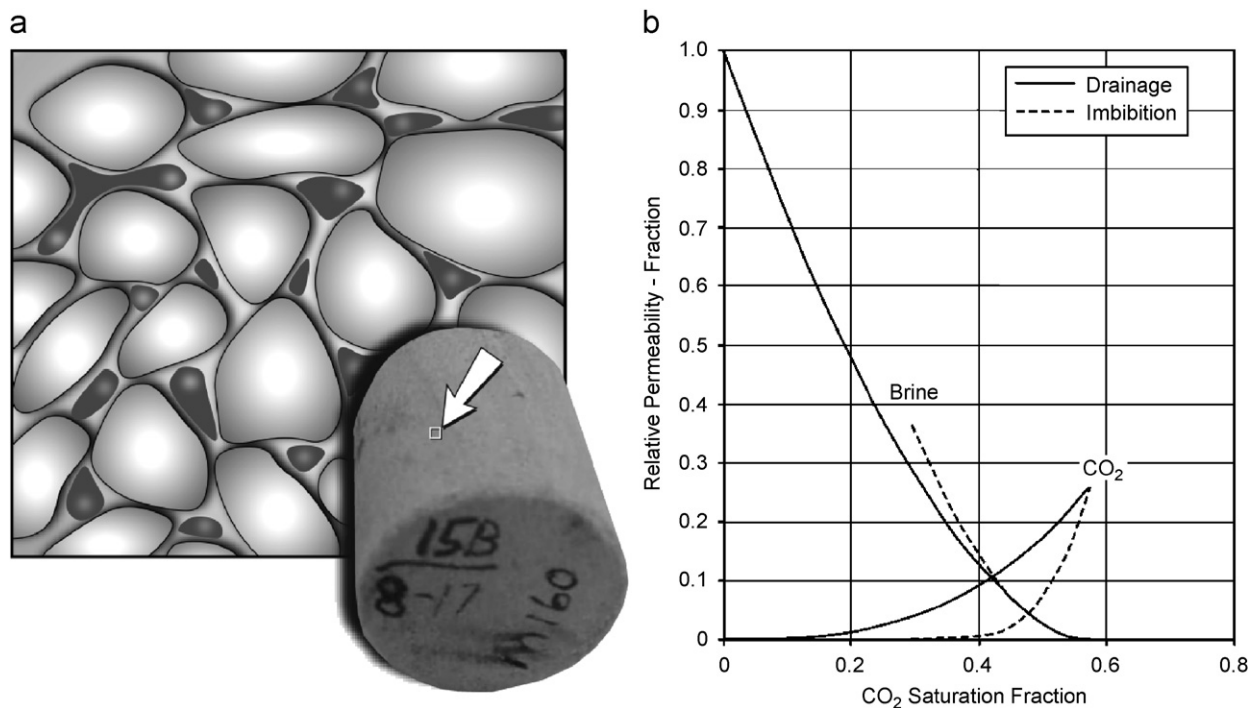

Fig. 3. Characteristics of residual-gas trapping: (a) diagrammatic illustration of disconnected bubbles of non-wetting gas in a water-wet porous medium and (b) relative permeability of CO_2 and brine at in situ conditions measured on a sandstone core from Alberta, Canada (from [40]).
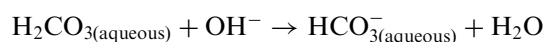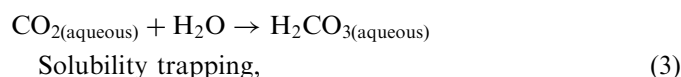
trapping occurs largely, if not entirely, after injection has stopped.

Chemical trapping occurs when CO_2 adsorbs onto organic materials contained on coals and shales (adsorption trapping—Fig. 1b), or dissolves in subsurface fluids (solubility and ionic trapping) and may then be involved in chemical reactions with the rock matrix (mineral trapping). Coal contains a natural system of fractures called cleats,

which imparts some permeability to the system. Between the cleats, the solid coal does not contain macropores through which fluids can flow, but does contain a very large number of micropores into which gas molecules can diffuse from the cleat. In the presence of multiple gases (e.g., CH_4, CO_2, N_2) the amount of each in the adsorbed state would be approximately in the proportion of their respective affinities (Fig. 1b) [43]. Because coal has higher

affinity for gaseous CO_2 than for methane,[3] which occurs naturally in coals, CO_2 storage in coal beds is based on the premise that the injected CO_2 will replace the methane in coal and remain adsorbed onto the coal surface. The freed methane, which is also a greenhouse gas with a radiative force 21 times stronger by weight than that of CO_2, has to be captured and used as a source of energy (should not be vented) to ensure a net greenhouse gas mitigation outcome, hence the name of the whole process as enhanced coalbed methane recovery (ECBMR). If the pressure in CO_2-saturated coal is subsequently lowered, some but not all CO_2 will desorb from the coal surface due to the hysteretic nature of gas adsorption and desorption [44]. However, if the coals are subsequently mined (i.e., coal pressure is brought to atmospheric), then all the CO_2 will desorb, cancelling the CO_2 storage and also posing a health and safety risk.

The most basic chemical reactions that lead to solubility trapping and mineral carbonation are [31]:

$$CO_{2(gaseous)} \rightarrow CO_{2(aqueous)}, \qquad (2)$$

$$CO_{2(aqueous)} + H_2O \rightarrow H_2CO_{3(aqueous)}$$
Solubility trapping, $\qquad (3)$

$$H_2CO_{3(aqueous)} + OH^- \rightarrow HCO_{3(aqueous)}^- + H_2O$$
Ionic trapping
$$HCO_{3(aqueous)}^- + OH^- \rightarrow CO_{3(aqueous)}^= + H_2O, \qquad (4)$$

$$CO_{3(aqueous)}^= + Ca^{2+} \rightarrow CaCO_{3(solid)}$$
Mineral trapping, $\qquad (5)$
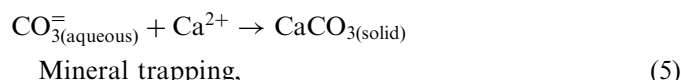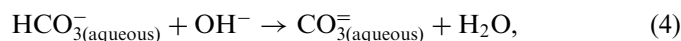
although more complex reactions may also take place with Ca and Mg rich minerals [31,45]. All the chemical trapping mechanisms depend, of course, on the amount of coal, formation water or rock that is available for reactions, but also on the contact area between free-phase CO_2 and coal, water or mineral, and on CO_2 saturation at the interface.

Under favourable circumstances, injected CO_2 may migrate in the subsurface at extremely low velocities such that it would take time on a geological scale (tens of thousands to millions of years) to potentially reach the surface, before which, under the right conditions, it is most likely to be trapped by a combination of the mechanisms outlined above in a process described as hydrodynamic trapping [46,47]. Very large amounts of CO_2 could be potentially stored this way.

When CO_2 is injected in the subsurface, it is first trapped by primary mechanisms, which are static and hydrodynamic trapping below the caprock in oil and gas reservoirs and deep saline aquifers, and adsorption onto the coal

surface in coal beds. Over time, a series of secondary trapping mechanisms start operating, mechanisms that do not necessarily increase the CO_2 storage capacity, but definitely increase the storage security (i.e., diminish the potential for leakage and/or the amount of CO_2 that may migrate or leak) [21]. This is due to the fact that these secondary trapping mechanisms: dissolution in reservoir oil or formation water, in situ mineral carbonation and CO_2 retention as an immobile phase trapped in the pore space of the storage formation, are much slower and have a much longer timeframe for operating, in the order of centuries to millennia, than the primary trapping mechanisms (Fig. 4a) [48–50]. The contribution of these trapping mechanisms is almost negligible during the operational (injection) phase of CO_2 geological storage but they contribute to increasing storage security (Fig. 4b) because the buoyant CO_2 is immobile in the pore space or does not exist anymore as a free phase, being either dissolved in formation water or precipitated as a carbonate mineral [21]. This discussion does not imply that CO_2 storage is not secure in the initial stages of a storage operation, it only indicates that storage security may increase in time if these secondary trapping mechanisms increase their contribution to the process.

By analogy with natural gas storage, man-made underground cavities (i.e., salt caverns), have also been proposed for CO_2 storage [51], but they have comparatively small capacity and are limited geographically; however, they may play an important role for temporary storage and/or as a buffer in collector and distributor systems between CO_2 sources and storage sites, being basically part of the CO_2 transportation system, and not of the storage system.

Suitable sedimentary successions that contain deep saline aquifers exist in all sedimentary basins, which are widespread worldwide, although of different characteristics and suitability for CO_2 storage [35,52]. Oil and gas reservoirs are found in hydrocarbon provinces, of which the most notable on a global scale are in the Middle East, Russia, North America, the Gulf of Mexico, the North Sea and on both sides of the south Atlantic (i.e., Nigeria, Angola, Brazil). Significant coal beds occur in North American sedimentary basins and in Australia, but also in regions that are quite poor in hydrocarbon reservoirs and deep saline aquifers such as China, India and South Africa.

4. Current status and potential of CO_2 geological storage

CO_2 storage in oil and gas reservoirs and in deep saline aquifers is a mature technology that can be applied immediately, as demonstrated by almost 100 years of natural gas storage at hundreds of sites in North America and Europe [53], more than 30 years of experience with CO_2 EOR, mostly in the US [54], and more than 15 years experience with acid gas injection in western Canada [55] (acid gas is a mixture of CO_2 and H_2S with minor hydrocarbon gases that is the result of sour gas processing). Carbon dioxide storage in oil reservoirs in conjunction with EOR is likely to be implemented where such

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[3] The interaction between coal and supercritical CO_2, and the effects of supercritical CO_2 on coal (see Section 4) are less understood and it seems that adsorption may change to absorption. This has implications on establishing the depth of CO_2 storage in coals, if CO_2 needs to be in gaseous phase.
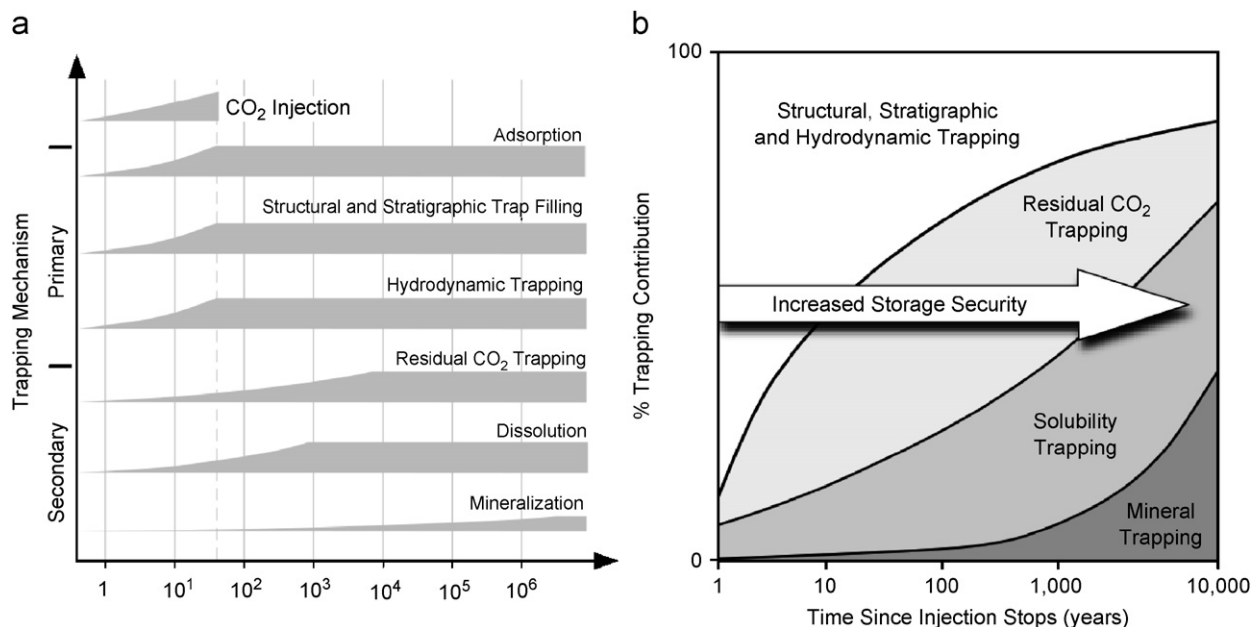
Fig. 4. Differences between various CO_2 trapping mechanisms in geological media: (a) operating timeframe, and (b) contribution to storage security (after [21]).

opportunities exist and where the cost of CO_2 storage can be reduced by producing additional oil; however, this option has limited capacity and geographic distribution [21]. Furthermore, while the stream of CO_2 from a large source is constant and may even increase with increasing production or power generation capacity, the amount of CO_2 needed by a CO_2 EOR operation decreases in time as CO_2 is produced with oil and recirculated. Thus, while the use and storage of CO_2 in EOR operations will potentially provide a cost-offset and even an economic benefit in the early uptake of CO_2 geological storage, the sources and supply of CO_2 will likely exceed the usage rates and capacity in EOR operations, leading to the need of accessing depleted hydrocarbon fields and deep saline aquifers concurrently.

Currently there are a number of commercial-scale projects in the world a by-product of which is injection and storage of CO_2 in geological media, and only a handful of projects whose primary objective is CO_2 storage, however, except for extremely few, none of them are driven by climate-change mitigation objectives (unless one considers the carbon tax imposed by the Norwegian government on CO_2 emissions from offshore gas production which spurred the Sleipner project in the North Sea, see below). Besides these, there are several pilot projects conducted for research purposes, the main objectives being to understand the fate of the CO_2 injected in the subsurface and to develop and test monitoring technologies.

There are close to 90 CO_2 EOR projects in the world, the majority of which are in the Permian Basin in west Texas, where approximately 30 Mt CO_2/yr are transported along a pipeline network approximately 3000 km long and injected [54]. However, most of the CO_2 used in west Texas and other CO_2 EOR operations in the USA originates in very

large natural CO_2 reservoirs in Colorado and New Mexico, such as the McElmo, St. John's and Jackson domes [56], and, in this regard, do not contribute to a reduction of anthropogenic CO_2 emissions into the atmosphere. The Weyburn CO_2 EOR operation in Saskatchewan, Canada, uses up to 5000 t/day CO_2 pipelined through a 326 km pipeline from a coal gasification plant in North Dakota, USA, and a monitoring research project was run on top of the EOR operation in the early 2000s [57]. Similarly, 1 Mt CO_2/yr stripped from natural gas produced from the Sleipner field in the North Sea is injected in the Utsira formation since the mid 1990s at ~800 m below the seabed, and a monitoring project has been running there since 1996 when the project started [58]. Another large-scale project is at In Salah in Algeria, where CO_2 stripped from produced natural gas is reinjected in the aquifer underlying the very gas reservoir from which it is produced [59]. The natural gas produced both at Sleipner and In Salah contains 9–10% CO_2, which has to be stripped before sending the natural gas to markets in Europe. Besides these operations, CO_2 is injected together with H_2S in depleted oil and gas reservoirs and deep saline aquifers at more than 40 acid gas injection operations in western Canada [55] and at more than 20 operations in the USA. The CO_2 and H_2S injected at these operations are produced at gas processing plants where these acid gases (the name derives from their corrosive nature in the presence of water) are stripped of produced sour gas to meet pipeline and market specifications. To date, approximately 3 Mt CO_2 and 3 Mt H_2S have been injected in western Canada. In all these cases the drivers for CO_2 injection have been economic and/or regulatory requirements. In the case of CO_2 EOR operations, additional oil production is the driver, facilitated by the availability of cheap CO_2 from natural sources or

industrial operations where high purity CO_2 streams are already produced as a result of the process itself, e.g., in ammonia and gasification plants. In the case of the Sleipner CO_2 injection operation, the driver is a carbon tax imposed by the Norwegian government on vented offshore-produced CO_2. In the case of acid gas injection operations, the driver is provided by regulatory requirements regarding H_2S emissions and by the (lack of) economics of separating H_2S from CO_2. Commercial-scale projects for CO_2 injection in deep saline aquifers are in an advanced planning stage by Statoil at Snøhvit in the Barents Sea, and by Chevron at Gorgon offshore northwestern Australia. In both cases the CO_2 is stripped from produced natural gas.

Besides these commercial-scale operations, a number of demonstration and pilot operations have been implemented or are planned around the world, mainly for testing and developing technology for monitoring the fate of the injected CO_2 and developing monitoring techniques. These pilot operations are run mainly by government research agencies and are not developed for commercialization. Such pilot projects are CO_2 injection in a deep saline aquifer at Frio in Texas, US, at Ketzin near Berlin in Germany and at Otway in Australia, and CO_2 injection in the K12B gas field in the Dutch sector of the North Sea [60–63]. One pilot project run by the industry rather than government is ZeroGen in Queensland, Australia,[4] where the goal is to demonstrate power generation from coal with associated CO_2 storage in a deep saline aquifer, similarly to the FutureGen[5] project in the USA that is in the process of being awarded to a site in either Illinois or in Texas.

In regard to CO_2 storage in coal beds, this is an immature technology that has yet to be proven and that has comparatively the lowest capacity of all geological media [21,64]. Permeability is a determining factor in the viability of CO_2 storage in coals, and currently it is considered that coal permeability has to be greater than 1 millidarcy (mD) for successful CO_2 injection and/or coalbed methane (CBM) production. Coal permeability varies widely and generally decreases with increasing depth as a result of cleat closure with increasing effective stress (e.g., [65]), such that the permeability of deep coals is on the order of microdarcies (μD), which is too low to allow CO_2 injection and flow without fracturing. In addition, coal is a polymer-like substance that is often affected by the gas with which it is in contact. Work to date shows that coal swells as CO_2 is adsorbed, which further reduces permeability and injectivity by up to two orders of magnitude [66,67]. Furthermore, the injected CO_2 may react with the coal and/or formation water, leading to solids precipitation and further permeability reduction [43,68]. Finally, CO_2 is a "plasticizer" for coal, lowering the temperature required to cause the transition from a glassy, brittle structure to a rubbery, plastic structure [69].

Coal plasticization, destroys the permeability that would allow CO_2 injection. Additional technical problems are the fact that the coal low permeability necessitates the use of many, densely spaced wells for injection, and the difficulty in ensuring that all the released methane can be securely captured and utilized.

The combined effects on permeability caused by the presence of CO_2 generally reduce the depth limit for CO_2 storage in coals to less than 800–1000 m, and also explains the limited success of pilot operations for CO_2 storage in coal beds run to date in Canada, Poland, China and Japan [70–73]. The only successful CO_2 ECBM project so far was run between 1995 and 2001 at the Allison Unit in the San Juan Basin in New Mexico, USA, by Burlington Resources as a pilot for CBM production [74], but no monitoring project was associated with this pilot.

Large CO_2 emitters need to have assured long-term storage capacity, which is not provided by CO_2 EOR and ECBMR operations where the need for new CO_2 decreases with time as CO_2 is produced at the well-head with the recovered oil or gas and recirculated. Storage of CO_2 in depleted oil and particularly gas reservoirs ultimately offers significant capacity [21], but the majority of the storage capacity is found in the major oil and gas producing regions (such as the Middle East, the North Sea, Russia, and Texas and Alberta in North America) and only as oil and gas reservoirs are depleted. Oil and gas production is going to be extended in a period of increasing oil prices, and, as long as reservoirs are producing, CO_2 storage in depleted oil and gas reservoirs is going to be delayed. In contrast, deep saline aquifers offer the advantage that they are present in most sedimentary basins, have the largest storage capacity of all geological media [21] and can potentially be used immediately. Furthermore, even in oil and gas producing regions it may be more economic in some cases to store produced CO_2 in a deep saline aquifer adjacent to a major CO_2 source than to transport the CO_2 to a depleted oil or gas reservoir some distance away, besides the fact that the oil and gas reservoirs may not be available yet for CO_2 storage because of continuing production [75].

From a storage efficacy point of view, it is desirable to store CO_2 at depths where its density is high (Fig. 1b), because more CO_2 is stored per unit of available pore volume. Thus, except for storage in coal beds, where the storage is based on gas adsorption rather than on volumetrics, the accepted conventional wisdom is that CO_2 should be stored at depths greater than the hydrostatic depth corresponding to the critical pressure P_c (i.e., greater than 740 m) such that CO_2 is in dense phase (liquid or supercritical, depending if temperature is less or greater than the critical temperature T_c). However, this should not be a hard-set criterion for selecting CO_2 storage sites, as long as the criteria of capacity, injectivity and confinement are being met. For example, hundreds of gas reservoirs in Alberta, Canada, found at depths shallower than 800 m have a cumulative storage capacity in the order of 100s

$MtCO_2$, and this resource should not be disregarded but rather used as long as CO_2 storage doesn't pose any risk. On the other hand, many coal beds that are uneconomic today and may be considered for CO_2 storage may become economic in the future or may be used for in situ coal gasification, and this energy resource should not be sterilized by storing CO_2.

5. Risks posed by CO_2 geological storage

As with any human activity, there are certain risks associated with CO_2 geological storage. Risk in its engineering definition is the product of the likelihood of an event to occur and the consequences of the event-taking place. Henceforth, since consequences are highly dependent on location and time, the following discussion will address only the various events that may take place and their potential consequences; furthermore, only the risks associated with CO_2 storage will be discussed because the risks associated with surface and injection/production facilities are well understood [76]. Risks associated with CO_2 geological storage may occur during the operational (injection) phase and/or afterwards.

During the operational phase, injection of any fluid in the subsurface has geomechanical and hydrodynamic effects. Pressure increases in the injection reservoir, aquifer or coal bed during fluid injection and decays slowly after its cessation (Fig. 5). Spatially, pressure is highest at the injection well and decays radially away from it. Depending on the injection pressure, geomechanical effects include opening of pre-existing fractures, rock fracturing, fault activation, induced microseismicity and even earthquakes

of moderate local magnitudes [77,78]. However, there is significant experience in assessing and controlling these geomechanical effects and generally regulatory agencies that permit and monitor deep injection of fluids do not allow bottom-hole pressures above a safe upper limit that is less than the minimum horizontal stress (necessary to open pre-existing fractures) and the rock fracturing threshold. Because of the pressure decay after cessation of injection, the geomechanical risks posed by injection decrease in time after the active operational phase of CO_2 storage (Fig. 5), thus increasing storage security. Of course, when multiple storage operations take place, possible overlapping and cumulative effects need to be taken into account. Also, in the case of CO_2 storage in depleted oil and gas reservoirs, possible geomechanical effects due to pressure depletion during hydrocarbon production and pressure buildup during CO_2 storage have to be considered, possibly limiting further the allowed maximum bottom-hole pressure during injection.

Fluids injected on the scale of current operations are accommodated in the subsurface through local displacement of resident fluids (water, oil or gas), compression of both injected and resident fluids, and expansion of the pore space that sometimes may lead to minor ground heaving. There is no experience with injection of fluids on the scale needed for CO_2 geological storage, and the hydrodynamic effect of injecting these volumes and correspondingly displacing the resident saline water needs further evaluation. For example, a single 500 MW coal-fired power plant emits annually several million tones of CO_2, which, assuming a CO_2 density of 500–600 kg/m³ at in situ conditions, will occupy a few million m³ of pore space.

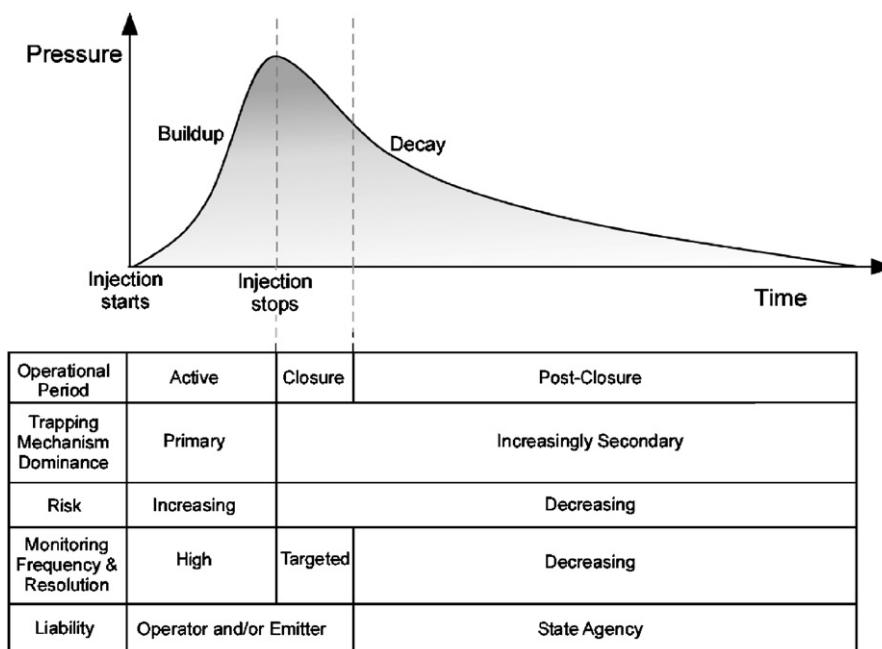| Operational Period	Active	Closure	Post-Closure
Trapping Mechanism Dominance	Primary	Increasingly Secondary	
Risk	Increasing	Decreasing	
Monitoring Frequency & Resolution	High	Targeted	Decreasing
Liability	Operator and/or Emitter	State Agency	

Fig. 5. Relation between pressure behavior and operational phases, dominance of CO_2 trapping mechanisms (see Fig. 4), monitoring frequency and resolution, and liability at a CO_2 storage site.

The magnitude of the storage space needed to reduce significantly CO_2 atmospheric emissions is staggering when a lifetime of 30–50 years is considered for thousands of power plants around the world.

Finally, CO_2 leakage poses different risks because of its potential consequences. Leakage is possible because, besides the pressure force that acts on CO_2 during injection, buoyancy acts on CO_2 at all times, pushing it upwards, and, if a pathways is available, CO_2 will flow along this pathway. Thus, leakage is possible both during injection and afterwards. From the point of view of retention efficacy and safety, CO_2 storage through static and hydrodynamic mechanisms is of most concern because CO_2 is mobile and may leak into overlying formations and possibly to shallow groundwater, the vadose zone and soils, and/or the atmosphere. Storage through residual-gas and mineral trapping is of no concern because the CO_2 is immobilized. Water saturated with CO_2 is slightly heavier (by 1–2%) than unsaturated water and its negative buoyancy will tend to drive it towards the bottom of the storage aquifer if certain conditions for the onset of free convection are met [48], and thus eventually will migrate downdip in the aquifer. Carbon dioxide adsorbed onto the coal surface will be immobile as long as the pressure does not drop, which would be the case if the coals are subsequently mined or depressurized. Thus, CO_2 stored through dissolution, ionic, and adsorption trapping may become of concern only when the in situ pressure and temperature conditions change such that CO_2 exsolves or desorbs, in which case it may regain its mobility and leak, basically reverting to the cases of CO_2 trapped in static and hydrodynamic traps. Only mobile free-phase CO_2 may pose risks due to its buoyancy which will move it up from its storage unit if a pathway is found, such as open faults and fractures, and defective wells [79].

The security of CO_2 storage increases after the injection phase not only as a result of pressure decay (Fig. 5) but also due to increasing CO_2 trapping by time-dependent secondary mechanisms that immobilize the CO_2 in the subsurface (Fig. 4). Thus, it is evident that, from a leakage-risk point of view, the most critical period in CO_2 geological storage is the operational (injection) one, when (most of) the injected CO_2 is in free, mobile phase and when the pressure is increasing as injection progresses. However, it is important to realize that geological structures that seem to be impermeable on a short time scale may be leaky on a geological time scale (and anywhere in between), as proven by the heavy oil and bitumen deposits that lost the volatile component of the originally light oil, by natural oil and gas seeps (e.g., [79,80]) and by gas reservoirs that are still recharging in areas of active gas generation. Hence, leakage may show itself well after the injection stage of a CO_2 storage operation. Nevertheless, leakage through CO_2 diffusion across caprock will take tens of thousands of years and longer [81], and only potential leakage along permeable pathways should be of interest in the context of CO_2 geological storage [79].

The primary risks associated with CO_2 leakage involve both acute (sudden, short and high rate) and chronic (slow, low rate and prolonged) leakage from the storage zone to the atmosphere or other subsurface zones containing resources that might be contaminated or biota that might be harmed. The consequences of leakage are global and local. The global consequence is associated with leakage back into the atmosphere, regardless of timing and rate, thus reducing the effectiveness of geological storage and contributing to increased CO_2 concentrations in the atmosphere. Over a long period of time, leakage at some sites should be expected [82], however from a climate stabilization point of view leakage rates in the order of 0.01–1%/yr would still be acceptable depending on the storage site [83,84]. It should be noted here that the leakage at surface back into the atmosphere will be in most cases less, sometimes significantly, than the leakage from the primary storage unit because some if not all of the CO_2 leaking from the latter will be caught by various trapping mechanisms and trapped along the leakage pathway (e.g., [85]) Thus, implementation of CO_2 geological storage should not be delayed until the potential for leakage is (almost) eliminated, because the alternative, continuing with full CO_2 emissions into the atmosphere, is much worse [86].

Local consequences of CO_2 leakage can be short- or long-term, and fall into three categories: health and safety, environmental and equity. In this regard, there are natural and anthropogenic analogues that help in assessing the risks associated with CO_2 geological storage. Natural emissions of geologically sourced CO_2 occur mainly in volcanic and tectonically active areas, such as in Japan and Italy, that are not suitable for CO_2 storage but that, nevertheless, provide effective analogues, while in sedimentary basins, natural CO_2 emissions appear as charged carbonated spring water and as gaseous seeps at the ground surface or vents at the sea bottom [87,88]. Anthropogenic analogues are well blowouts and leakage incidents from natural gas pipelines and storage sites [53,89,90]. However, numerical simulations suggest that, unlike in the case of natural gas, CO_2 leaks from a deep storage site along highly permeable pathways may have a cyclical behaviour (alternating high and low rates) because of the cooling Joule–Thompson effect associated with rapid CO_2 decompression and relative-permeability effects in the presence of liquid and gaseous CO_2 phases [91,92].

Short-term consequences of CO_2 leakage are mainly those that pose an acute danger to life, such as asphyxiation. At normal atmospheric conditions, CO_2 is a physiologically active, colourless, odorless and non-flammable gas slightly heavier than air that is fundamental in photosynthetic and respiratory processes. Thus, from a health and safety point of view, CO_2 is dangerous only at increased concentrations, usually more than 0.5–1.5% (compared with the current atmospheric concentration of 0.038%). Higher concentrations and/or long exposures to elevated concentrations, as in the case of well blowouts

[90], are hazardous either by reducing the oxygen concentration in the air (hypoxia) to below the 16% level required to sustain human life, or by entering the body, especially the bloodstream, and/or altering the amount of air taken during breathing and causing direct toxicity [93]. Acute exposure to CO_2 concentrations above 3% may significantly affect health, with effects such as hearing loss, impaired vision and mental confusion. Carbon dioxide acts as an asphyxiant at concentrations in the 7–10% range and can be fatal; at concentrations above 20% death occurs in 20–30 min [93,94].

Because its density is greater than that of air, CO_2 released or leaked at the surface will flow to low levels, and, in the absence of wind or air circulation, will accumulate under stagnant conditions in enclosures such as open pits, tanks, buildings and topographic depressions, where it can reach dangerous concentrations. Occupational protective standards have been developed for exposure to CO_2, and the safety risks posed by acute CO_2 leakage from CO_2 storage projects are considered to be comparable to those posed generally in the oil and gas industry [21], and one may argue that the risks are actually smaller due to the non-flammable and non-explosive character of CO_2 [76]. Another possible short-term effect of CO_2 leakage is killing of low-lying and small animals that may find themselves in low-level enclosed areas where CO_2 has accumulated if leakage happens on land, or locally changing the water pH and affecting marine life if leakage occurs at the sea bottom. In general, CO_2 concentrations are largely dependent on the size of the release and ambient atmospheric conditions. Large volume leaks with high-release rates will likely induce atmospheric mixing, while small leaks are expected to disperse at or near background levels. Furthermore, large leaks are very unlikely to go unnoticed by operators and regulatory agencies, and will likely be mitigated. The greatest likely hazard is posed by moderately sized leaks that do not induce sufficient mixing or that collect in a confined space.

Long-term consequences of CO_2 leakage are generally those that affect ecosystems. Environmental effects of CO_2 leakage are the death of vegetation exposed to high CO_2 soil concentration, such as is the case of natural leakage at Mammoth Mountain in California [95], if leakage occurs on land, and affecting and even killing sensitive marine biological systems such as coral reefs if leakage occurs at the sea floor. Elevation of CO_2 concentrations in the soil is likely to affect the soil pH and adversely impact the chemistry of nutrients, redox-sensitive elements and trace metals, and plant growth [96]. Plants usually have a higher resistance to CO_2 than animals, but persistent leaks over weeks to months in duration could suppress respiration and water uptake in the root zone. Another environmental effect that may even pose a health threat is the contamination of shallow potable groundwater. Dissolved CO_2 will form a weak carbonic acid, altering the water pH and potentially mobilizing heavy (toxic) metals, sulphate and chloride (e.g., [97]). Carbon dioxide seeping at the sea

floor may affect the sediment biota. Depending on the depth of the sea floor, the leaked CO_2 may be heavier than seawater, in which case it will accumulate as a liquid on the sea floor, or it will be buoyant, in which case it will raise through the water column. In both cases CO_2 will dissolve in seawater, locally affecting water pH and, consequently, marine vegetation and life.

Equity consequences of CO_2 leakage occur when CO_2 migrates or leaks into other energy and mineral resources, such as oil and gas reservoirs or lead–zinc deposits, contaminating them. Also, in a credit-based system where the stored CO_2 has a market value, leakage reduces the credits allocated to a CO_2 storage operation, hence lowering its value.

Well-head and pipeline failures may lead to relatively large flows of CO_2, but these are usually short lived and, based on statistics of underground gas storage, the frequency of such incidents is likely to be very low [76]. As long as pipelines and/or injection wells are not located in densely populated areas, the risk posed by such failure events is very small. The experience with deep waste injection and natural gas storage also shows that the risk of seismicity is minimal, and the risk posed by brine displacement is likely to be minimal as well, but needs to be assessed individually because it depends on site geology and hydrogeology [76]. Some coal seams have held methane for millions of years, and, given the CO_2 higher affinity to coal, again, the risk of CO_2 leakage from coal seams is expected to be low [76]. The potential for leakage from the storage site is the greatest for oil and gas reservoirs because of the high density of wells that penetrate them (e.g., [98]). Improperly drilled, completed and/or abandoned wells may provide a CO_2 leakage pathway [79], as demonstrated by the existence of surface casing vent flow and gas migration [99]. While the risk associated with any individual CO_2 storage operation is most likely to be very low, the extremely large number of such operations that will be needed by 2050 and the general magnitude of CO_2 storage operations required to make this technology viable as a climate change mitigation strategy [6] will undoubtedly increase the overall risk.

Monitoring for, and assessing leakage on a local scale is important for safety, permitting, and leakage-remediation, while, from a climate-change mitigation point of view is important for emissions reduction and credits. Monitoring the injection characteristics along transportation pipelines and at injection wells, such as pressure, temperature, gas composition and flow rate, is standard practice in the oil and gas and other industries. Monitoring the fate of the CO_2 in the subsurface can be done using intrusive and non-intrusive technologies, reviewed extensively in Chapter 5.6 of the IPCC Special Report on CCS [21]. Intrusive, or direct, methods are based on pressure measurements and sampling subsurface fluids through observation and monitoring wells for the presence of CO_2 or of tracers introduced together with the injected CO_2 for monitoring purposes. Non-intrusive, or indirect, methods are based on

imaging of the subsurface using various geophysical techniques, such as time-lapse three-dimensional seismic imaging and vertical seismic profiling (VSP), to detect the presence of, and track the movement of the plume of injected CO_2. These technologies, based on fluid sampling and seismic imaging, have long been used in the oil and gas industry for hydrocarbon exploration. However, it should be noted that seismic imaging does not work in many circumstances found in sedimentary basins, particularly below black coal deposits and salt beds. Non-seismic geophysical techniques include the use of electrical, electromagnetic and self-potential techniques [100]. Various techniques are currently being developed for the detection and monitoring of leaked CO_2 in soils, at the land surface and in the atmosphere, such as infrared imaging for vegetation stress, soil gas sampling and eddy covariance. The challenge in the case of soil and atmospheric monitoring for leaked CO_2 is to differentiate it from the background CO_2 that occurs naturally and whose levels vary daily and seasonally as a result of biological processes in plants and soils, which in turn depend on the amounts of sunlight, moisture levels and temperature. There are no similar monitoring techniques for leakage detection in a marine environment. However, it should be stressed that it is difficult if not impossible to monitor the fate of a volume of injected CO_2, and that various monitoring tools and techniques can be used for detecting the presence of CO_2, but not to quantify CO_2 volumes or flow rates.

6. Challenges and barriers to deployment of CO_2 geological storage

If CO_2 injection into geological media is technologically feasible, as indicated by CO_2 EOR and acid gas injection operations, including the more recent CO_2 storage operations at Sleipner and In Salah, then the question arises as to what are the challenges and barriers to deployment. There are many who argue that the economics of such operations is not right and that this is the main barrier to large-scale implementation. Indeed, economics will likely affect implementation as long as there is no value for stored CO_2, but even if a value is established for stored CO_2 through a tax system or carbon market, companies may still decide to vent and pay the tax rather than store CO_2 if the former option is cheaper. In enhanced hydrocarbon recovery operations, CO_2 is a commodity purchased on the market and, hence, it has a value above the ground, not in the ground, and these operations are optimized to maximize hydrocarbon recovery and minimize CO_2 loss. As a result, the CO_2 that is produced at the pump with the recovered oil is separated and reinjected, and at the end of the operations the reservoir is blown down and the recovered CO_2 is sold. If the stored CO_2 had a market value, then the enhanced hydrocarbon operations will be optimized to maximize the combined value of produced hydrocarbons and stored CO_2. In other operations, like acid gas disposal or CO_2 storage at Sleipner, deep injection

represents a direct business cost, although it will likely be a cost-effective operation for a variety of reasons. Carbon dioxide storage costs, in the order of 0.5–5.0 US\$/t CO_2 net injected for onshore operations and 6–12 US\$/t CO_2 for offshore operations [21,101], are the lowest in the capture and storage chain, comparable with those for transportation and significantly lower than the cost of CO_2 capture. Thus, lowering the cost of CO_2 capture is a challenge, but it is not a barrier to the implementation of CO_2 geological storage because, ultimately, the cost of CCS may and most likely will be passed to the consumer.

There are well-founded concerns that public acceptance is a key element and may pose a barrier to large-scale implementation of CO_2 geological storage and indeed this may likely be the case. From the public's perspective there are two basic questions that need to be satisfactorily answered: will CO_2 leak, and what will happen if it does leak? The public may perceive risk differently from the engineer, who is concerned with likelihood and hazard, in a subjective manner that considers more the qualitative nature and characteristics of risks ("social constructivist paradigm") [102]. Public opinion studies have shown that the public by and large is unaware of CO_2 geological storage as a climate-change mitigation technology, and, without any prior knowledge, consistently rates it toward the bottom of various options for addressing global warming, higher only than ocean storage and nuclear energy but significantly lower than improving energy efficiency and use of renewable energy [103–106]. However, public support and acceptance increase when explanations are provided and when CCS is presented as being part of a portfolio of climate-change mitigation measures, while, on the other hand, the willingness of the public to pay decreases as the cost passed to the consumer increases [104,106]. The public is very quick in identifying the risks associated with CO_2 geological storage, namely the risk of leakage [106]. General public attitude should not be confused with the attitude of the local population around a capture and geological storage project, which most likely will form around two competing positions: desire for jobs and economic development in the local community versus concerns about possible leakage of CO_2 from the storage site. To that one should add the "not in my back yard" (NIMBY) syndrome, whereby the *wider* public accepts the technology and its benefits, but the *local* public does not want to accept the locally concentrated costs (economic and societal) resulting from the facility. It seems that public acceptance may pose a challenge that can, nevertheless, be overcome with information, education and use of a transparent process for the selection, permitting and operation of CO_2 storage sites. In this respect, environmental non-governmental organizations (E-NGOs) have an important role to play because they are trusted by the public more than governments and industry. Some E-NGOs are completely and unequivocally opposed to CCS, which they see as a ruse for extending the use of fossil fuels, while others (e.g., Natural Resources Defense Council

and Bellona) are supportive, fully realizing that this climate-change mitigation technology has an important role to play in a portfolio of mitigation measures [86,107].

The real barrier to deployment of CO_2 capture and geological storage at the present time is the absence of a comprehensive policy, legislation and regulatory framework for implementation. Some jurisdictions may have regulatory elements that are applicable to CO_2 geological storage, but they are incomplete and insufficient. The capture and transportation of CO_2 are industrial processes that are active only during the operational phase of CCGS and that are extensively regulated, with precedents and analogues from other industries. Similarly, deep injection of fluids is a process that is well regulated, at least in most if not all developed countries, and for which extensive experience exists. These regulations can be easily adopted and/or adapted to other countries and/or circumstances. It is the post-operational, storage part of the whole process that currently lacks policy and regulations because environmental laws and regulations (including international treaties to protect the marine environment) were enacted before CO_2 emissions became a concern. It is this current lack of policy and regulations regarding the post-injection stage of CO_2 storage operations that at present constitutes a barrier to large-scale deployment. The industry needs policy and regulatory certainty in order to assess the financial risk, raise the money and proceed with investments, hence deployment will not occur until policy creates a ''price'' for CO_2 and/or a requirement for storage, and a regulatory framework is put in place. Currently, Australia is the most advanced on the path of creating a regulatory framework for offshore CO_2 geological storage.

The first issue to be addressed is CO_2 classification, which varies from jurisdiction to jurisdiction, and even within the same jurisdiction varies depending on its origin and use. Mineral acts in some jurisdictions consider CO_2 produced from the ground (e.g., from CO_2 reservoirs or with natural gas) as a commodity, and certainly it is a commercial commodity that is traded for use in the food industry and in enhanced hydrocarbon recovery. On the other hand, given its greenhouse gas properties, some jurisdictions have legislated its designation within environmental protection acts variously as pollutant, toxic substance, waste (since it is injected) and even hazardous. The classification of CO_2 is critical because, depending on it, CO_2 will be subject to more or less stringent controls and regulations regardless of its intrinsic characteristics.

The relationship between international, national and subnational jurisdictions has to be clearly sorted out before large-scale deployment of CO_2 geological storage will occur, particularly in the case of CO_2 storage under the seabed where international treaties, such as the London Convention and the London Protocol, apply. If CO_2 is stored within national boundaries and territorial waters, then, in the case of federal countries such as USA, Canada and Australia, the relationship between federal and state/provincial jurisdiction and legislation needs to be clarified,

and in some cases legislation by different levels of government will have to be harmonized. Within this framework, the trans-border movement of CO_2 (across state/provincial or international boundaries), either at surface (e.g., pipelines) or in the subsurface (CO_2 plume spread and migration) will have to be addressed.

Other policy issues that need addressing are ownership of the pore space and the competition between storage rights and other mineral rights. In most jurisdictions around the world the subsurface is owned by the state, but there are sufficient cases where the subsurface, including the mineral rights, is owned by the surface landowner. Large-scale CO_2 storage projects will likely cover large areas, and the issue of access to the pore space is critical to implementation. Furthermore, if the pore space is leased for production of energy or minerals, then issues of priority or co-optimization of usage arise.

Another policy issue that needs addressing is long-term liability and third party transfer. At the time of storage, if the entire process is contained within a single legal entity (e.g., an oil company), then the ownership, credits and operational liability are clearly assigned. However, if the CO_2 emitter is one entity (e.g., a power plant), using a carrier (pipeline company) for transportation, and a third party for injection, then it is not clear which entity will get the credits for storage and which entity retains operational liability. Furthermore, for CO_2 storage to be an effective climate-change mitigation technology, the stored CO_2 should remain in the ground at least for centuries, which requires the assumption of long-term operational and financial liability that would cover the implementation of a long-term monitoring program and remediation in case of CO_2 leakage. Industry will not assume an indefinite and undefined risk, notwithstanding that most likely the company taking on the risk will not have the necessary longevity. For this reason, the current thinking is that, after the active injection period, a closure period should follow during which the operator, while maintaining liability, should demonstrate to the designated state agency the safety of storage, after which the state will assume long-term liability for the site (Fig. 5). In this vein, the states of Texas and illinois passed legislation for assuming liability for the FutureGen project (zero-emissions coal-fired power plant) if is located within the state. Even for the short term, the issue of liability and third party transfer has to be clarified in case of mergers, acquisitions or bankruptcy.

A proper regulatory framework needs to be put in place for the entire process and duration of CO_2 storage projects. In some jurisdictions, such as Texas in the USA and Alberta in Canada, there is currently in place a regulatory framework for the injection of CO_2 in geological media, either for EOR or for acid gas disposal, and this regulatory framework can be easily adopted and/or adapted for the active stage of CO_2 storage projects. However, no jurisdiction currently has any regulatory framework for the post-injection stage of CO_2 storage operations, when continuing monitoring, albeit likely at decreasing frequency

and resolution, will be required (Fig. 5), and remediation will be needed in case of leakage. Proper application, permitting and reporting processes need to be put in place within the regulatory framework that needs to be created.

Finally, the issue of type and amount of impurities allowed in the injected CO_2 stream has to be resolved from both economic and regulatory points of view. Streams originating from gas processing plants may contain H_2S, while streams originating from power plants will contain SO_x and NO_x. The level of H_2S in acid gas disposal operations in western Canada reaches 83% [55], which shows that, technologically and operationally, the presence of impurities in the injection stream is not an issue. However, the type and amount of acceptable impurities clearly affect the economics and the risk of CO_2 storage operations [108]. Achieving a high level of purity and/or eliminating certain impurities increase the cost of CO_2 separation and capture, while allowing them will likely affect and increase the costs of transportation and injection (higher volumes of gas to be compressed, pipelined and injected; special materials may be needed; special safety measures) and will increase the size of the space needed for storage. In this respect, the London Protocol adopted a resolution in October 2006 in regard to acceptable impurities in the stream of CO_2 injected in geological media under the sea bed that does not specifically limit the amount of impurities, but restricts the type of impurities to only those that are the direct result of the CO_2 generation and separation processes (i.e., no addition of impurities is allowed for getting rid of them at the same time). The presence of impurities, such as H_2S, will increase the consequence side of the risk posed by leakage. This may also affect the economics of CO_2 geological storage by requiring monitoring at higher resolution and frequency.

Thus, while scientific, technological and economic challenges still remain and need to be overcome, CCGS will not be deployed on a commercial scale unless proper policy and regulatory frameworks are developed and implemented. This may include, possibly, a regulatory requirement to reduce atmospheric CO_2 emissions similar to the regulatory requirement in Alberta, Canada, to reduce H_2S emissions that led to the deployment of acid gas disposal as a compliance and mitigation strategy.

7. Conclusion

Fossil fuels, mainly coal, will continue to be used for power generation and combustion in industrial processes well into this century because no other sources of energy are so abundant, cheap, available and distributed globally such that the security and stability of energy systems is at least enhanced, if not assured. While nuclear energy is likely to be part of any energy portfolio, and renewables will play an increasing role, the share of fossil fuels in the world energy mix will likely increase slightly over the next few decades. Each form of energy production has its downside, which in the case of fossil fuels is the generation of CO_2, whose concentration increase in the atmosphere most likely contributes to global warming and climate change. Thus, the challenge is to find ways to reduce anthropogenic CO_2 emissions into the atmosphere from burning of fossil fuels while, at the same time, continuing to use them at the pace required by the increase in world population and improvement in standards of living.

Carbon capture and geological storage represents an option that could play a prominent role in reducing anthropogenic CO_2 emissions into the atmosphere, comparable in size with improving energy efficiency and energy conservation. The principle is quite simple: capture CO_2 from large sources before it would be vented into the atmosphere, transport it to a storage site, usually by pipeline but also by ship where warranted, and inject it at least several hundreds of meters deep below the ground surface if onshore, or below the seabed if offshore. Geological media suitable for CO_2 storage must have the necessary capacity to store the intended volumes of CO_2, must have the injectivity needed to take in the CO_2 at the rate that it is supplied, and must confine the CO_2 to the storage site and impede its lateral migration and/or vertical leakage to other strata, shallow potable groundwater, soils and/or atmosphere. Such geological media are oil and gas reservoirs and deep saline aquifers that are found in sedimentary basins. Storage of gases, including CO_2, in these media has been demonstrated on a commercial scale by EOR operations, natural gas storage and acid gas disposal. There are other geological media thought to have potential for CO_2 storage, such as coal beds, shales and even basalts, but the technology has yet to be proven, and their capacity, injectivity and confinement properties have still to be demonstrated. Carbon dioxide is trapped in geological media through a series of physical and chemical mechanisms, such as simple immobilization in a volume bounded by low-permeability rocks, residual-gas saturation in the pore space, adsorption onto organic material in coals and shales, dissolution in formation fluids such as oils and brine, and mineral precipitation as a result of a series of geochemical reactions. These trapping mechanisms operate on various time scales that vary from immediate (concurrent with CO_2 injection) to thousands of years.

Like any human endeavor, CO_2 storage in geological media is not risk free. There are risks associated with the capture, transportation and injection of CO_2 that are similar to and comparable with any other industrial activity, particularly in the oil and gas industry, and for which an extensive safety and regulatory framework is in place. The specific risks associated with CO_2 storage relate to the operational (injection) phase, mainly geomechanical and hydrodynamic, and to the post-operational phase. The geomechanical risks refer to rock fracturing, ground heaving and induced seismicity, while hydrodynamic risks

refer to fluid displacement in the subsurface. However, the risks of most concern are those posed by the potential for acute or chronic CO_2 leakage from the storage site. Notwithstanding the global climate effect of CO_2 returning to the atmosphere, the local risks to health and safety, environment and equity need to be properly assessed and managed. Consequently, proper monitoring frameworks and remediation plans need to be put in place for each CO_2 geological-storage operation.

Currently there are very few operations in the world where CO_2 is injected and stored in the ground, mostly if not exclusively as a by-product of an operation driven by other considerations than just climate change. Carbon dioxide is stored in oil reservoirs at close to 90 CO_2 EOR operations in the world, and at close to 70 acid gas disposal sites. In these cases, the driver is either additional oil production or meeting regulatory requirements regarding H_2S emissions, which, together with CO_2, forms the acid gas that is the result of sour gas processing prior to being sent to markets. Storage of CO_2 at Sleipner in the North Sea is driven by a carbon tax on CO_2 emissions from offshore oil and gas production. Several pilot and demonstration projects were recently implemented or are in advanced planning stages around the world, mostly with government support to advance the science and technology of CO_2 storage in geological media. The existence of all these operations indicates that there are no major technological barriers to this technology.

The reason that there are no large-scale operations implemented with the specific goal of reducing anthropogenic CO_2 emissions into the atmosphere is that a series of challenges and even barriers stands in the way of broad technology penetration. A major challenge in the implementation of CO_2 geological storage is the high cost of CO_2 capture, particularly for dilute streams like those from power plants. However, this is only a challenge because the cost will likely be passed to the consumer. There are concerns that public opinion, and acceptance or rejection of this technology will likely affect the large-scale implementation of CO_2 geological storage. This challenge can be overcome with information, education and use of a transparent process for the selection, permitting and operation of CO_2 storage sites. The absence of policy, legislation and a proper regulatory framework is currently a barrier to the deployment of CO_2 geological storage. Issues that need addressing through policy, legislative and regulatory processes are CO_2 regulatory classification, type and amount of impurities allowed in the CO_2 stream, ownership of the storage space, long-term liability and third party transfer, and finally separation and overlap of international, national and subnational jurisdictions. The resolution of these issues will affect the economics and financial risk of CO_2 geological storage and will accelerate or delay the deployment of this technology for reducing anthropogenic CO_2 emissions into the atmosphere.

References

[1] IPCC (Intergovernmental panel on climate change). Climate change 2007: The physical science basis. Fourth assessment report, IPCC Secretariat, Geneva, Switzerland, 2007.

[2] Bryant E. Climate process and change. Cambridge, UK: Cambridge University Press; 1997.

[3] AGU (American Geophysical Union). Position statement. EOS Trans AGU 1999;80:49.

[4] AGU (American Geophysical Union). AGU position statement on human impacts on climate change. EOS Trans AGU 2003; 84:574.

[5] IEA (International Energy Agency). Prospects for CO_2 capture and storage. Paris, France: IEA/OECD; 2004.

[6] IEA (International Energy Agency). Energy technology perspectives: scenarios and strategies to 2050. Paris, France: IEA/OECD; 2006.

[7] Kaya Y. The role of CO_2 removal and disposal. Energy Convers Manage 1995;36:375–80.

[8] Hoffert MI, Caldeira K, Jain AK, Haites EF, Harvey LDD, Potter SD, et al. Energy implications of future stabilization of atmospheric CO_2 content. Nature 1998;395:881–4.

[9] Balzhiser RE, Samuels MR, Elasassen JD. Chemical engineering thermodynamics—the study of energy, entropy and equilibrium. Englewood Cliffs, NJ, USA: Prentice-Hall; 1972.

[10] IPCC (Intergovernmental panel on climate change), Climate change 2001: synthesis report. In: Watson RT, the Core Writing Team, editors. Cambridge, UK, and New York, NY, USA: Cambridge University Press, 2001.

[11] Huesemann MH. Can advances in science and technology prevent global warming? Mitigat Adapt Strateg Glob Change 2006;11: 539–77.

[12] Huesemann MH. The limits of technological solutions to sustainable development. Clean Technol Environ Pol 2003;5:21–34.

[13] Holdren JP, Morris G, Mintzer I. Environmental aspects of renewable energy sources. Annu Rev Energy 1980;5:241–91.

[14] Pimentel D, Fried C, Olson L, Schmidt S, Wagner-Johnson K, Westman A, et al. Environmental and social costs of biomass energy. Bioscience 1984;34(2):89–94.

[15] Hoffert MI, Caldeira K, Benford J, Criswell DR, Green C, Herzog HJ, et al. Advanced technology paths to global climate stability: energy for a greenhouse planet. Science 2002;298:981–7.

[16] Jackson RB, Banner JL, Jobbágy EG, Pockman WT, Wall DH. Ecosystem carbon loss with woody plant invasion of grasslands. Nature 2002;418:623–6.

[17] Stephens BB, Gurney KR, Tans PP, Sweeney C, Peters W, Bruhwiler L, et al. Weak northern and strong tropical land carbon uptake from vertical profiles of atmospheric CO_2. Science 2007;316: 1732–5.

[18] Chrisholm SW, Falkowski PG, Cullen JJ. Discrediting ocean fertilization. Science 2001;294:309–10.

[19] Buessler KO, Boyd PW. Will ocean fertilization work? Science 2003;300:67–8.

[20] Broecker WS. Thermohaline circulation, the Achilles heel of our climate system: will man-made CO_2 upset the current balance? Science 1997;278:1582–8.

[21] IPCC (Intergovernmental Panel on Climate Change). In: Metz B, Davidson O, de Coninck HC, Loos M, Mayer LA, editors. Special report on carbon dioxide capture and storage. Cambridge, UK, and New York, NY, USA: Cambridge University Press; 2005.

[22] Aya I, Yamane K, Shiozaki K. Proposal of self sinking CO_2 sending system: COSMOS. In: Eliasson B, Riemer PWF, Wokaun A, editors. In: Proceedings of the 4th international conference on greenhouse gas control technologies. Amsterdam: Pergamon; 1999. p. 269–74.

[23] Caldeira K, Jain AK, Hoffert MI. Climate sensitivity uncertainty and the need for energy without CO_2 emissions. Science 2003;299: 2052–4.

[24] Seibel BA, Walsh PJ. Potential impacts of CO_2 injection on deep-sea biota. Science 2001;294:319–20.

[25] Klara SM, Srivastava RD, McIlvried HG. Integrated collaborative technology development program for CO_2 sequestration in geologic formations—United States Department of Energy R&D. Energy Convers Manage 2003;44:2699–712.

[26] Haszeldine RS. Deep geological CO_2 storage: principles reviewed, and prospecting for bio-energy disposal sites. Mitigat Adapt Strateg Glob Change 2006;11:377–401.

[27] Turkenburg WC. Sustainable development, climate change, and carbon dioxide removal (CDR). Energy Convers Manage 1997;38S:3–12.

[28] Pacala S, Socolow RH. Stabilization wedges: solving the climate problem for the next 50 years with current technologies. Science 2004;305:968–72.

[29] Socolow RH. Can we bury global warming? Scientific American 2005;293(1):49–55.

[30] McGrail BP, Schaef HT, Ho AM, Chien Y-J, Dooley JJ, Davidson CL. Potential for carbon dioxide sequestration in flood basalts. J Geophys Res 2006;111(B12201).

[31] Gunter WD, Bachu S, Benson SM. The role of hydrogeological and geochemical trapping in sedimentary basins for secure geological storage for carbon dioxide. In: Baines SJ, Worden RH, editors. Geological storage of carbon dioxide, vol. 233. London, UK: Geological Society Special Publication; 2004. p. 129–45.

[32] Chikatamarla L, Bustin MR. Sequestration potential of acid gases in Western Canadian coals. In: Proceedings of the 2003 international coalbed symposium, Tuscaloosa, AL: University of Alabama, May 5–8, 2003. p. 16.

[33] Kohl AL, Nielsen RB. Gas purification. Houston, TX, USA: Gulf Publishing Company; 1997.

[34] Enick RM, Klara SM. CO_2 solubility in water and brine under reservoir conditions. Chem Eng Commun 1990;90:23–33.

[35] Bachu S. Screening and ranking of sedimentary basins for sequestration of CO_2 in geological media in response to climate change. Environ Geol 2003;44:277–89.

[36] Holm LW, Josendal VA. Effect of oil composition on miscible-type displacement by carbon dioxide. SPE J 1982;22(1):87–98.

[37] Taber JJ, Martin FD, Seright RS. EOR screening criteria revisited—part 1: introduction to screening criteria and enhanced recovery field projects. SPE Reserv Eng 1997;12(3):189–98.

[38] Bondor PL. Applications of carbon dioxide in enhanced oil recovery. Energy Convers Manage 1992;33:579–86.

[39] Holt T, Jensen JJ, Lindeberg E. Underground storage of CO_2 in aquifers and oil reservoirs. Energy Convers Manage 1995;36:535–8.

[40] Bennion DB, Bachu S. Supercritical CO_2 and H_2S—brine drainage and imbibition relative permeability relationships for intergranular sandstone and carbonate formations, *SPE paper 99326*, SPE Europec/EAGE Annual conference and exhibition, Vienna, Austria, June 12–15, 2006. p. 13.

[41] Kumar A, Noh MH, Sepehrnoori K, Pope GA, Bryant SL, Lake LW. Simulating CO_2 storage in deep saline aquifers. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO_2 capture project, vol. 2, geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 877–98.

[42] Juanes R, Spiteri EJ, Orr Jr. FM, Blunt MJ. Impact of relative permeability hysteresis on geological CO_2 storage. Water Resour Res 2006;42:W12418. 13p.

[43] Reeves SR, Schoeling L. Geological sequestration of CO_2 in coal seams: reservoir mechanisms, field performance, and economics. In: Williams DJ, Durie RA, McMullan P, Paulson CAJ, Smith AY, editors. In: Proceedings of the 5th international conference on greenhouse gas control technologies. Collingwood, VIC, Australia: CSIRO Publishing; 2001. p. 593–8.

[44] Orr Jr FM. Storage of carbon dioxide in geologic formations, SPE paper 88842. J Petrol Technol 2004;56(9):90–7.

[45] Gunter WD, Perkins EH, Hutcheon I. Aquifer disposal of acid gases: modeling of water–rock reactions for trapping acid wastes. Appl Geochem 2000;15:1085–95.

[46] Bachu S, Gunter WD, Perkins EH. Aquifer disposal of CO_2: hydrodynamic and mineral trapping. Energy Convers Manage 1994;35(4):269–79.

[47] McPherson BJOL, Cole BS. Multiphase CO_2 flow. Transport and sequestration in the Powder River basin, Wyoming, USA. J Geochem Explor 2000;69–70:1161–6.

[48] Ennis-King JP, Paterson L. Role of convective mixing in the long-term storage of carbon dioxide in deep saline formations. SPE J 2003;10:349–56.

[49] Xu T, Apps JA, Pruess K. Reactive geochemical transport simulation to study mineral trapping for CO_2 disposal in deep arenaceous formations. J Geophys Res 2003;108(B2):2071–84.

[50] Perkins EH, Czernichowski-Lauriol I, Azaroual M, Durst P. Long term predictions of CO_2 storage by mineral and solubility trapping in the Weyburn Midale Reservoir. In: Wilson M, Morris T, Gale JJ, Thambimuthu K, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. II. London, UK: Elsevier; 2004. p. 2093–101.

[51] Dusseault MB, Bachu S, Rothenburg L. Sequestration of CO_2 in salt caverns. J Can Petrol Technol 2004;43(11):49–55.

[52] Bradshaw J, Dance T. Mapping geological storage prospectivity of CO_2 for the world's sedimentary basins and regional source to sink matching. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 583–91.

[53] Perry KF. Natural gas industry experience and technology: potential applications to CO_2 geological storage. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO_2 capture project, vol. 2: geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 815–26.

[54] Moritis G. CO_2 injection gains momentum. Oil Gas J 2006; 104(15):37–57.

[55] Bachu S, Gunter WD. Overview of acid gas injection operations in western Canada. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 443–8.

[56] Stevens SH. Natural CO_2 fields as analogs for geologic CO_2 storage. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO_2 capture project, vol. 2: geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 687–97.

[57] Wilson M, Monea M. IEA GHG Weyburn monitoring and storage project, summary report. In: In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. III. Regina, SK, Canada: Petroleum Technology Research Center; 2004. p. 273.

[58] Torp AT, Gale JJ. Demonstrating storage of CO_2 in geological reservoirs: the Sleipner and SACS projects. In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 311–6.

[59] Riddiford FA, Tourqui A, Bishop CD, Taylor B, Smith M. A cleaner development: the In Salah gas project, Algeria. In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 601–6.

[60] Hovorka SD, Benson SM, Doughty C, Freifeld BM, Sakurai A, Daley TM, et al. Measuring permanence of CO_2 storage in saline formations: the Frio experiment. Environ Geosci 2006;13(2):105–21.

[61] van der Meer LHG, Hartman J, Geel C, Kreft E E. Re-injecting CO_2 into an offshore gas reservoir at a depth of nearly 4000 metres subsea. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 521–30.

[62] Förster A, Norden B, Zink-Jørgensen K, Frykma P, Kulenkampff J, Spangenber E, et al. Baseline characterization of the CO_2Sink geological site at Ketzin. Germany, Environ Geosci 2006;13(3): 145–61.

[63] Cook PJ. Carbon dioxide capture and geological storage: research, development and application in Australia. Int J Environ Stud 2006;63(6):731–49.

[64] Gale JJ. Using coal seams for CO_2 sequestration. Geologica Belgica 2004;7(3–4):99–103.

[65] Bustin RM. Importance of fabric and composition on the stress sensitivity of permeability in some coals, northern Sydney Basin, Australia: relevance to coalbed methane exploration. AAPG Bull 1991;81:1894–908.

[66] Shi J-Q, Durucan S. A numerical simulation study of the Allison Unit CO_2-ECBM pilot: the effect of matrix shrinkage and swelling on ECBM production and CO_2 injectivity. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 431–9.

[67] Cui X, Bustin RM, Chikatamarla L. Adsorption-induced coal swelling and stress: implications for methane production and acid gas sequestration into coal seams, J Geophys Res 2007; 112, B10202, in press, doi:10.1029/2004JB003482.

[68] Zhang CJ, Smith M, McCoy BJ. Kinetics of supercritical fluid extraction of coal: physical and chemical processes. In: Kiran E, Brennecke JF, editors. Supercritical fluid engineering science: fundamentals and applications. Washington, DC: American Chemical Society; 1993. p. 363–79.

[69] Larsen JW. The effects of dissolved CO_2 on coal structure and properties. Int J Coal Geol 2003;57(1):63–70.

[70] Gunter WD, Mavor MJ, Robinson JR. CO_2 storage and enhanced coalbed methane production: field testing at Fenn-Big Valley, Alberta, Canada. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 413–22.

[71] van Bergen F, Pagnier H, Krzystolik P. Field experiment of enhanced coalbed methane–CO_2 in the upper Silesian basin of Poland. Environ Geosci 2006;13(3):201–24.

[72] Wong S, Law D, Deng X, Robinson J, Kadatz B, Gunter WD, et al. Enhanced coalbed methane and CO_2 storage in anthracitic coals— micro-pilot test at south Qinshui, Shanxi, China. Int J Greenhouse Gas Control 2007;1(2):215–22.

[73] Yamaguchi S, Ohga K, Fujioka M, Nato M, Muto S. Field experiment of Japan CO_2 geosequestration in coal seams project (JCOP). In: Gale JJ, Rokke N, Zweigel P, Svenson H, editors. In: Proceedings of the 8th international conference on greenhouse gas control technologies. London, UK: Elsevier; 2006 CD-ROM.

[74] Reeves SR. Coal-Seq project update: field studies of ECBM recovery/CO_2 sequestration in coal seams. In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 557–62.

[75] Dahowski R, Bachu S. Timing of availability and impacts on CO_2 storage in the Alberta Basin, Canada. In: Gale JJ, Rokke N, Zweigel P, Svenson H, editors. In: Proceedings of the 8th international conference on greenhouse gas control technologies. London, UK: Elsevier; 2006 CD-ROM.

[76] Damen K, Faaij A, Turkenburg W. Health, safety and environemntal risks of underground CO_2 storage—overview of mechanisms and current knowledge. Climatic Change 2006;74(1–3): 289–318.

[77] Sminchak J, Gupta N, Byrer C, Bergman P. Issues related to seismic activities induced by the injection of CO_2 in deep saline aquifers. J Energy Environ Res 2002;2:32–46.

[78] Streit JE, Siggins A, Evans B. Predicting and monitoring geomechanical effects of CO_2 injection. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations— results from the CO_2 capture project, vol. 2. Geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 495–500.

[79] Bachu S, Celia MA. Assessing the potential for CO_2 leakage, particularly through wells, from geological storage sites. In: McPherson BJOL, Sundquis E, editors. The science of CO_2 storage, AGU monograph. Washington, DC: American Geophysical Union; 2008, in press.

[80] Kvenvolden KA, Harbaough JW. Reassessment of the rates at which oil from sources enters the marine environment. Environ Res 1983;10:223–43.

[81] Lindeberg E, Bergmo P. The long-term fate of CO_2 injected into an aquifer. In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 489–94.

[82] Celia MA, Bachu S. Geological sequestration of CO_2: is leakage unavoidable and acceptable? In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 477–82.

[83] Pacala S. Global constraints on reservoir leakage. In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 267–72.

[84] Hepple RP, Benson SM. Geologic storage of carbon dioxide as a climate change mitigation strategy: performance requirements and the implications of surface seepage. Environ Geol 2005;47:576–85.

[85] Nordbotten JM, Celia MA, Bachu S. Semi-analytical solution for CO_2 leakage through an abandoned well. Environ Sci Technol 2005;39(2):602–11.

[86] Hawkins DG, Bachu S. Deployment of large-scale CO_2 geological storage: do we know enough to start now? In: Gale JJ, Rokke N, Zweigel P, Svenson H, editors. In: Proceedings of the 8th international conference on greenhouse gas control technologies. London, UK: Elsevier; 2006 CD-ROM.

[87] Morner NA, Etiope G. Carbon degassing from the lithosphere. Glob Planet Change 2002;33:185–203.

[88] Shipton ZK, Evans JP, Dockrill B, Heath J, Williams A, Kirchner D, et al. Natural leaking CO_2-charged systems as analogs for failed geologic storage reservoirs. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO_2 capture project, vol. 2: Geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 699–712.

[89] Gurevich AE, Endres BL, Robertson JO, Chilingar GV. Gas migration from oil and gas fields and associated hazards. J Petrol Sci Eng 1993;9:223–38.

[90] Skinner L. CO_2 blowouts: an emerging problem. World Oil 2003;224(1):38–42.

[91] Pruess K. Numerical simulation of CO_2 leakage from a geologic disposal reservoir, including transitions from super- to subcritical conditions, and boiling of liquid CO_2. SPE J 2004;9(2):237–48.

[92] Pruess K. Numerical studies of fluid leakage from a geologic disposal reservoir for CO_2 show self-limiting feedback between fluid flow and heat transfer. Geophys Res Lett 2005;32:L14404.

[93] Hepple RP. Human health and ecological effects of carbon dioxide exposure. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO_2 capture project, vol. 2: geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 1143–72.

[94] Fleming EA, Brown LM, Cook RI. Overview of production engineering aspects of operating the Denver Unit CO_2 flood. SPE paper 24157. In: Proceedings of the SPE/DOE enhanced oil recovery symposium, vol. 2. Tulsa, OK, April 22–24, 1992, p. 23–36.

[95] Gerlach TM, Doukas MP, McGee KA, Kessler R. Soil efflux and total emission rates of magmatic CO_2 at the Horseshoe Lake tree kill, Mammoth Mountain, California, 1995–1999. Chem Geol 1999;177:101–16.

[96] Saripalli KP, Mahasenan NM, Cook EM. Risk and hazard assessment for projects involving the geological sequestration of CO_2. In: Gale JJ, Kaya Y, editors. In: Proceedings of the 6th international conference on greenhouse gas control technologies, vol. I. Amsterdam: Pergamon; 2003. p. 511–6.

[97] Wang S, Jaffe PR. Dissolution of trace metals in potable aquifers due to CO_2 release from deep formations. Energy Convers Manage 2004;45(18–19):2833–48.

[98] Gasda SE, Bachu S, Celia MA. Spatial characterization of the location of potentially leaky wells penetrating a deep saline aquifer in a mature sedimentary basin. Environ Geol 2004;46:707–20.

[99] Watson TL, Bachu S. Evaluation of the potential for gas and CO_2 leakage along wellbores. SPE paper 106817, synopsis. J Petrol Technol 2007;59(7):78–9.

[100] Hoversten GM, Gasperikova E. Non-seismic geophysical approaches to monitoring. In: Benson SM, editor. *Carbon dioxide capture for storage in deep geologic formations—results from the CO_2 capture project*, vol. 2: geologic storage of carbon dioxide with monitoring and verification. London, UK: Elsevier; 2005. p. 1071–112.

[101] Senior B, Adams J, Espie T, Wright I. Investigation of how capture and storage could evolve as a large scale CO_2 mitigation option. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 943–51.

[102] Kasperson RE, Renn O, Slovic P, Brown HS, Emel J, Goble R, et al. The social amplification of risk: a conceptual framework. Risk Anal 1988;8(2):177–87.

[103] Palmgren CR, Morgan MG, De Bruin WB, Keith DW. Initial public perceptions of deep geological and oceanic disposal of carbon dioxide. Environ Sci Technol 2004;38(24):6441–50.

[104] Curry T, Reiner DM, Ansolabehere S, Herzog HJ. How aware is the public of carbon capture and storage. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 1001–9.

[105] Reiner D, Curry T, de Figueiredo M, Herzog H, Ansolabehere S, Itaoka K, et al. An international comparison of public attitudes towards carbon capture and storage technologies. In: Gale JJ, Rokke N, Zweigel P, Svenson H, editors. In: Proceedings of the 8th international conference on greenhouse gas control technologies. London, UK: Elsevier; 2006 CD-ROM.

[106] Shackley S, McLachlan C, Gough C. The public perception of carbon capture and storage in the UK: results from focus groups and a survey. Climate Pol 2005;4:377–98.

[107] Hawkins DG. Policies to promote carbon-less energy systems. In: Wilson M, Morris T, Gale JJ, Thambimuthu K, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. II. London, UK: Elsevier; 2004. p. 1525–30.

[108] Haines M, Leslie J, MacDonald D. Co-capture and storage of CO_2 with other impurities from coal and other heavy fuel-fired power plant flue gases. In: Rubin ES, Keith DW, Gilboy CF, editors. In: Proceedings of the 7th international conference on greenhouse gas control technologies, vol. I. London, UK: Elsevier; 2005. p. 295–301.