Health, safety and environmental risks of underground CO_2 sequestration

Overview of mechanisms and current knowledge

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Abstract

Carbon dioxide removal is considered to be a potential key strategy to reduce global CO_2 emissions. The principle of carbon dioxide removal is to capture CO_2 produced with the conversion of fossil fuels and sequester the CO_2 in a geological reservoir (also referred to as underground CO_2 sequestration) or the ocean. Insight in the risks associated with CO_2 sequestration is one of the key factors affecting public acceptance and is indispensable to facilitate the formulation of standards and a regulatory framework required for large-scale application of underground CO_2 sequestration. This essay gives an overview of the current (gaps in) knowledge of health, safety and environmental risks caused by underground CO_2 sequestration and research areas that need to be addressed to increase our understanding in those risks.

Health, safety and environmental risks can be caused by surface and injection installations and sequestration of CO_2 in a geological reservoir. The risks caused by a failure in the surface installations are understood and can be minimised by risk abatement technologies and safety measures. A wellhead failure can result in a relatively large flow of CO_2 out of the reservoir, but statistics of underground gas storage (UGS) on leakage through wellhead failure have indicated that the frequency of incidents is low. Less is known on the risks caused by underground CO_2 sequestration, which can mainly be explained by the lack of experience. Underground CO_2 sequestration is a relatively young area; most of the (demonstration) projects are still in their early stages. Also the number of projects and the variety in projects is limited. Due to the limited knowledge on underground CO_2 sequestration, the chance and consequences of the risks can generally not be quantified. Also a common risk assessment methodology to assess long-term consequences of geological CO_2 sequestration is not yet available, but is being developed.

The potential risks of underground CO_2 sequestration include escape of CO_2 and CH_4 from the reservoir (leakage), seismicity, ground movement and displacement of brine. Experience with UGS has indicated that the risk of seismicity is minimal, which is expected to be true for CO_2 sequestration as well. The mechanisms of ground movement are understood, but prediction is difficult. Brine displacement when injecting CO_2 in an aquifer depends too much on local/regional conditions to draw general conclusions on the risks caused by it. Although there are still uncertainties with regard these risks, the main research topic in risks associated with underground CO_2 sequestration is leakage. Leakage of CO_2 and CH_4 from the reservoir can occur through or along (abandoned) wells and by a cap rock failure. Diffusion of CO_2 through the cement or steal casing caused by corrosion is a slow process. However, it is the question what the impact of CO_2 on well integrity will be for a sequestration period of 100 to 10,000's of years. A cap rock failure encompasses various mechanisms resulting into CO_2 migration through high permeability zones in the cap rock or through faults and fractures, which extend into the cap rock. Leakage through faults and fractures is generally considered to be the most important natural leakage pathway.
The type of reservoir, in which CO_2 is injected, is an important factor for the risk of leakage. Hydrocarbon fields, which are well studied, are generally considered to be safe reservoirs for CO_2 sequestration, since they have held oil, gas and often CO_2 for million of years. Although a spontaneous, large release of CO_2 is unlikely, all hydrocarbon reservoirs are likely to leak over (geologic) time. Moreover, exploitation of these reservoirs might have affected the seal integrity. Deep saline aquifers and unminable coal seams on the other hand have not been studied extensively. The risk of leakage might be very relevant for aquifers (considering the enormous potential CO_2 storage capacity), for which the seal integrity has not been proven. Once the CO_2 is completely dissolved, leakage is not likely to occur, since no free CO_2 is available. Coal seams have held methane for million of years and moreover, CO_2 is adsorbed more easily than methane, so the risk of CO_2 leakage is expected to be low.

Considering the present knowledge on risks associated with underground CO_2 sequestration, one of the principal objectives in future R&D is to assess (a range of) leakage rates for the various geological reservoirs discussed. Therefore, more insight is required in the interaction of CO_2 and the reservoir, cap rock and well (cement), migration pathways and the overburden integrity. Leakage rates at its turn are required to quantify the effects on human beings, animals, ecosystems and groundwater quality. Although the effects of elevated concentrations of CO_2 on human beings, animals and even some biota are understood, the effects on groundwater quality and (marine) ecosystems need further research.

Various research programmes on geological CO_2 sequestration exist, in which health, safety and environmental risks (and especially leakage) are important research topics. Most of these programmes are still running, but will be finished in the time period 2003-2005. Research items include the issue of leakage, cap rock and well integrity, interaction between CO_2 and the reservoir and cap rock and possible migration pathways of CO_2. Quite a variety of reservoirs are being studied: aquifers, hydrocarbon reservoirs and coal seams in the USA, Europe, Australia and Japan. There are several ongoing programmes studying industrial and natural analogues. Industrial analogues where CO_2 is injected (CO_2-EOR and acid gas injection) offer the opportunity to study the behaviour of CO_2 in geological reservoirs, leakage through (abandoned) wells and the risks of CO_2 injection (well failure, blow-out). Natural analogues are considered to be useful in providing a better understanding of leakage rates, migration pathways, long-term physical and chemical interactions between CO_2 and the reservoir/cap rocks and effects on groundwater and ecosystems.
Monitoring plays an essential role in R&D programmes as technique to detect CO_2 and to study the development and behaviour of CO_2 in geological reservoirs. Although the existing monitoring techniques enable to study the movement of the CO_2 front in the reservoir and detect CO_2 in air, water and soil, it is difficult to quantify the amount of CO_2 leakage due to limited resolution. Various research programmes investigate the possibilities to optimise and combine different monitoring techniques to increase resolution.

It can be concluded that the R&D programmes currently being undertaken do cover a large part of the research needs. However, risks depend on reservoir and site-specific conditions (which vary strongly among different reservoirs) and the number of R&D programmes focussing on risks associated with underground CO_2 sequestration is limited. Therefore, it is unlikely that all risks will be completely understood and can be quantified after existing and planned R&D programmes have been finished. The reservoir dependence of risks pleads for more pilot projects to allow thorough risk assessment, management and standard setting.

Contents

1 Introduction

In order to stabilise the concentration of greenhouse gasses in the atmosphere, many countries have committed themselves to reduce their greenhouse gas emissions. The required emission reductions (which are dominated by CO_2) can be realised by means of a diverse portfolio of options covering energy and material efficiency improvements, afforestation, increased use of renewable and nuclear energy and decreasing the carbon intensity of fossil fuels. The latter option comprises a shift in fuels (from coal to gas) and carbon dioxide removal, in which CO_2 emitted at stationary sources is captured and sequestered[1] in geological reservoirs or the ocean. It is becoming clear that energy and material efficiency improvements and the use of renewable energy sources cannot yet achieve the required emission reductions alone. The use of nuclear energy meets public resistance in many countries. Given the large amounts of fossil fuels that can be produced at low costs, carbon dioxide capture and sequestration in geological reservoirs is considered to be a potential key element of any strategy to substantially reduce global CO_2 emissions (see e.g. (Herzog et al., 1997; IPCC, 2001; Turkenburg, 1997)). The technical potential (see table 1) is sufficient to sequester worldwide emissions for several decades, although this potential might be reduced when stringent risk standards are applied.

Table 1 Geological reservoir types and estimated global storage capacity (Hendriks et al., 2002; IEA GHG, 1998; IEA GHG, 2000; IEA GHG, 2001)

Reservoir type	Global capacity (Gt CO_2)
Depleted oil and gas fields [a]	920
Deep saline aquifers	240-10,000
Unminable coal seams [b]	40-270

[a] Including oil and gas fields approaching the end of their economically productive life (by primary and secondary production). In these reservoirs, injection of CO_2 may enhance the oil/gas yield (enhanced oil/gas recovery or EOR/EGR).
[b] In these reservoirs, injection of CO_2 can result in the production of coal bed methane (enhanced coal bed methane recovery or ECBM).

Many studies investigated the technical feasibility, potential, economics and barriers of CO_2 capture and sequestration (see e.g. (Hendriks, 1994; Holloway, 1996; IEA GHG, 2000; IEA GHG, 2000)). The risks associated with underground CO_2 sequestration have not been studied so extensively. Insight (or a lack of it) in the risks associated with underground CO_2 sequestration is a key factor affecting public acceptance. Understanding those risks is indispensable to facilitate the formulation of standards and a regulatory framework required for large-scale application of underground CO_2 sequestration.

The Advisory council for research on spatial planning, nature and the environment (RMNO), which advises the Dutch government on the content and organisation of research on environmental issues on the mid and long term, initiated a project on early detection of environmental risks. The purpose of this project is to develop an approach to assess the risks of new technologies and to get an overview of the current scientific status on risks of several large transitions. This essay aims to give an overview of the knowledge and especially the gaps in knowledge with regards health, safety and environmental risks of underground CO_2 sequestration by means of a 4-step procedure:

[1] Sequestration differs from storage in respect to the time window. Storage activities come to an end as soon as the engineering facilities will be decommissioned (10-50 years). The lifetime of sequestration extends beyond the abandonment of the site (100 to 10,000 years) (Wildenborg et al., 2002).

1. The potential risks are identified and described.
2. Scientific publications and reports are analysed to summarize the present knowledge and gaps in knowledge on risks associated with CO_2 sequestration. Also information generated in ongoing R&D projects on CO_2 sequestration is used and interviews with several experts were part of this review activity.
3. Knowledge on industrial and natural analogues for CO_2 sequestration in geological formations is assessed to get insight into which factors/processes might be (ir)relevant to the risks of CO_2 sequestration.
4. On the basis of the outcome of step 2 and 3, research areas are formulated to identify missing information and reduce gaps in knowledge.

Health, safety and environmental risks[2] can be caused by surface and injection installations and by sequestration of CO_2 in the reservoir. Since capture of CO_2 by means of absorption and compression are commonly applied technologies in industry, associated risks are considered to be acceptable according current industry standards and therefore not discussed in this paper. The risks associated with surface and injection installations are discussed very briefly (Holloway, 1996; Gale and Davison, 2003). We will focus on the risks associated with CO_2 sequestration in geological reservoirs. CO_2 sequestration in the ocean is not considered, since this option is not feasible for the Netherlands.

Outline
In chapter 2, the risks of surface and injection installations are described, followed by a more extensive discussion of risks associated with underground CO_2 sequestration in chapter 3. The lessons learned from industrial and natural analogues are given in chapter 4 to come up with future R&D topics in chapter 5. Chapter 6 elaborate on monitoring followed by the main findings and conclusions in chapter 7.

2 Risks associated with surface and injection installations

A CO_2 sequestration scheme requires a surface installation, consisting of a CO_2 transmission pipeline[3], a CO_2 delivery station, a pipeline distribution network and a monitoring system. The injection installation will consist of a number of injection wells. When hydrocarbons are produced simultaneously, the system also comprises production wells and surface facilities to clean, compress and transport extracted hydrocarbons.

CO_2 is transported and injected for enhanced oil recovery (CO_2-EOR) in the USA, Canada, Turkey and Trinidad and Tobago. Worldwide, approximately 3100 km of pipeline exists with a capacity of circa 45 Mt CO_2/yr (Gale and Davison, 2003). The major risk associated with pipeline transport is a pipeline failure, resulting in CO_2 release. A pipeline failure, which can be either a (pin)hole or rupture, can be caused by external interferences, hot tapping by utility workers, corrosion, construction defects and ground movement. Both the likelihood and the possible consequences of a CO_2 pipeline failure have been analysed. The accident record for CO_2 pipelines in the USA shows eight accidents from 1968 to 2000 without any injuries or fatalities[4] (Benson et al., 2002), corresponding to a frequency of approximately 3.10^{-4} incidents per km year. The estimated frequency of a major incident involving large losses of

[2] A risk is defined as the product of chance (frequency) and effects (which can be either health, environmental and economic damage). The economic risks and social risks associated with public acceptance of the technology are not considered in this study.
[3] Although CO_2 transport generally occurs by high-pressure pipelines, trucks can be applied as well and also transport by tankers might be possible in some situations.
[4] It should be mentioned that these pipelines are mainly sited in areas of low to medium population density.

CO_2 from a pipeline of 250 mm (release rates of 0.24 up to 10 t CO_2/s for a pipeline hole and rupture, respectively) using statistics on natural gas pipeline is about 1.10^{-5} per km year (Holloway, 1996). Statistics of incidents with natural gas and hazardous liquid pipelines between 1986 and 2001 in the USA show a frequency of 2.10^{-4} and 8.10^{-4}, respectively (Gale and Davison, 2003). Since CO_2 is not explosive or inflammable, the consequences in case of leakage are expected to be smaller than for natural gas. On the other hand, CO_2 tends to form a blanket on the earth's surface due to the higher density of CO_2 compared to air, while natural gas tends to disappear into the air. The possible consequences of a rupture of a buried pipeline transporting 250 t liquid CO_2/hr at 60 bar have been analysed in (Kruse and Tekeila, 1996). The results of the model indicate that the safety distances to the pipe at which concentrations of minimal 5% will occur for 60 seconds, lie between 150 and 600 m, depending on the distance between safety valves (Kruse and Tekeila, 1996).

The major risk associated with injection is a wellhead failure, which could be caused by unsuitable construction/execution, leaking pipe connections, defective materials and collapse of the well. The likelihood of a sudden escape of all CO_2 stored in an underground reservoir is very small due to the limited capacity of the injection system (Holloway, 1996). In the majority of well failures, an amount equal to the content of the well tubing will be released. In normal cases, this leak will be detected by the monitoring system, resulting in the closure of the back flow preventer and the emergency shutdown valve at the wellhead (Holloway, 1996). Failure of the back-flow preventer or packer may result in a well blow-out (Holloway, 1996). A blowout is an uncontrolled flow of reservoir fluids (which can be CO_2, but also salt water, oil, gas or a mixture of these) into the well bore to the surface. Apart from CO_2 release, the potential consequences are casualties (lethal, injuries) among operators and economic damage caused by explosion or fire when upcoming hydrocarbons are ignited or by parts of the well, which can be launched by the pressure release. The frequency of blow-outs from offshore gas wells has been estimated at 1.10^{-4} per well year, based on a database of blow-outs in the Gulf of Mexico and the North Sea between 1980 and 1996 (CMPT, 1999).

Summarizing, the risks associated with surface and injection/production facilities are well understood. Since the early production of oil and gas, many wells have been drilled and pipelines were constructed to transport the products to the market. So there is a lot of experience with hydrocarbon extraction, processing and transport, which is partly applicable to CO_2 as well. A large amount of data is available on operating experience with surface and injection/production installations, and failure rates of the equipment and the impact on the environment in case of failure (Holloway, 1996).
CO_2 is used in various industrial applications (carbonisation of beverages, cooling, drinking water treatment, welding, foam production etc). Industrial experience with CO_2 and gases shows that the risks from industrial facilities are manageable using standard engineering controls and procedures (Benson et al., 2002). Accidents have happened and people have been killed, but the incidents described were preventable and experience teaches us how to operate these facilities even more safely (Benson et al., 2002). Obviously, safety systems and procedures should be applied consistently.

3 Risks associated with CO_2 sequestration in geological reservoirs

In this chapter, the risks associated with underground CO_2 sequestration are described and gaps in knowledge identified. For each risk, the mechanisms causing the risk and the possible effects will be discussed.

The risks of CO_2 sequestration in a geological reservoir can be divided into 5 categories:

- **CO_2 leakage**: CO_2 migration out of the reservoir through the subsurface and finally into the atmosphere
- **CH_4 leakage**: CO_2 injection might cause CH_4 present in the reservoir to migrate out of the reservoir, through the subsurface and finally into the atmosphere
- **Seismicity**: The occurrence of (micro) earth tremors caused by CO_2 injection
- **Ground movement**: Subsidence or uplift of the earth surface as a consequence of pressure changes induced by CO_2 injection
- **Displacement of brine**: Flow of brine to other formations (possibly sweet water formations) caused by injection of CO_2 in open aquifers

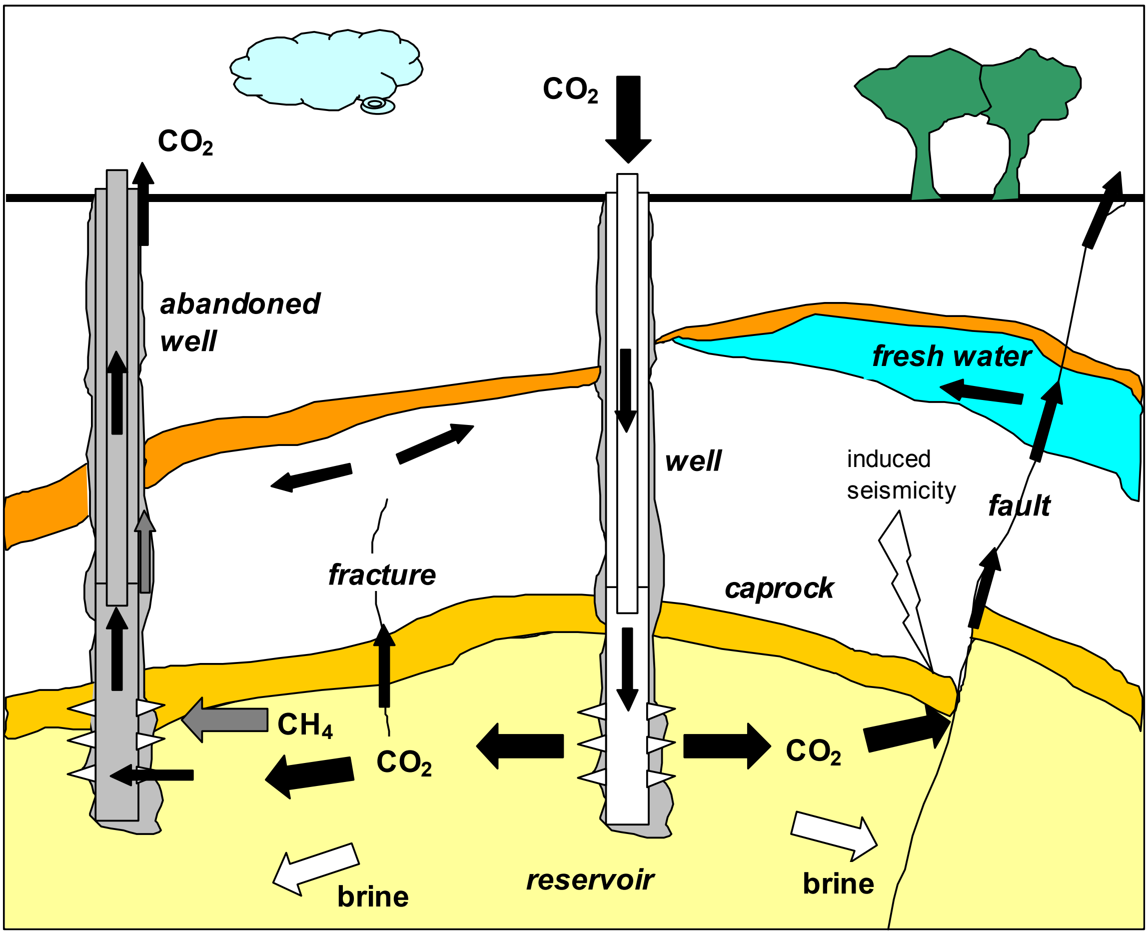

Figure 1 Risks of underground CO_2 sequestration. Black and grey arrows represent CO_2 and CH_4 flows (along abandoned wells, fractures and faults). White arrows represent brine displacement as a consequence of CO_2 injection.

3.1 CO_2 leakage

When CO_2 is injected in geological reservoirs, it might potentially migrate out of the reservoir through the subsurface and finally to the atmosphere/biosphere. The potential for leakage will depend on well and cap rock (seal) integrity and the trapping mechanism, which can be categorized into hydrodynamic trapping, solubility trapping, mineral trapping and adsorption (Reichle et al., 1999):

- When injecting CO_2 in a reservoir, it will primarily be trapped as a gas or supercritical fluid (hydrodynamic trapping). In this state, CO_2 can be considered as “free” and will rise up due to buoyancy effects until it reaches the cap rock, where it will accumulate.

- Since CO_2 is highly soluble in water and also dissolves in oil, solubility trapping is an important trapping mechanism in deep saline aquifers, depleted oil and gas fields. When injecting CO_2 in an aquifer, CO_2 will mainly be present as supercritical fluid before it fully dissolves. Model calculations of CO_2 injection in the Upper Plover formation (Australia) indicate that complete dissolution is expected to take place on a time scale ranging from 10,000 to 100,000 years (Ennis-King and Paterson, 2003). Simulations of CO_2 injection into the Utsira formation at Sleipner suggest that CO_2 will be dissolved completely after 5,000 years (Lindeberg and Bergmo, 2003). The solubility of CO_2 under field conditions remains an uncertainty (van der Meer, 2003). When the CO_2 is completely dissolved, leakage is no longer possible, since free CO_2 is not present anymore, provided that no CO_2 is released as a consequence of pressure and temperature changes in the reservoir.
- CO_2 can also react with minerals and organic matter present in the geologic formations to become part of the solid matrix, also referred to as mineral trapping. However, the extent to which injected CO_2 reacts with minerals present in either sandstone or carbonate reservoirs is low. Reservoir simulations of aquifers similar to the Utsira formation at Sleipner revealed that less than 1% precipitates as carbonate minerals (Johnson and Nitao, 2003).
- In coal seams, CO_2 will be trapped by adsorption to the coal surface displacing adsorbed methane and by physical (hydrodynamic) trapping in the cleats within the coal. Due to adsorption to the coal surface, less “free” CO_2 is present. Consequently, the risk of leakage in coal seams is expected to be smaller than for hydrocarbon reservoirs and deep saline aquifers, where CO_2 is predominantly present in free state.

The permeability of the overburden formations is another critical factor for leakage, since it determines the retention time of CO_2 in the subsurface. Generally, only reservoirs below 800 m are considered for CO_2 sequestration, because at this depth CO_2 will reach supercritical state, where the density of CO_2 ensures optimal storage (van der Meer, 1993). Various models have been developed to predict the movement of CO_2 through the overburden. Simulation of CO_2 diffusion through the 700 m overburden above the Utsira formation at Sleipner indicate that it will take more than 500,000 years for the CO_2 to reach the sea floor (Lindeberg and Bergmo, 2003). A model simulating the release of CO_2 from an aquifer at 1000 m depth in the North-eastern part of the Netherlands indicated a breakthrough time of CO_2 to reach the surface of about 5500 years (Holloway, 1996).

3.1.1 Mechanisms of CO_2 leakage

CO_2 can migrate by several mechanisms from the reservoir through the subsurface and finally to the atmosphere/biosphere. These mechanisms are discussed below for each reservoir type.

Depleted oil and gas fields

Hydrocarbon reservoirs, which generally have been well researched, are considered to be safe sinks for CO_2 sequestration, since these media have held oil/gas for millions of years without large, spontaneous releases. Many gas reservoirs are holding significant quantities of CO_2 as well, giving further confidence that CO_2 can be stored safely without large releases of CO_2. However, there is a risk that CO_2 escapes from the reservoir through or along wells or by means of a cap rock failure. CO_2 might also escape via spill points[5] or dissolve in fluid flow in the reservoir rock beneath the CO_2 accumulation to surrounding formations.

[5] The structurally lowest point in a hydrocarbon trap that can retain hydrocarbons. Once a trap has been filled to its spill point, further storage or retention of hydrocarbons will not occur for lack of reservoir space within that trap.

CO_2 leakage through or along wells after the injection phase can be caused by casing or cementation defects due to improper design or construction, corrosion of the casing and deterioration of cement plugs by CO_2 and/or brine. Leakage may occur through or along abandoned wells and improperly constructed operative wells (for extraction/ injection of hydrocarbons or water). Modern petroleum well completion practices typically include pressure testing of steel tubulars and cement within the well to check for leakage. If identified, leakages are then squeezed off using zone isolation packers and cement (IEA GHG, 2000). Abandoned wells can be an important migration pathway, since depleted oil/gas reservoirs are generally "punctured" by a large number of non-operative exploration and production wells, some of them in bad condition. Especially unidentified and poorly (improperly plugged) abandoned wells are potential point sources. Moreover, control and maintenance of abandoned wells is a complex matter in several regions in the world.
Diffusion of CO_2 through the cement or steal casing caused by corrosion is a process, which will progress very slowly (in the order of 20 cm in 100 years) (Seinen et al., 1994). However, it is uncertain how the well bore integrity (and especially the cement) is affected by CO_2 and brine considering a sequestration timescale of 100's to 10,000's of years. Over such long time scales, abandoned wells may serve as preferential leakage pathways and may therefore represent a significant (long-term) risk (Celia and Bachu, 2003).
In order to assess potential leakage of a certain reservoir, detailed information must be available on the number, type and age of wells, completion technique and type of materials used. This information will not always be available in some regions, making it hard to get a quantitative estimation of leakage potential.

A *cap rock failure* is a generic term for various mechanisms described below:

- Capillary leakage occurs when the pressure difference of fluid phase and the water phase in the pores adjacent to the cap rock is higher than the capillary entry pressure of the cap rock. Since the capillary entry pressure of a cap rock has generally been sufficient to retain hydrocarbons and the capillary entry pressure can be measured by means of core testing, capillary leakage of CO_2 is not considered to be a problem (Jimenez and Chalaturnyk, 2003).
- Diffusion of CO_2 (caused by a difference in CO_2 concentration) through the cap rock is expected to be a very slow process, but can be the controlling mechanism for leakage on the long-term (Jimenez and Chalaturnyk, 2003).
- CO_2 might leak through man-made fractures, also referred to as hydraulic fracturing. Fractures can be created by over pressuring the reservoir. When injecting CO_2 in oil fields, fracturing of the seal might occur as a consequence of the pressure fluctuations in the reservoir (Wildenborg and van der Meer, 2002). Also the (earlier) production/injection processes to exploit hydrocarbon reservoirs may have created fractures. It is possible that fractures will be sealed in time by precipitation of newly formed minerals, but could also be re-opened as a consequence of changes in stresses and/or pressures during CO_2 sequestration (Jimenez and Chalaturnyk, 2003).
  In order to prevent fracturing, the maximum injection pressure should always be kept below the level at which the cap rock may shear (fracture pressure) (Over et al., 1999). The risk of leakage through fracturing is low as long as the storage pressure does not exceed the initial reservoir pressure. However, there is a certain level of overpressure, at which CO_2 can be safely contained. This "safety factor" depends on the stress state of the cap rock, which depends on depth, pore pressure, rock properties and sedimentary and tectonic history.
- Dilatant[6] shear formation and fracturing may occur in cap rocks, which can ultimately create preferential flow paths and increasing the cap rock permeability. However, shear deformation can also result in a reduced permeability (Jimenez and Chalaturnyk, 2003).

[6] Dilantacy is the increase in the volume of rocks as a result of deformation

- High-permeability zones might be formed by reaction of CO_2 with the cap rock, causing the cap rock to dissolve. CO_2 can also dehydrate clay shales in the cap rock, thereby increasing its permeability.
- CO_2 might leak through open (non-sealing) faults, which extend into the cap rock. The risk for leakage along faults can be minimised by performing a detailed analysis of the geological setting of the reservoir prior to injection (IEA GHG, 2003).
- Seismic disturbances might cause cap rock failure (Saripalli et al., 2003).

Of these mechanisms, leakage along or trough wells, faults and fractures are generally considered to be the most important leakage pathways. CO_2 leakage through the cap rock is less controllable and more dependent upon geological characteristics than CO_2 migration through or along wells. Hardly any measurements of CO_2 leakage via these mechanisms have been performed. This makes it rather difficult to quantify the chance it may occur and the possible health, safety and environmental consequences.
Recently, soil gas measurements have been taken at the Rangely Weber oil field, where CO_2 is injected to enhance oil recovery. These measurements indicate annual fluxes of circa 3800 t CO_2 originating from deep sources over an area of 78 km^2 (Klusman, 2003), corresponding to approximately 0.01% of the annual injection CO_2 rate[7].

Deep saline aquifers
Leakage from deep saline aquifers basically occurs via the same mechanisms as discussed above. A major difference with hydrocarbon reservoirs is that aquifers generally do not have cap rocks or seals that have stood the test of time. Since deep saline aquifers are not of economical interest such as hydrocarbon-reservoirs, the number of wells in aquifers, and consequently the potential for CO_2 leakage through/along wells is relatively low. However, exploration and production wells have been drilled through some deep saline aquifers, and this might have created potential leakage pathways.
Another difference with hydrocarbon reservoirs is the fact that CO_2 storage in an aquifer will induce a (temporary) pressure increase in the reservoir, because the space to store CO_2 only becomes available as a result of compression of the fluids and rock in the reservoir, or displacement of formation water into adjacent formations or to the surface (Holloway, 1996).

Deep saline aquifers have not been researched that well as hydrocarbon reservoirs. The Sleipner project is the first commercial CO_2 injection in a deep saline aquifer (the Utsira formation) where an extensive research programme is running to study and monitor CO_2 behaviour in the aquifer. Reactive transport model simulations indicate that after 120 years, mineral precipitation caused by CO_2 will have decreased the porosity and permeability of the cap rock base from 5% to 2.3% and from 3 to 0.3 mDarcy, respectively (Johnson and Nitao, 2003). These results suggest that the sealing properties of the cap rock are enhanced by CO_2 sequestration.

Leakage from a "typical" deep saline aquifer has been modelled to estimate leakage rates from wellhead and cap rock failure, which is used as input for risk assessment. Results indicate that leakage through a failed cap rock poses the highest risk to all environmental media (Saripalli et al., 2003). The calculated flux from a continuous fracture aperture of 2000 microns corresponds to a leakage rate of 0.1% of the total volume stored per year. Leakage rates through permeable zones in the cap rock are estimated at 0.05% of the total volume scored per year. Spatial frequency of cap rock failures within the area of review was estimated at 0.01 for both a fractures cap rock and high-permeability zones, assuming that 1% of the cap rock area spread over an area of review of 50 km radius is fractured and another 1% is highly

[7] In 1998, circa 3 Mt CO_2 was injected at Rangely Weber. The injection rate has decreased slightly in the period 1998-2003 (Wackowski, 2003).

permeable[8]. Although the estimated frequency of 0.00002 for a major wellhead failure based on statistics of underground gas storage (UGS) accidents in the USA and Canada is much lower, the consequences (CO_2 flux) of such event are larger (Saripalli et al., 2003). Moreover, in other regions in the world, the frequency of well failures might be much higher.

Unminable coal seams

Coal seams are unique in the sense that injected CO_2 is to a large extent adsorbed to the coal matrix, replacing methane adsorbed to the coal matrix (coal bed methane). CO_2 is more easily adsorbed to coal than methane. It is argued that if coal seams have held methane for millions of years, it will probably retain CO_2 for another thousand of years as well, provided that CO_2 is sequestered at reservoir pressure. When operating at overpressure, the risk of CO_2 leakage is higher.

The methane content of the target coal seams gives an indication of the sealing capacity of the overburden. Coal can be undersaturated with methane due to degassing in geological history. When a coal seam is undersaturated with methane, the methane must have escaped. Insight in degassing and the sealing capacity of the overburden can be provided by information on the burial history. For each targeted coal seam for CO_2 sequestration, the burial history should be studied to draw conclusions upon the overburden integrity (Wolf, 2003).

The development of this storage technology is behind those of other reservoirs (Gale, 2003). There are still several aspects to be studied on the interaction between CO_2 and coal seams. Especially the chemical and physical reactions that could occur during CO_2 injection into coal seams and their impact on the integrity of the coal seams require further research. One of these reactions is swelling of the coal matrix when injecting CO_2, which might cause a reduction in the permeability. Swelling might also induce stresses on the overlying and underlying rock strata in non ideal coal seams (thin, low permeable and highly faulted), that could cause faulting and possible migration pathways out of the coal seam (Gale, 2003).

3.1.2 Local effects of CO_2 leakage

CO_2 might cause health effects when exposed to humans, animals and ecosystems at elevated concentrations. Health effects of elevated CO_2 concentrations on human beings and animals are well understood. Prolonged exposure to high CO_2 levels, above 20–30%, will cause death by suffocation to humans and the majority of air-breathing animals (Benson et al., 2002). Deaths from catastrophic releases of CO_2 are known from industrial accidents and natural disasters. The sudden release of CO_2 from Lake Nyos (Cameroon) in 1986 caused the deaths of at least 1700 people and many animals. The most widely accepted hypothesis to explain the sudden release is an overturn of the lake, the hypolimnium of which became oversaturated with CO_2, caused by a slow leak of CO_2 from magmatic sources into the deep lake waters (Holloway, 1997). This illustrates that the health hazard caused by CO_2 releases depends mainly on the nature of the incident rather than the initial size of the release. Since CO_2 is heavier than air, leakage of relatively small quantities of CO_2 poses a lethal threat when CO_2 is able to accumulate in confined spaces such as valleys or cellars. The topography around Lake Nyos played a crucial role in the disaster, since it provides ideal conditions for the emitted CO_2 cloud to remain concentrated rather than disperse (Holloway, 1997).

A similar disaster in which anthropogenic CO_2 leaking from a geological reservoir is able to accumulate in a lake is possible, but can simply be prevented by selecting only those reservoirs without any lakes in vicinity. The potential impact on human beings of a sudden release of CO_2 from an offshore reservoir will be lower than from an onshore reservoir. From that perspective, offshore reservoirs deserve preference in selecting reservoirs for sequestration practices.

[8] Obviously, cap rock failure is strongly dependent upon the site-specific geological characteristics and should be evaluated based on a geological characterization.

When migrating upwards from the reservoir, CO_2 may also affect the quality of ground and surface water, soil, energy and mineral resources, which may affect (sub)surface, aquatic and marine ecosystems. In general, the environmental and ecological effects are less well understood as health effects on humans.
Fresh, potable groundwater, located in the 100-200 m of the subsurface, could be contaminated by leakage of CO_2. Even small CO_2 leaks may possibly cause significant deteriorations in the quality of potable groundwater. An increase in CO_2 concentration might cause a decrease in pH to a level of 4-5, which might cause calcium dissolution, increase in the hardness of water and change in the concentration of trace elements (Holloway, 1996). A model simulating the pH change and the enhanced dissolution of trace metals caused by CO_2 dissolution shows that in poorly buffered aquifers, trace metals can be released (by dissolution/desorption) to levels that exceed drinking water standards (Jaffe and Wang, 2003). However, mineral dissolution kinetics, an important parameter affecting trace metal concentration, have not been characterised completely yet.
Surface water could also be contaminated by leakage, which could affect aquatic ecosystems by decreasing the pH, especially in stagnant or stably stratified waters (Benson et al., 2002).
Elevation of CO_2 concentrations in the soil due to leakage is likely to lower the soil pH, and adversely impact the chemistry of nutrients, redox sensitive elements and trace metals, as well as plant growth (Saripalli et al., 2003). Plants usually have a higher resistance against CO_2 than mammals, but persistent leaks could suppress respiration in the root zone. Tree kills associated with soil gas concentrations in the range of 20 to 30% CO_2 have been observed at Mammoth Mountain, California, where volcanic outgassing of CO_2 has been occurring since at least 1990.
The effects of CO_2 on subsurface organisms dwelling in deep geologic formations and the effects on marine ecosystems (when CO_2 is injected in an offshore reservoir) are not well known (Benson et al., 2002). Various studies ((Herzog et al., 1996; Takeuchi et al., 1997)) and research projects (CO_2 Deep Ocean Storage R&D Project) have been/are conducted in which the impact of pH decrease caused by CO_2 injection in the ocean on marine ecosystems (plankton) were/are studied. However, there is a large difference between injection of relatively large quantities CO_2 in the ocean and small leaks of CO_2 from offshore reservoirs to the seafloor.

3.1.3 Global effects of CO_2 leakage

From a global perspective, leakage of CO_2 from reservoirs would make CO_2 sequestration less effective, or even ineffective as mitigation option (depending on the leakage rate). The crucial question is what leakage rates are acceptable to assure stabilisation of atmospheric greenhouse concentrations in the coming century is not endangered. Obviously, the acceptable leakage rate depends on stabilisation targets and the extent and timing of CO_2 sequestration. Let us assume 1000 GtC will be sequestered between now and 2300. In order to stabilise greenhouse gas emissions at a level of 450-750 ppm around 2300, annual anthropogenic greenhouse gas emissions must be reduced to circa 2 to 4 GtC per year (Wigley et al., 1996). If we assume only 1 to 10% of the allowable emission of 3 GtC per year on average may be caused by leakage from underground reservoirs, the maximum leakage rate would be circa 0.003-0.03%. In this simplified calculation we set the leakage rate from the reservoir equal to the leakage rate at the surface into the atmosphere.
Various studies have been performed in which acceptable leakage rates have been assessed by means of simple calculations as performed above and with more advanced models. Hawkins (2003) calculated the emission caused by leakage in a scenario in which the CO_2 reduction required to reach a stabilization level of 450 ppm from the IPCC IS92a reference case emissions to 2100 is completely covered by underground CO_2 sequestration (total sequestration of circa 800 GtC). The results show that with a 99.9 % storage retention time (0.1% annual leakage rate), emissions from leaks rise to the total allowable 450 ppm annual global emission rate by 2200. According calculations performed by Hepple and Benson

(2003), leakage rates must be less than 0.01% per year for stabilisation targets of 350, 450 and 550 ppm CO_2, and be less than 0.1% per year to meet stabilisation targets of 650 and 750 ppm.
Lindeberg (2003) used a more realistic model, in which geological and physical features are accounted for, to calculate required average residence time of CO_2 in geological reservoirs. According his calculations, an average residence time of at least 10,000 years is required.
Although there is a certain range in the acceptable leakage rate, most authors seem to agree that leakage rate should be lower than 0.1% per year.

3.2 CH_4 leakage

The injection of CO_2 in depleted hydrocarbon reservoirs, coal beds and deep saline aquifers might result in leakage of methane and light alkanes, which is ubiquitous in hydrocarbon reservoirs and coal beds and moderately common in deep saline aquifers (Klusman, 2003). An important feature of CH_4 is that it is more mobile than supercritical CO_2. Soil gas measurements at the Rangely Weber CO_2-EOR field indicate annual fluxes of 400 t of thermogenic CH_4 originating from deep sources over an area of 78 km^2 (Klusman, 2003).
Like CO_2 leakage, CH_4 leakage may have both local and global impacts. On a local scale, CH_4 may affect shallow water quality and poses a lethal threat when accumulating in confined spaces such as basements. Since the global warming potential (GWP) of methane is circa 23 times that of CO_2 (IPCC, 2001), CH_4 leakage is an important factor to be assessed in order to verify the effectiveness as greenhouse gas mitigation option[9].

3.3 Seismicity

The injection of large amounts of fluid into a sediment layer or fractured rock modifies its mechanical state. High-pressure liquid injection in geological reservoirs as such cannot lead to the development of earth tremors. However, liquid injection may modify existing underground stress fields such that earth tremors are triggered (Over et al., 1999). Oil and gas reservoirs may be sources of reservoir-induced seismicity, generally when fluids are injected for enhanced oil recovery causing pressure changes in the reservoir (Holloway, 1996). Also when injecting CO_2 in aquifers, the pressure build-up will affect stability of the reservoir, which may cause earth tremors (Over et al., 1999). The risks with regard seismicity for aquifers depend on the type of aquifer. In an aquifer with fractures, a small pressure increase may cause geological instability. For an aquifer without fractures, this is less critical (Over et al., 1999).
Potential effects of reservoir-induced seismicity are CO_2 leakage from the reservoir and damage to buildings and infrastructure. A seismic hazard assessment (as part of the risk assessment of CO_2 sequestration) requires a careful examination of the conditions at the sequestration site, including historical seismicity, structural study of the area, evaluation of the critical fluid pressure for failure and pre-injection seismic monitoring of the area to define "zero-state" seismicity (Holloway, 1996). The problem of seismicity might be more serious when CO_2 is injected into a reservoir in tectonically active regions, which can be found in e.g. Japan and California (Li et al., 2003).

3.4 Ground movement

It is possible that the earth's surface will sink or rise because of man-made pressure changes, which might cause damage to buildings and infrastructure and might also trigger seismicity. Several cases of subsidence in history (mainly during exploitation of oil and gas fields) are

[9] Leakage of 400 t CH_4 corresponds to 25,300 t CO_2 equivalents, which is significantly higher than the measured CO_2 leakage rate at the Rangely Weber field (3800 t per year).

known and well documented. For all these cases, the mechanism is well understood, but prediction of subsidence is found to be difficult (Holloway, 1996).
It is not envisaged that uplift will take place in a CO_2 reservoir as long as the maximum storage pressure is kept below the geostatic pressure. However, in a reservoir that is under high tectonic stresses, any significant reduction of the grain pressure (pressure acting between individual rock particles) may trigger faults. This may lead to uplifting or down-faulting of the surface (Holloway, 1996). Another cause of subsidence may be the chemical reaction between aqueous CO_2 and the reservoir rock, which may cause dissolution of the reservoir rock (chemical compaction). Consequently, the reservoir may cave in under the weight of the overburden formation. Chemical compaction or dissolution of the reservoir rock will particularly be a matter of concern in carbonate rocks with a high (secondary) porosity (Holloway, 1996).

3.5 Displacement of brine

The injection of CO_2 in aquifers might cause displacement of saline groundwater (brine). This may cause undesirable effects such as a rise of the water table and an increase in salinity of drinking water in extraction wells. The fate of brine displaced by the injected CO_2 will be site specific and uncertain (Benson et al., 2002).

4 Industrial and natural analogues for underground CO_2 sequestration

Industrial analogues for underground CO_2 sequestration can be found in enhanced oil recovery with CO_2 (CO_2-EOR), acid gas injection, disposal of industrial and nuclear waste in underground reservoirs and underground storage of natural gas (UGS). At least some of these analogues are common practices in several countries, for which extensive risk assessments have been performed.
Natural analogues include reservoirs where CO_2 has been successfully trapped for geological timescales and reservoirs where CO_2 is leaking at the surface. Oil and gas fields contain CO_2 to various extents. One in ten fields contain 1-5% CO_2 and one in hundred contain on average 50% CO_2 (Bains and Worden, 2001). There are also numerous CO_2 reservoirs, where CO_2 has been held for thousands of years (e.g. Bravo Dome in New Mexico) and where CO_2 is leaking at the surface (e.g. Mammoth Mountain in California).
The experience and knowledge obtained from industrial and natural analogues indicate that CO_2 can be sequestered safely in geological reservoirs, although underground CO_2 sequestration differs from industrial and natural analogues in various aspects. Nevertheless, there are strong similarities, which make analogues valuable to get insights that might increase our understanding in the risks of underground CO_2 sequestration. Industrial analogues might also provide useful insights in risk assessment, management (like monitoring) and mitigation for geologic sequestration of CO_2 (Benson et al., 2002).

4.1 Enhanced oil recovery with CO_2

In most oil fields, only a proportion of the original oil in place is recovered using standard petroleum extraction methods. By injecting CO_2 into those reservoirs, oil recovery can be enhanced by mobilizing the oil through miscible or immiscible displacement, depending on reservoir pressure and oil composition. In many CO_2-EOR projects, CO_2 injection is alternated with water injection to improve oil recovery. At the production well, oil, water, CO_2 and natural gas are produced and separated and CO_2 is recycled to the injection well. Only a part of the injected CO_2 is sequestered by dissolution in immobile oil.

Commercial CO_2-EOR operations are underway in the USA, Canada, Turkey and Trinidad. The USA accounts for the majority of CO_2-EOR oil production with 74 projects in 2000, injecting around 30 million tonnes per year (IEA GHG, 2000).
Although the purpose of CO_2-EOR is primarily oil production and not CO_2 sequestration, CO_2-EOR practices enable us to study the behaviour of CO_2 in the reservoir and the risks of leakage. Monitoring CO_2 in the reservoir might increase our insight in CO_2 sequestration in immobile oil and leakage through abandoned wells and via fractures and faults extending into the cap rock. Unfortunately, CO_2 storage characteristics in the EOR industry have not been well documented (IEA GHG, 2000). The Weyburn Monitoring Project currently investigates the performance of CO_2 sequestration in the Weyburn oil field.

4.2 Acid gas injection

Oil and gas produced from geological reservoirs generally contain varying amounts of hydrogen sulphide (H_2S) and CO_2, acidic components that have to be removed before the product is sent to the market. After the acid gases have been removed by absorption, H_2S can be converted into elemental sulphur and CO_2 vented to the atmosphere. Alternatively, the gases can be flared or re-injected into a geological formation (IEA GHG, 2002).
In western Canada, increasingly more oil and gas producers are turning to acid gas re-injection. The main reason is that sulphur recovery is costly and efforts have been made to reduce flaring. Although the purpose of acid gas injection is to dispose H_2S, significant quantities of CO_2 are injected simultaneously, because it is not economic to separate the gases. The acid gas, with a CO_2 content varying between 15 and 98%, is injected mainly in a supercritical phase, or to a lesser extent as a gas or liquid, or mixed with wastewater from hydrocarbon production (IEA GHG, 2002).
Since 1989, 42 acid gas injection operations have been approved in western Canada, of which 39 active. By the end of 2002, close to 1.5 Mt CO_2 and 1 Mt H_2S have been successfully injected into depleted hydrocarbon reservoirs and saline aquifers. In the USA, another 16 acid gas injection operations exist (IEA GHG, 2002). These acid gas injection operations provide a unique, commercial scale analogue for CO_2 geological sequestration, since CO_2 is injected in similar formations[10] and conditions as considered for underground CO_2 sequestration, also with the purpose of permanent sequestration (in contrast to CO_2-EOR). Monitoring the injected acid gas might increase the insight on long-term containment of CO_2 and leakage by cap rock and well failures. In addition, information on reservoir characteristics of acid gas injection operations can be used to identify sites for underground CO_2 sequestration.

4.3 Underground disposal of industrial waste

The technology of deep well injection of hazardous industrial liquid wastes has many similarities to the technology of CO_2 sequestration in deep saline aquifers. Many of the formations currently used for deep well disposal of industrial waste are also suitable candidates for CO_2 sequestration (Benson et al., 2002).
The risks involved in underground disposal of industrial waste also play a role in underground CO_2 sequestration. Examples of reservoir induced seismicity have been observed for injection of industrial waste (Holloway, 1996). The re-injection of liquid waste in the Rocky Mountain Arsenal (USA) well caused several earthquakes ranging between 0.5 and 5.3 on the Richter scale. Also a blow-out of liquid waste has been reported (Benson et al., 2002).
Early performance of underground disposal of industrial waste in the USA (before the introduction of more stringent regulations) showed many examples of well failures and contamination of drinking water aquifers. Failures were attributed to poor characterization of

[10] The geological conditions at acid gas injection operations are representative of the general conditions encountered within on-shore sedimentary basins, which are considered to be important reservoirs for underground CO_2 sequestration (Bachu et al., 2003).

the confining units, improper well completion techniques, use of well construction materials that were incompatible with the waste streams and consequently corroded, inconsistent or inadequate monitoring, and leakage through abandoned wells (Benson et al., 2002). Recently, the Chemical Manufacturers Association (MCA) undertook a probabilistic risk assessment of component failure of a hazardous waste well system and showed that failure of any of the system components under current regulations was very unlikely, in most cases, much less than 10^{-6} per year (Benson et al., 2002).

However, the chemical and physical features of CO_2 are different from industrial waste such as industrial organic waste or brine water co-produced with oil/gas production. The density of CO_2 is lower than that of liquid waste and therefore, buoyancy forces will tend to drive CO_2 upward, whereas injected fluid wastes tend to migrate away from the injection well with little buoyant force driving it up or down. The effects caused by leakage are comparable neither. This makes the use of underground disposal of industrial waste for underground CO_2 sequestration rather limited (Benson et al., 2002).

4.4 Underground disposal of nuclear waste

Like CO_2 sequestration, safe nuclear waste disposal requires understanding the complex, coupled physical-chemical-mechanical processes that will occur over periods of hundreds to thousands of years (Benson et al., 2002). However, underground disposal of nuclear waste differs in so many aspects from geological CO_2 sequestration. The physical and chemical features of nuclear waste, its potential effects and toxicity and the way nuclear waste is disposed (in waste canisters) make underground disposal of nuclear waste completely different than underground CO_2 sequestration. Moreover, nuclear waste is generally stored in rock-salt formations or deep clay deposits (Commissie Opberging Radioactief Afval, 2001).

The lessons to be learned from underground disposal of nuclear waste should be found in the area of risk assessment methodology, monitoring, and public outreach.

The systematic survey of FEP (features, events, and processes) developed in the nuclear waste area might be suitable to assess the long-term risks associated with underground CO_2 storage (Benson et al., 2002). The FEP framework is a procedure to identify, classify and screen all relevant features, events, and processes that may cause risks. *Features* refer to geologic features, such as stratigraphic layering and faults or fracture zones. *Events* refer to occurrences such as changes in precipitation fluxes, seismic activities, and mining enterprises. *Processes* refer to physical/chemical and other processes active at the site such as buoyancy flow of variable-density fluids and chemical-sorption. By combining critical FEPs, scenarios are constructed and selected for performance assessment (Benson et al., 2002). These scenarios describe possible future evolutions or states of the sequestration facility (Wildenborg et al., 2002). Within the so-called Samcards project, which makes part of the CO_2 capture project, a research programme set up by a large international industrial consortium, this method is currently adapted for the purposes of CO_2 sequestration (Wildenborg et al., 2002). The objective of Samcards is to develop and apply a methodology for the safety assessment of underground CO_2 storage. In addition to the FEP analysis, probabilistic approaches such as the use of complementary cumulative distribution functions (CCDF) for calculating reasonable expectations (for ranges of parameter variability, conceptual uncertainties, and scenario uncertainties) could be very useful for the performance assessment of CO_2 sequestration at a given site (Benson et al., 2002).

4.5 Underground storage of natural gas

Underground (natural) gas storage (UGS) in depleted gas fields and in aquifers is applied to help meet cyclic seasonal and/or daily demands for gas. The practice of UGS might provide useful insights to risk assessment, management and mitigation for geologic sequestration of CO_2.

Like CO_2, natural gas is less dense than water and tends to rise to the top of the storage structure. There are differences as well: CO_2 is denser and more viscous (and thus less mobile), reactive (in particular when dissolved in water) and not explosive nor flammable. Moreover, the duration of CO_2 sequestration is longer than it is for UGS and much larger volumes are involved. These differences deserve special attention in a risk assessment of underground CO_2 sequestration.

While UGS has been applied safely and effectively, there have been a number of documented cases where leakage has occurred. In the vast majority of the cases, leakage is caused by defective wells. Over time, fewer accidents have occurred and modern procedures (among which monitoring) have made UGS a safe and effective operation (Benson et al., 2002). A record of incidents of underground gas storage over a period of 25 years reports only five incidents of 432 underground gas storage facilities, of which none were serious (Gas Research Institute, 1995).
Reservoir induced seismicity has been observed in gas storage reservoirs at two locations (Holloway, 1996). Recent investigations have shown the risk of earth tremors in case of gas storage in empty gas fields to be slight, even at an over-pressure of 10% above initial pressure (if no fundamental changes in reservoir conditions have occurred) (Over et al., 1999). Micro-seismicity might occur as a consequence of underground gas storage, but the magnitudes are generally low. The risk of seismicity caused by CO_2 sequestration in depleted gas fields is likely to be small as well and can be minimised by controlling the injection pressure.

4.6 Natural analogues

Several studies are now underway to investigate natural CO_2 reservoirs and what they may tell us about the effectiveness of geologic sequestration, many of them as part of the NASCENT project contracted by the EU. In this project, several CO_2 accumulations in Europe are studied (Florina in Greece, Mátraderecske and Mihályi in Hungary, Vorderrhön in Germany, Latera in Italy and Montmiral in France) (Pearce et al., 2003). Other research programmes studying natural analogues are NACS (Natural Analogues for Geologic CO_2 Sequestration) and GEODISC. NACS evaluates large commercial CO_2 fields in the USA, mainly for use in enhanced oil recovery projects. GEODISC evaluates the technological, environmental and commercial feasibility of geological sequestration of CO_2 in Australia.

Reservoirs where CO_2 is trapped for geologic timescales are ideal to assess long-term effects of underground of CO_2 sequestration, which is generally not possible with current injection field tests and laboratory experiments. In the Ladbroke Grove and Katnook gas fields in South Australia, CO_2 originating from nearby volcanoes has migrated into these reservoirs between 1 million and 4500 years ago. These natural analogues have been studied within the GEODISC project. Mineralogical analysis of the cap rock has revealed that the porosity has increased slightly due to the presence of CO_2, whereas the permeability is reduced (Watson et al., 2003). This is quite coherent with the model results for CO_2 impact on the cap rock of the Utsira formation (see section 3.1.1).

At sites where CO_2 is actively leaking, leakage rates and pathways can be assessed by soil gas and flux measurements. At Mammoth Mountain, the leakage rate varies between 25 and 7000 g CO_2/day/m^2. At Mátraderecske, the average gas flux is 240 to 480 g CO_2/day/m^2, with a maximum at 18,000 g CO_2/day/m^2, which can result in lethal concentrations in basements and soil gas concentrations resulting in tree/crop death (IEA GHG, 2003).
Soil gas surveys, geophysical (seismic) evidence and laboratory-based migration experiments performed within the NASCENT project indicate that CO_2 migrates predominantly through cap rocks along fractures to the surface. Migration via diffusion and solution in cap rock porewaters is relatively minor (Pearce et al., 2003).

5 R&D topics

In general, there is still a considerable lack of knowledge in many mechanisms and processes involved with underground CO_2 sequestration. There are several reasons for this, the lack of experience being one of the most important. Underground CO_2 sequestration is a relatively young area; most of the (demonstration) projects are still in their early stages. Also the number of projects and the variety in projects is limited. Since each reservoir differs from another and many risks are reservoir specific, it is necessary to do a wide variety of storage projects to get better insight. Finally, not all results of laboratory experiments cannot simply be extrapolated to field conditions, because certain field conditions are difficult to simulate in a laboratory (van der Meer, 2003).

From the previous sections, it can be concluded that the gaps in knowledge with regard the risks of underground CO_2 sequestration lay principally in various aspects related to the issue of leakage:

- realistic leakage rates (fluxes) through various migration pathways (faults, fractures, along wells)
- well integrity and (long-term) impact of CO_2 on cement and casings (especially for abandoned wells)
- cap rock integrity (permeability, chemical and mechanical impact of CO_2 injection). This is a major issue especially for aquifers, for which the sealing capacity for gasses has not been proven.
- overburden integrity
- frequencies of well and cap rock failures
- CO_2 solubility in brine under field conditions
- chemical and physical reactions that could occur when injecting CO_2 in coal seams
- effects of leakage on groundwater (and potential risks this implies to potable water reservoirs) and ecosystems

The overview of current and planned R&D activities (see table 2) shows that priorities are indeed given to CO_2 behaviour and leakage. The current research programmes pay less attention to the risks of CH_4 leakage, seismicity, ground movement and brine displacement, because the mechanisms causing these risks are understood or because the risk is expected to be small or can be minimised by applying control technologies and procedures. Although specific research topics could not always be derived from the available information on these research projects, we feel that many of the gaps identified in this study are being addressed in current and planned R&D programmes.

Scientifically based flux rates should be forthcoming from a number of risk assessment R&D programmes (Gale, 2003).

Well failure and the impact of CO_2 on cement and casings are being studied (amongst others in CCP project). The experience with CO_2-EOR and acid gas injection might be used to get an indication of frequencies and leakage rates.

Cap rock performance and the impact of CO_2 is an important issue that is studied in various research programmes. A core sample from the cap rock above the Utsira formation in the North Sea has recently been taken and is now subjected to a detailed analysis (IEA GHG, 2003). Long-term physical and chemical interactions between the stored gas and the reservoir rock and the cap rock are being assessed within the NASCENT project. Field measurements are particularly useful to determine the large-scale features of the cap rock that could not be tested on laboratory samples, such as continuity and the presence of faults or fractures (Benson et al., 2002) and whether faults are sealing or non-sealing.

Table 2 Summary of research work on risks of underground CO_2 sequestration (see http://www.co2sequestration.info/ for detailed description of all projects)

Project	Funding source(s)	Systems	Country	Project aims (related to risks of underground CO_2 sequestration)	Completion
CO_2 capture project (CCP) (SMV team)	- European Commission - US Department of Energy - Klimatek - industry sources	CO_2-EOR CO_2-EGR CO_2-ECBM aquifers	USA and Europe	Develop tools and methodologies for risk assessment, risk mitigation and risk remediation, long term monitoring and verification of CO_2 movement in geological formations, among which: • Develop a methodology for comprehensive risk assessment of long-term storage in oil fields and recommend a monitoring strategy that provides assurance of long-term storage (NGCAS project) • Develop a methodology to conduct detailed probabilistic risk assessment, mitigation and remediation methodology for CO_2 injection and sequestration into coal beds • Assess sealing capacity of tubulars & cement • Develop and apply a methodology for the safety assessment of underground CO_2 storage	2004
GEODISC	- The Australian Greenhouse Office - industry sources	CO_2-EOR aquifers natural analogues	Australia	• Monitor CO_2 injection via modelling of seismic characteristics • Assess and quantify risks associated with CO_2 injection • Develop enhanced understanding of CO_2 trapping through study of natural analogues	2003
RITE CO_2 underground storage project	-	aquifers (on & offshore)	Japan	• Understanding of CO_2 behaviour and interactions in an aquifer • Evaluation of monitoring methods for the assessment of environmental impact and safety	2005
NACS	- US Department of Energy - industry sources	natural analogues	USA	To evaluate the safety and security of geological sequestration processes	2004/2005
NASCENT	- European Commission - industry sources	natural analogues	Europe	Addressing key issues associated with geological CO_2 sequestration that include long-term safety, stability of storage underground, and potential environmental effects of leakage: • Relation between CO_2-charged porewaters and both reservoirs and their cap rocks (geochemistry) • Geomechanical testing and gas migration studies in low permeability cap rocks • Identification of pathways through soil gas surveys for CO_2 and associated tracer gases • Perform geochemical analyses of carbonated waters to assess the effects of CO_2 on groundwater	2004
SACS	- European Commission - national authorities - industry sources	aquifer offshore	Norway	• Undertake geochemistry evaluations and geophysical modelling (phase 1) • Assess well monitoring requirements (phase 1) • Undertake data interpretation studies and verify models developed (phase 2)	Finished in 2002
GEO-SEQ	- US Department of Energy - industry sources	CO_2-EOR CO_2-EGR CO_2-ECBM aquifers	USA	Optimise a set of monitoring technologies ready for full-scale field demonstration in oil, gas, brine formations, and coal formations	2003
Weyburn Monitoring Project	- European Commission - Natural Environment Research Council - British Geological Survey - industry sources	CO_2-EOR	Canada	• Assessment of geochemical impacts on the formation's CO_2 storage integrity and capacity • Monitoring of the movement of various fluids within the reservoir • Fluid and phase behaviour characterisation to establish the mechanisms that govern the distribution and displacement of the CO_2-rich fluids • Applied research for the development of better sequestration monitoring tools and techniques	2004

When the target injection site is a hydrocarbon reservoir, a study should be carried out to determine how the primary, secondary and possibly, tertiary recovery processes[11] may have affected the hydraulic integrity of the bounding seals (Jimenez and Chalaturnyk, 2003).
The NASCENT project is studying the effects of CO_2 leakage from natural CO_2 accumulations on underground and surface water and ecosystems. Since many storage reservoirs are located offshore, it is also important to study the impacts of CO_2 leakage on marine ecosystems. There are several research projects on ocean sequestration also studying the impact of CO_2 on marine organisms, which might increase our insights in this field.

Although many of the research items discussed in this chapter will be covered in R&D programmes, risks strongly depend on reservoir and site-specific conditions (cap rock, stratigraphic layers overburden, onshore/offshore, presence of water resources, ecosystems), for which a large variety exists. Also the number of R&D programmes focussing on the risks associated with underground CO_2 sequestration is limited. Therefore, it is unlikely that all risks will be completely understood and can be quantified after existing and planned R&D programmes have been finished.

6 Monitoring

Monitoring will play an important role in studying the research topics treated in the previous section required to qualify and quantify the risks involved in underground CO_2 sequestration, which is needed to ensure that it will be a safe, effective and acceptable greenhouse mitigation option. The functions of monitoring are (Benson and Myer, 2002):

1. Observe the development of the CO_2 plume
2. Implementation of effective controls on injection well completion, injection rates, and wellhead and formation pressures.
3. Get insight in a broader range of parameters relevant for the performance of CO_2 sequestration:
    - performance of the reservoir and cap rock
    - possible migration pathways (i.e. faults and fractures)
    - solubility
    - geochemical interactions (among which mineral trapping)
    - groundwater and soil quality
    - ecosystem impacts
    - micro-seismicity caused by CO_2 injection (to record the stability of the reservoir)
    - evaluation how effectively the storage reservoir is being used
4. Monitoring also enables modification and fine-tuning of models developed to predict the fate of CO_2 in the reservoir.

In this paragraph, we will briefly discuss the different monitoring techniques and the role these techniques have in providing insight in the risks of CO_2 sequestration. The following techniques can be distinguished (Benson and Myer, 2002; Wildenborg et al., 2002):

- Devices to measure CO_2 flow rate, injection and formation pressures
- Direct measurement methods for CO_2 detection in air, water or soils, including sensors, remote sensing, geochemical methods and tracers.
- Indirect measurement methods for CO_2 plume detection (to track migration of CO_2 plume in locations where there are no monitoring wells). These methods include well logs, geophysical methods (seismic, electromagnetic and gravity) and satellite and airplane based monitoring. Geophysical monitoring techniques are commonly applied in the oil

[11] After primary recovery (pressure depletion) and secondary recovery (waterflooding, injection of water), oil recovery can be increased by means of tertiary recovery techniques such as CO_2 or steam injection

and gas industry. Among these techniques, seismic methods are by far the most highly developed and can cover a large area with high resolution. One of the shortcomings of geophysical techniques is the difficulty in quantifying the amount of CO_2 that is present and the rate of leakage might it occur. Myer et al (2003) studied the resolution of seismic monitoring and concluded that a plume of circa 20,000 t CO_2 at 2000 m depth may be detectable. Other work suggests that the detectable volume of CO_2 would be much smaller (Benson and Myer, 2002). Only by combining geophysical measurements with other techniques, such as formation pressure measurements and reservoir simulation, it will be possible to obtain more quantitative estimates of leakage rates (Benson and Myer, 2002). This will require additional research efforts and field-testing.

- For monitoring earthquakes, subsidence and uplift, the use of tilt meters or a water-levelling network in combination with satellite radar observations is recommended.

At this moment, there are various R&D and demonstration programmes running (or finished), in which the fate and behaviour of CO_2 in different reservoirs is monitored, where plans exist for monitoring or in which monitoring techniques are studied, developed and improved:

- Since October 1996, Statoil has injected annually circa 1 Mt CO_2 captured at the Sleipner platform, which treats natural gas, into a saline aquifer under the North Sea. The multi-institutional research project SACS (Saline Aquifer CO_2 Storage) was formed to predict and monitor the migration of CO_2 injected in the aquifer by means of time-lapse seismic surveys. It appeared that the overall effect of the accumulated CO_2 on the seismic signal is significant, making time-lapse seismic surveying a highly suitable geophysical technique for monitoring CO_2 injection into a saline aquifer (Arts et al., 2003).
- Geochemical monitoring is done within the IEA Weyburn CO_2-EOR Monitoring programme. At the Weyburn oil field (Saskatchewan, Canada), where more than 5000 t CO_2 is injected per day, well samples are taken of produced fluids before and after injection. The trends in chemical composition and the isotope data suggest that the reaction of injected CO_2 with the formation water lowered pH resulting in dissolution of carbonate minerals and production of bicarbonate. Also, the water chemistry suggests that several silicate minerals are influencing water composition and may be in sufficient quantity to buffer pH. These reactions would result in the further production of bicarbonate and lead to precipitation of injected CO_2 as carbonate minerals. The detailed examination of mineral modes and mineral compositions, reservoir and related rocks is underway, allowing a more definitive statement regarding the possibility that CO_2 will be stored as carbonate minerals by silicate-carbonate reactions (Emberley et al., 2003).
- Cost-effective monitoring technology is being developed and tested as part of the USA Department of Energy GEO-SEQ project. Experiments are conducted with cross well seismic and electromagnetic techniques during injection in the Lost Hills oil reservoir in California. It was concluded that the demonstrated methodology, combining crosswell seismic and electromagnetic monitoring, can provide a detailed small-scale understanding of CO_2 flow in a reservoir, that is not achievable from surface geophysical or well log sampling methods (Hoversten et al., 2003). A pilot test is underway at the Vacuum oil field in New Mexico (USA), where electrical resistance tomography (ERT) is developed to track CO_2 movement within a well field (Newmark et al., 2003). Partners of the GEO-SEQ will also conduct a series of field monitoring experiments before, during, and after CO_2 injection into an aquifer (Hovorka and Knox, 2003).
- In the RECOPOL project, which aims at the development of a demonstration site of CO_2 sequestration in coal seams in Poland, two types of monitoring are foreseen: direct CO_2 measurement (sensors will be placed at the surface and in a nearby abandoned mine gallery) and seismic monitoring. Because seismic monitoring has never been applied for CO_2 in coal, 3 different techniques are currently being evaluated (van Bergen et al., 2003).
- Methods for monitoring the integrity (cement plugs, corrosion of casing) of abandoned wells are studied within the CCP project (Wildenborg et al., 2002).

- The studies on natural analogues also enable to evaluate monitoring techniques, particularly with regard detecting and quantifying leakage and ecosystem impacts (Benson and Myer, 2002).

Summarizing, today's monitoring technology makes it possible to detect the presence of CO_2, but the ability to make quantitative estimates of CO_2 leaks is limited. Various research programmes are running to optimise existing monitoring techniques. While improvements can be made and are expected in all of these areas, today's technology provides a good starting point (Benson and Myer, 2002).

7 Conclusions and recommendations

The review of the (gaps in) knowledge of risks associated with underground CO_2 sequestration and research topics that need to be addressed are summarised in table 3. The risks associated with pipeline transport and surface and injection facilities of CO_2 are known and can be minimised by risk abatement technologies and safety measures. The risks of CO_2 sequestration in a geological reservoir are less well understood. Although industrial and natural analogues suggest that CO_2 can be sequestered safely in geological reservoirs for thousands of years, various issues need to be studied in more detail to assess (long-term) risks of underground CO_2 sequestration. There is generic knowledge on the mechanisms and effects of the risks, but the probability of these risks and the consequences of different failure mechanisms can generally not be quantified. This is mainly caused by the lack of experience as underground CO_2 sequestration is a relatively young area and most of the (demonstration) projects are still in their early stages. Another complicating factor is that underground sequestration encompasses long-term effects, which are difficult to assess by means of CO_2 injection operations or laboratory experiments.

Leakage of CO_2 from the reservoir is the main R&D topic. The potential for leakage will depend on trapping mechanism and well, cap rock and overburden integrity. Leakage through or along wells, faults and fractures are generally considered to be the most important leakage pathways. In general, CO_2 leakage through the cap rock is less controllable and more dependent upon geological characteristics than CO_2 migration through or along wells.
The type of reservoir in which CO_2 is sequestered is an important factor for leakage. Hydrocarbon fields are generally well studied and considered to be safe reservoirs for CO_2 sequestration, since they have held oil, gas and often CO_2 for millions of years. Deep saline aquifers and unminable coal seams have not been studied that comprehensively. Especially aquifers need to be studied in more detail considering the enormous potential CO_2 storage capacity. The risk of leakage might be relevant for these reservoirs, for which the seal integrity has not been proven. Coal seams generally have held coal bed methane for million of years and, moreover, CO_2 is adsorbed more easily than methane, so the risk of CO_2 leakage is expected to be low.

One of the principal objectives in future R&D is to assess (a range of) leakage rates for various geological reservoirs. Hereto, cap rock and overburden integrity, the interaction between CO_2 and cap rock and migration pathways such as fractures and faults need to be studied. Although experiments and models suggest that the impact of CO_2 on the cap rock integrity is minimal or even positive, further work is required in this area. The risk of leakage through/along wells (including interaction CO_2 and cement) should be quantified, for which experience from CO_2-EOR and acid gas injection operations might be useful. The leakage rate at its turn is required to quantify the effects on human beings, ecosystems and groundwater quality. Although the effects of elevated concentrations of CO_2 on human beings, animals and even for some biota are understood, the effects on groundwater quality and (marine) ecosystems need further research.

Table 3 Overview available knowledge on risks of underground CO_2 sequestration

Risk	Chance	Potential consequences/effects	R&D topics
Pipeline, surface and injection facilities			
Pipeline failure	- Frequency minor incident in order of 10^{-4} per km year	CO_2 escape (effects see "CO_2 leakage") The consequences can be minimised by application of risk abatement technologies and safety procedures	(1)
Surface equipment failure	Can be estimated from long industrial experience with CO_2 (inc. CO_2-EOR) and other gases	CO_2 escape (effects see "CO_2 leakage") The consequences can be minimised by application of risk abatement technologies and safety procedures	(1)
Well failure (during injection)	Can be estimated from CO_2-EOR, acid gas injection and UGS experience Frequency well blow-out off-shore gas estimated at 10^{-4} per well year	- CO_2 escape (effects see "CO_2 leakage") - well blow-out (might cause casualties among operators) The consequences can be minimised by application of risk abatement technologies and safety procedures	(1)
Underground sequestration			
CO_2 and CH_4 leakage	- Frequency well failure (after injection) unknown, might be estimated from experience with CO_2-EOR, acid gas injection and UGS - Frequency cap rock failure unknown. Problem is that chance is site/reservoir specific - Chance on CO_2 leakage is generally expected to be lowest for coal seams and highest for deep saline aquifers	- Health hazard to people and animals (understood) - Ecosystem impact (not completely understood) - Affect soil and groundwater quality (not completely understood) - Make CO_2 sequestration ineffective as mitigation option	- Determine chance and rate of leakage for different reservoirs - Well, cap rock and overburden integrity require more research - Effects on ecosystems and groundwater quality need to be studied - Hydrocarbon reservoirs relatively well studied, deep saline aquifers and coal seams require more research - Improve monitoring techniques to detect and quantify small CO_2 leaks
Seismicity	Can be estimated from CO_2-EOR, acid gas injection and UGS experience	- Damage to buildings and infrastructure (expected to be small based on UGS experience) - CO_2 leakage	(1)
Ground movement	Can be estimated from CO_2-EOR, acid gas injection and UGS experience	- Damage to buildings and infrastructure - Seismicity	(1)
Displacement of brine	Unknown	- Rise water table - Increase salinity drinking water resources	(1)

(1) These risks are generally understood and considered to be minimal or controllable with risk abatement technologies and safety procedures. Therefore, research topics for these risks are not discussed in literature.

Various research programmes and projects on geological CO_2 sequestration exist, in which risks are important research topics. Most of these programmes are still running and will be finished in the period 2003-2005. Research items include the issue of leakage, cap rock and well integrity, interaction between CO_2 and the reservoir and cap rock, and possible migration pathways of CO_2. Quite a variety of reservoirs are being studied: deep saline aquifers, hydrocarbon reservoirs and coal seams in the US, Europe, Australia and Japan. There are several ongoing programmes studying industrial and natural analogues. Industrial analogues where CO_2 is injected (CO_2-EOR and acid gas injection) offer the opportunity to study the behaviour of CO_2 in geological reservoirs, leakage through (abandoned) wells and the risks of CO_2 injection (well failure, blow-out). Natural analogues are considered to be useful in providing a better understanding of leakage rates, migration pathways, long-term physical and chemical interactions between CO_2 and the reservoir/cap rocks and effects on groundwater and ecosystems.
Monitoring plays an essential role in these projects as technique to detect CO_2 and study the development and behaviour of CO_2 in geological reservoirs. With state of the art monitoring techniques, CO_2 can be detected, but it is difficult to quantify the amount of leakage should it occur. Various research programmes investigate the possibilities to optimise and combine different monitoring techniques.

It can be concluded that R&D programmes currently being undertaken or planned for the future do cover a large part of the research needs. However, risks depend on reservoir and site-specific conditions (cap rock, stratigraphic layers overburden, onshore/offshore, presence of water resources, ecosystems), for which a large variety exists. Also the number of R&D programmes focussing on the risks associated with underground CO_2 sequestration is limited. Therefore, it is unlikely that all risks will be completely understood and can be quantified after existing and planned R&D programmes have been finished. The reservoir dependence of risks pleads to perform (and analyse) a wide variety of storage projects.

Besides the required R&D to increase our insight in risks, also a common risk assessment methodology able to assess long-term effects of underground CO_2 sequestration should be developed. The FEP methodology currently being developed within the CCP project may provide a useful framework for evaluating the risks of geological CO_2 sequestration. This might be an important step to assess the long-term risks of underground CO_2 sequestration consistently.
Risk assessment is needed to ensure that risks will comply with safety standards long after injection has stopped and on-site monitoring is not performed anymore. Simultaneously, risk assessment is the basis for the formulation of a regulatory framework, since it indicates the importance of potential risks, needed to specify standards for sequestration sites. In addition, risk assessment is an important element to set up risk management and control strategies to minimise risks of underground CO_2 sequestration facilities and make it a safe and viable greenhouse gas mitigation option. Much more work needs to be done in this field.

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