

Natural Releases of CO₂

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Cover image taken by Alexandre Halbwachs.

The cover image shows Lake Nyos, Cameroon with degassing operations underway.

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INTRODUCTION

THE NEED TO ENSURE SECURITY OF CO₂ STORAGE

Increasing concentrations of CO₂ in the Earth's atmosphere are enhancing global warming and subsequent climate change. One option for reducing anthropogenic CO₂ emissions to the atmosphere is the deployment of technologies for the capture and storage of CO₂ produced by the combustion of fossil fuels. This option, however, would be deployed as part of a portfolio of measures, including renewable energy, nuclear power, fuel switching and energy efficiency. The technology for capturing CO₂ from power plant is already available and could lead to significant reductions in CO₂ emissions, providing options are available for disposing of the captured CO₂. One of the most attractive methods being considered, which offers potential long-term containment of significant quantities of CO₂, is geological storage.

Geological storage of anthropogenic CO₂ involves injecting the CO₂ underground, for example in depleted oil and gas reservoirs, deep saline reservoirs and unminable coal seams, where it becomes secured in a similar way to hydrocarbons that have remained naturally trapped in gas and oil fields for millions of years.

Storage of CO₂ in gas or oil reservoirs is currently being demonstrated at a commercial scale at a number of sites. For example, since 1996 the Sleipner project has been capturing CO₂ from the natural gas extracted from the Sleipner West gas field in the North Sea and reinjecting it into a deep saline formation above the gas field.

Concerns have been expressed that if CO₂ capture and storage becomes widely deployed possible seepage from these underground storage sites could have a deleterious effect on the environment. These concerns have arisen largely because, over the past few decades, a few natural events involving the rapid emissions of large masses of CO₂ in volcanic areas have resulted in serious incidents.

To understand the circumstances that lead to these natural release incidents, the IEA Greenhouse Gas R&D Programme commissioned eminent geologists from the British Geological Survey and CRIEPI in Japan to provide a factual and balanced overview of natural CO₂ releases from underground sources and their relevance to geological CO₂ storage. This report provides a summary of their findings.

IEA GREENHOUSE GAS R&D PROGRAMME

This report has been produced by the IEA Greenhouse Gas R&D Programme (IEA GHG). IEA GHG is an international collaboration of governments and industries from many countries with several linked objectives:

- To identify and evaluate technologies that could be used to reduce the emissions of greenhouse gases arising from the use of fossil fuels;
- To disseminate the results of those evaluations;
- To identify targets for research, development and demonstration, and promote the appropriate work.

IEA GHG was established in 1991 and, since then, its main focus has been on capture and storage of CO₂. It has also examined a wide range of other technologies, including carbon sequestration in forests, renewable energy sources (biomass and wind energy) and methods for reducing emissions of non-CO₂ greenhouse gases. This helps to put in perspective the potential of capture and storage of CO₂.

NATURAL RELEASES OF CO₂

CO₂ EMISSIONS FROM VOLCANIC ACTIVITIES

The most important process by which naturally occurring CO₂ from underground sources can be emitted into the atmosphere is through the degassing of magma (molten rock) in volcanic areas. When magma rises towards the Earth's surface, the pressure on it is lowered and dissolved CO₂ is released. Most of the CO₂ originating from magma degassing is emitted through volcanoes and associated fissures, or hydrothermal sites.

Volcanic regions by their very nature are prone to eruptions, ground movement, earth tremors and explosions that can fracture the surrounding rocks. They may also contain magma chambers or voids that are capable of holding large volumes of gas (mostly water vapour) that can be suddenly released at high pressure as a result of these fractures.

Although CO₂ is also released rapidly from the central conduit(s) of volcanoes during violent eruptions. It has recently been recognised that non-eruptive

diffuse degassing may be the principle mode of gas release from sites of both active and dormant volcanic activity. For instance around the Yellowstone hydrothermal area in the USA, diffuse degassing has been measured at 16 million tonnes CO₂ per year. In diffuse degassing, the CO₂ can percolate to the surface through porous zones on volcano flanks and through hydrothermal areas (Box 1).

Although they are not common, dormant or extinct volcanoes can also contain crater lakes; worldwide there are around 20-30 such examples.

Crater lakes are located at the top of volcanoes and are commonly surrounded by high crater walls. The lakes overflow down a spillway leading to a valley system. In tropical areas such lakes may be deep and still and the water column within them can become stratified, as there is little seasonal mixing of the lake waters. CO₂, or other gases percolating up highly permeable fissures and fractures into the crater lake floors can dissolve into the lower levels of the lake waters (increasing their density) until they become saturated with respect to CO₂.

BOX 1. AN EXAMPLE OF DIFFUSE DEGASSING



An eruption of Old Faithful, perhaps the world's best known geyser and a major tourist attraction, rises above Yellowstone's Upper Geyser Basin.

Yellowstone is the site of one of the world's largest hydrothermal systems and contains a number of different types of hydrothermal features; all of which release CO₂ by means of diffuse degassing. Geysers occur when CO₂-charged heated water rising from deep within the ground is released periodically and explosively. With hot springs, the water charged with CO₂ is released at a steady, non-explosive rate, whereas with mud pots (sometimes known as mud volcanoes) CO₂ release occurs through clayey mud. (Image courtesy of Smithsonian Institution)

BOX 2. THE DIENG INCIDENT



The Dieng incident was associated with a phreatic explosion that resulted in the formation of a new crater and the reactivation of a pre-existing fracture. Phreatic explosions normally release large volumes of superheated water with only small amounts of CO₂. It was considered that the pure gaseous CO₂ released must have accumulated in a shallow reservoir as a high density fluid before the explosion and was then released through fractures as they opened up due to the pressure build-up in the volcano prior to the explosion. (Image courtesy of Sumarna Hamidi, Volcanological Survey of Indonesia).

BOX 3. LAKE NYOS AND LAKE MONOUN INCIDENTS



Lake Nyos (image above after the CO₂ release) and Lake Monoun are both tropical crater lakes at considerable elevation compared to much of the surrounding topography. The lakes are not seasonally overturning and, due to low-level volcanic activity, springs in the lake bottoms are constantly supplying CO₂ to the bottom of the lakes. This dissolves in the lake water and results in a layer of dense, CO₂-saturated water building up above the bottom of the lake. At Lake Monoun an earthquake is thought to have upset the density stratification of the lake, whereas at Lake Nyos, geologists are uncertain what triggered the sudden release of CO₂; although some suspect a landslide. Whatever the cause, the event resulted in the rapid mixing of the CO₂ supersaturated deep water with the upper layers of the lake, where the reduced pressure allowed the stored CO₂ to effervesce out of solution leading to the sudden release of CO₂ from the crater lake. The cold CO₂ was confined by the crater walls and flowed down into adjoining valleys suffocating people and animals before it could dissipate.

become saturated with respect to CO₂. Once saturated, any disturbance that causes part of the lower lake waters to rise could cause CO₂ to come out of solution. Only a very few, like those at Lake Nyos and Lake Monoun in Cameroon (see below), have become saturated with CO₂. In contrast, the lakes commonly found in temperate regions are seasonally overturning and therefore pose much less potential danger from CO₂ build up, should it occur.

Impact of CO₂ emissions from volcanic activities

The impact of natural CO₂ emissions from volcanic activities on the environment is mainly dependent on the scale and location of the incident. Although CO₂ is non-toxic, a large rapid release of the gas is of concern because CO₂ is an asphyxiant. There are a small number of examples of natural disasters in volcanic areas caused by sudden emissions of large volumes of CO₂ that have led to loss of life.

One of these incidents occurred at the Dieng volcano complex in Indonesia and provides an example of the danger presented by sudden CO₂ emissions from volcanoes following a build-up of gas within them. In 1979, at the Dieng complex, diffusive CO₂ emissions occurred prior to a major eruption. About 200 000 tonnes of pure CO₂ was released and flowed from the volcano to the plain below as a dense layer resulting in the asphyxiation of 142 people (see Box 2).

The two other recorded disasters, however, were associated with sudden emissions of CO₂ from volcanic crater lakes at Lake Nyos and Lake Monoun, both of which are in Cameroon in West Africa (see Box 3). When Lake Monoun overturned in 1984, the sudden release of volcanic CO₂ led to the death of 37 people. In a similar incident at nearby

BOX 4. DIFFUSE DEGASSING AT MAMMOTH MOUNTAIN



Tree kill on the shore of Horseshoe Lake, Mammoth Mountain, California, was caused by CO₂ emerging through the ground along fault zones on the volcano's flanks, following a period of enhanced seismic activity. The gray area in bottom centre of the photo marks the location of trees killed by high concentrations of carbon dioxide gas in the soil. (Photograph by S.R. Brantley)

Lake Nyos in 1986, approximately 1.24 million tonnes of CO₂ was released from the lake in just a few hours and asphyxiated 1700 people. These releases, however, involved a set of specific geographical features and geological processes that contributed to each event and the loss of life that followed.

In addition to these major incidents, there have been a number of smaller incidents that can be attributed to natural CO₂ releases and which have lead to asphyxiation of animals and damage to plant life. In volcanic areas, diffuse degassing of CO₂ is commonplace. The CO₂ normally mixes with air, dissipates rapidly and generally is not considered to be hazardous to man. However, if the dispersion is restricted or there is a sudden increase in seismic activity, high concentrations of CO₂ can accumulate. Notable examples

include the diffuse degassing of CO₂ through soil on the flanks of Mammoth Mountain, California, which resulted in localised ecosystem damage (see Box 4) and the sudden release of CO₂ in the Cava dei Sielci region of the Alban Hills volcanic complex in Italy, which resulted in the deaths of more than 30 animals. Both were associated with an increase in seismic activity in the area.

CO₂ EMISSIONS FROM SEDIMENTARY BASINS

CO₂ also occurs as a result of geological processes in large, sometimes high purity (>90% CO₂) reservoirs in many sedimentary basins. Sedimentary basins are widely spread around the world and many occur in tectonically stable regions, where there is little or no volcanic/hydrothermal activity.

CO₂ is commonly trapped within the porous and permeable reservoir rocks as a supercritical phase (a highly compressed gas) but may also dissolve in any salt water remaining in the rock formation. An overlying impermeable cap rock is often present which acts as a natural seal, in a similar manner to the presence of oil and natural gas fields in sedimentary basins. Naturally occurring CO₂ may also be retained in other geological settings, for example, confined in the pore spaces of sedimentary rocks folded into domes or other structures.

The best documented natural CO₂ field, as well as the worlds' largest supply of commercially traded CO₂, is the McElmo Dome in Colorado. The CO₂ reservoir is capped by over 700m of impervious salt, shale and sandstone which provides an effective seal and, at the time of discovery in 1948, contained an estimated 1.6 billion tonnes of high purity CO₂. A further

notable example is the giant CO₂ field in the Pisgah Anticline, Mississippi, USA which is thought to be around 65 million years old and holds over 200 million tonnes of CO₂.



Mofettes are openings in the earth's surface from which carbon dioxide and other gases escape. The mofettes pictured here, where bubbles of gas constantly rise to the surface, is in the nature reserve Soos near Frantiskovy Lazne, Czech Republik. Image courtesy of André Künzelmann/UFZ



The Bublák mofette in the Eger Basin, Czech Republik. Here, the gas rises spontaneously from the earth's mantle to the surface and is more than 99 per cent CO₂. Image courtesy of André Künzelmann/UFZ

CO₂ leaks from sedimentary basins can occur through permeable rock and/or along any faults or fissures in the rock, although CO₂ can also be accidentally emitted from via boreholes. In some areas CO₂ leakages along faults can result in CO₂ charged groundwater emerging visibly in springs and through old well bores. More typically, however, CO₂ appearing at the ground surface is already dispersed to the surrounding strata, so that it emerges at very low seepage rates and over a larger area than that of the point of origin.

In offshore areas the migration of gases through the seabed commonly produces pockmarks or, where gases emerge along with mud, a mound on the sea floor called a mud volcano. Mud volcanoes may also occur onshore. The best documented natural CO₂ emission from the sea bed occurs in the Tyrrhenian Sea offshore from the Aeolian Islands in Italy. Here 25,000 tonnes of CO₂ per year are released over an area of 15km², most of which dissolves into the sea water.

Impact of CO₂ emissions from sedimentary basins

There are numerous natural CO₂ fields within sedimentary basins around the world some of which, due to the presence of an overlying impermeable cap rock, have held CO₂ for millions of years without evidence of leakage or environmental impact. Many others, however, do leak although there are no recorded incidents involving sudden large emissions of CO₂ from sedimentary basins. Leakage generally manifests itself as carbonated springs or dry seeps and can result in very localized ecosystem damage.

The environmental impact resulting from these leaks is significantly smaller than those occurring in volcanic regions. They depend ultimately on many factors that control the migration and accumulation of this gas. In many cases CO₂ emissions through the ground are not a significant hazard to man because they are dispersed by the wind. The main threat to man is where CO₂ is emitted in situations where it can build up to high concentrations, for example in buildings or in hollows in the ground. Leakages are more likely to have an adverse impact on vegetation, killing it or damaging it depending on the levels of CO₂ released.

There are a number of notable examples of CO₂ emissions from sedimentary basins which present, at most, only very local hazards to man or the natural environment. These include the Southeast Basin in France where several small CO₂ fields are located along major fault systems. The CO₂ dissolves in the groundwater and emerges in carbonated springs, many of which are exploited by the sparkling mineral water industries, such as Badoit, Vichy and Perrier.

The Colorado Plateau is also an interesting example because it contains both major CO₂ fields and areas where CO₂ is leaking. In some areas, such as the Paradox Basin, CO₂ seepage along faults results in CO₂ charged groundwater in several springs and through old well bores. The Crystal Geyser is a dramatic example of leakage along a well bore, which has since become a tourist attraction. The geyser first erupted in 1935 when a well

being drilled intersected a CO₂-charged aquifer. Today the geyser erupts every 4 to 12 hours as a result of pressure changes in the aquifer.

Mátradereske in northern Hungary provides an example of CO₂ leakage as a result of the presence of permeable caprocks above CO₂ fields. High levels of CO₂ have been recorded for some time in this area; however, in 1992 residents in two houses in the village suffered from headaches and since then control flushing systems have been installed.

The impacts of CO₂ emissions in off-shore areas are not well known. CO₂ may emerge at the seabed dissolved in water or as a free gas. If in a free gas phase it may form a train of bubbles that will rise through the water column and is unlikely to build up in high concentrations; although unless the emission rate is very high, the CO₂ is more likely to dissolve in the water column. The dissolution of CO₂ into seawater lowers its pH (increases its acidity), at least locally, and may impact on the marine environment, depending on the dispersion and duration of emissions.



This is the strongest vent in the Panarea degassing field. The average depth is around 10 meters and the seafloor is characterized by a gravel cover. The position is very close to the north point of the Bottaro islet. Image courtesy of Giorgio Caramanna, University La Sapienza, Roma

GEOLOGICAL STORAGE SITES FOR ANTHROPOGENIC CO₂

Geological storage of CO₂ involves injecting the CO₂ underground, such that it becomes trapped in the pore spaces between grains of sedimentary rock in exactly the same way that hydrocarbons are naturally trapped in oil and gas fields. The procedure offers the opportunity to remove large quantities of CO₂ to an underground storage site, using techniques that are both currently available and constantly improving.

ENVIRONMENTAL CONCERNS

Significant quantities of CO₂ are already injected underground around the world in enhanced oil recovery projects. Underground storage of natural gas, an analogous technique, is also widely practised. Nevertheless, because CO₂ is an asphyxiant and heavier than air, there may be concerns about the safety of underground CO₂ storage, either from possible slow seepage or sudden large-scale emission resulting from well failure. Slow seepage is unlikely to give cause for safety concerns unless the gas is inadvertently trapped. The risk of sudden large-scale release of CO₂ would have to be avoided in the same way as for other gases, such as by avoiding unsuitable sites. It is also important that CO₂ remains in the underground storage sites for a long period of time (up to 1000 years) to minimise climate change.

DEVELOPING CO₂ STORAGE SITES

Sites for the geological storage of anthropogenic CO₂ are most likely to be situated in stable sedimentary basins because storage sites will need to be contained in tectonically stable locations with a reasonable storage capacity. Depleted oil and gas reservoirs, in particular, have a number of attractive features as CO₂ storage reservoirs:

- the reservoirs are proven traps, known to have held liquids and gases for millions of years;
- the reservoirs have well known geology;
- a large number of potential sites exist, as thousands of oil and gas fields are approaching the ends of their economically productive lives; and
- exploration costs would be small.

Geological storage of CO₂ can be considered as closely analogous to natural CO₂ fields that occur in sedimentary basins. CO₂ storage sites would need to be sited at carefully selected locations, to take advantage of the geological factors that prevent gas leakage. For a storage operation to earn a permit, regulators would want assurance that any potential gradual CO₂ seepage would only occur at a very slow rate, that sudden releases are extremely unlikely and that any seeps cannot migrate to belowground confined spaces that are vulnerable to sudden release.

The regulatory process is likely to include:

- a rigorous characterisation of the storage site and surrounding area;
- the construction of geological models of the site and surrounding area;
- the simulation of CO₂ injection into the storage reservoir;
- a risk evaluation/management process
- monitoring of the stored CO₂.

To cover the unlikely event that seepage might occur a remediation plan will also likely to be required. If the potential for seepage is identified a remediation plan may be required. During the site characterisation, any concerns over the integrity of the rock cap and its ability to contain CO₂ for the necessary timescales would need to be addressed. During CO₂ injection, monitoring and modelling of the site would be required to provide information needed to demonstrate the selected sites ability to contain CO₂ for the necessary timescales.

CO₂ STORAGE PROJECTS

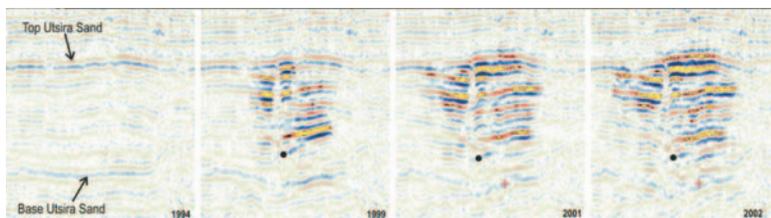
There are a number of current geological CO₂ storage operations being undertaken worldwide. Many of the first CO₂ storage sites were old oil fields

where CO₂ could be injected to boost production of crude oil (known as CO₂ enhanced oil recovery or CO₂-EOR). More recently, underground CO₂ storage is being performed at gas production sites, where raw natural gas produced at the site contains too much CO₂ for commercial use, so the excess is removed, compressed and then injected underground. Examples of such projects that are undergoing detailed monitoring of the surface and subsurface include the Sleipner project in the North Sea and the CO₂-EOR projects at Weyburn in Saskatchewan, Canada and Rangely, in Colorado, USA.

At the Sleipner gas field CO₂ is injected under pressure into the Utsira formation, which is a saline-water-saturated sandstone formation extending under a large area of the North Sea at a depth of about 800m. Approximately 1 million tonnes of CO₂ is removed annually from the raw natural gas and injected into the deep saline reservoir

above the gas field. The CO₂ injection operation started in October 1996 and over the lifetime of the project, a total of 20 million tonnes of CO₂ is expected to be stored. The project has been closely monitored and no migration from the storage reservoir has been detected (see Box 5).

BOX 5. SEISMIC PROFILES OF THE SLEIPNER CO₂ INJECTION SITE



Time lapse seismic profiles through the Utsira Sand and CO₂ plume at the Sleipner CO₂ injection site acquired over the injection point (marked by a black dot) and storage area. The first was acquired in 1994, prior to any CO₂ injection. The subsequent surveys were taken as injection progressed between 1999 and 2002. The difference in reflectivity between the baseline survey (1994) and later surveys is due to the presence of CO₂ in the pore spaces of the reservoir rock.

The seismic profiles demonstrate that the CO₂ has spread out laterally from the injection point in a series of discrete layers. There is no evidence of faults or fractures in the cap rock above the injection site and no evidence that CO₂ is migrating out of the storage reservoir.

BOX 6. THE IEA GHG WEYBURN CO₂ MONITORING AND STORAGE PROJECT



The project has undertaken a comprehensive programme of sub-surface and surface monitoring. This has involved repeat seismic surveying, geochemical sampling of production fluids and soil gas sampling.

Soil gas sampling is designed to detect injected CO₂ that may have escaped from the reservoir and seeped to the surface. Sampling and analysis of gas above the injection site found fluxes for CO₂ and O₂ within the range of that for natural soils and comparable to an off-set reference location, indicating that there is no evidence so far for seepage of injected CO₂ from depth. Image courtesy of PTRC.

The Weyburn Project (Box 6) in Canada combines CO₂-EOR with a comprehensive monitoring and modelling programme to evaluate CO₂ storage. CO₂ injection commenced in 2000 and is anticipated that over the project lifetime some 20 million tonnes of CO₂ will be stored; currently 5 000 tonnes of CO₂ are injected daily. No leakage from the reservoir has been detected to date. Furthermore, long-term predictions indicate that the majority will remain permanently stored for 5000 years.

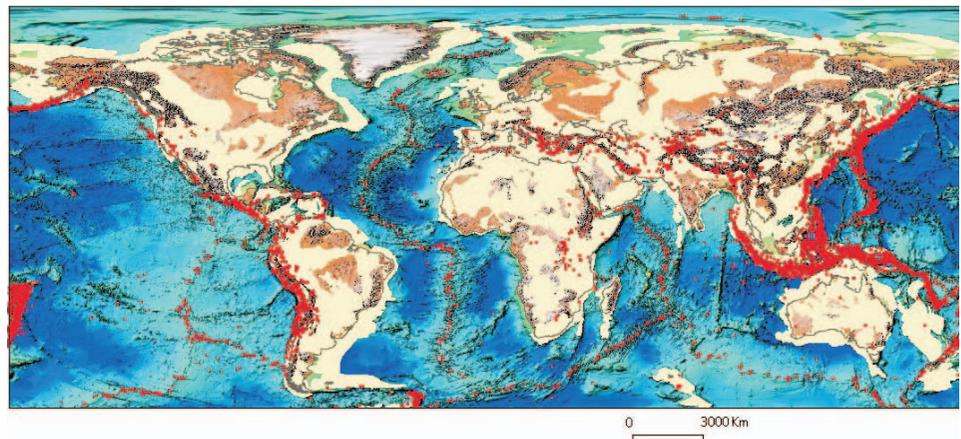
At the Rangely oil field in the USA around 23 million tonnes of CO₂ have been injected into the field since 1986. In 2000, a survey of the field and adjacent areas showed that CO₂ was emerging through the ground surface, albeit at very low seepage rates. Further investigations, however, suggest that this was largely due to the oxidation of methane originating from the oil reservoir or overlying strata, rather than leakage of injected CO₂.

RELEVANCE OF NATURAL CO₂ RELEASES TO GEOLOGICAL STORAGE

DISTINCTION BETWEEN NATURAL CO₂ RELEASES FROM SEDIMENTARY BASINS AND VOLCANIC AREAS

A major distinction can be made between natural CO₂ emissions that occur in volcanic areas and those that occur in sedimentary basins. Volcanic regions and associated hydrothermal areas, where natural emissions of CO₂ occur, are commonly tectonically unstable and may be liable to ground heave and fracturing. Moreover, because heat and steam are commonly present they can contain gas under great pressure, often in voids. The occasional large sudden emissions of CO₂ that have occurred in volcanic and hydrothermal areas are generally associated with seismic activity.

Volcanoes are located mainly around the Pacific rim, the east African rift, and the Atlantic ridge; the majority of the earth's surface is devoid of volcanic activity (see figure below).



Location of world earthquake centre. The red marks indicate earthquake centres above magnitude 5 for the previous 10 years. The yellow shading indicates high prospective or prospective areas. Courtesy of Geoscience Australia

By contrast, sedimentary basins are widely spread around the world and many occur in tectonically stable regions (see figure above). They commonly contain both porous/permeable reservoir rocks and impermeable cap rocks that can act as natural seals and prevent gases reaching the surface. The existence of natural barriers is proven by the presence of oil and natural gas fields in sedimentary basins.

RELEVANCE OF NATURAL CO₂ RELEASES

The major natural CO₂ emissions that have occurred can be regarded as representing fairly exceptional geological situations. These are either tropical crater lakes that do not seasonally overturn and are actively filling with CO₂ due to volcanic activity, or are the result of shallow CO₂ accumulations in voids or magma chambers (again originally from volcanic activity) that are released as a precursor to a volcanic eruption. Such geological situations have nothing in common with the stable sedimentary formations where it is proposed to store CO₂.

For example, at the Dieng volcano, the CO₂ was thought to have accumulated in a shallow reservoir as a high density fluid before the explosion and then released through fractures created due to the pressure build-up in the volcano prior to the explosion. This combination of large volumes of CO₂ gas in shallow reservoirs coupled with fracture development prior to an explosion would not occur in a sedimentary basin.

Similarly, the CO₂ releases at Lakes Nyos and Monoun were again the result of exceptional circumstances unlikely to be found at or near purpose designed CO₂ storage sites. These circumstances included the presence of stratified lakes at considerable elevation, the presence of a slow CO₂ leak into the bottom of the stratified lakes and the unobserved CO₂ saturation of the lower layer of the lake waters.

There are no recorded incidents involving sudden large emissions CO₂ from sedimentary basins. Seepage has been detected from some natural CO₂ fields along faults or as a result of boreholes, which in a few cases has resulted in very localized environmental damage. Although the environmental impact resulting from seepage are significantly smaller than those occurring in volcanic regions. With a rigorous site selection process, the risk of seepage occurring from geological storage sites in sedimentary basins can be minimised.

CONCLUSIONS

Geological storage offers the potential for long-term storage of significant quantities of CO₂. However, concerns over the security of underground storage of CO₂ have arisen largely because of a few natural events involving rapid emissions of large masses of CO₂ that have resulted in serious incidents.

The main incidents involving CO₂ emissions have all arisen in volcanically active regions and can be regarded as representing fairly exceptional geological situations.

Sites considered for geological storage of CO₂ are most likely to be situated in stable sedimentary basins and have nothing in common with the geological situations which resulted in the incidents that occurred in volcanic regions.

Seepages from natural CO₂ fields within sedimentary basins have been detected. However, any resulting ecosystem damage is generally localized and of modest impact. Some sedimentary basins have stored CO₂ for millions of years without any evidence of seepage.

Worldwide, there are a number of on-going geological CO₂ storage projects monitoring the fate of the injected CO₂ in geological formations which have given confidence in this option offering an effective solution for long term storage of significant quantities of CO₂.