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## Publication Date

2002-03-01

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# Lessons Learned from Natural and Industrial Analogues for Storage of Carbon Dioxide in Deep Geological Formations

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| | |
|---|---|
| ACGIH | American Conference of Governmental Industrial Hygienists |
| AEC | Atomic Energy Commission |
| AER | Annual Energy Report |
| AGU | American Geophysical Union |
| ANSI | American National Standards Institute |
| AoR | Area of Review |
| ASHRAE | American Society of Heating, Refrigerating, and Air-conditioning Engineers |
| ASME | American Society of Mechanical Engineers |
| ASR | Aquifer Storage and Recovery |
| ATP | adenosine tri-phosphate |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BCF | billion cubic feet |
| Billion | $10^9$ |
| CAM | Crassulacean acid metabolism |
| CCA | compliance certification application |
| CCA PA | compliance certification application performance assessment |
| CCDF | complementary cumulative distribution function |
| CCGG | Carbon Cycle – Greenhouse Gas |
| CCP | Carbon Capture Project |
| CDC | Center for Disease Control and Prevention |
| CEQA | California Environmental Quality Act |
| CERCLA | Comprehensive Environmental Response, Compensation, and Liability Act |
| CFR | Code of Federal Regulations |
| CGA | Compressed Gas Association |
| CGMP | current good manufacturing practice |
| CMA | Chemical Manufacturers Association |
| CMDL | Climate Monitoring and Diagnostics Laboratory |
| COSPEC | Correlation Spectrometer/Spectroscopy |
| CPCN | Certificate of Public Convenience and Necessity |
| CPUC | California Public Utilities Commission |
| CWA | Clean Water Act |
| DEP | Department of Environmental Protection |
| DHHS | Department of Health and Human Services |
| DIAL | differential absorption lidar |
| DOA | Department of Agriculture |
| DOC | Department of Commerce |
| DOE | Department of Energy |
| DOGGR | Division of Oil, Gas, and Geothermal Resources (California) |
| DOI | Department of the Interior |
| DOL | Department of Labor |
| DOT | Department of Transportation |
| DP | disturbed performance |
| ECOR | eddy-flux correlation |
| EDF | Environmental Defense Fund |
| EEG | Environmental Evaluation Group (State of New Mexico) |
| EIA | Energy Information Administration |
| EOR | enhanced oil recovery |
| EPA | Environmental Protection Agency |
| FAA | Federal Aviation Administration |
| FACE | free air $CO_2$ enrichment |

| | |
|---|---|
| FDA | Food and Drug Administration |
| FEMA | Federal Emergency Management Agency |
| FEP | features, events, and processes |
| FIFRA | Federal Insecticide, Fungicide, and Rodenticide Act |
| FTIR | Fourier-transform infra-red |
| FWQA | Federal Water Quality Administration |
| GAO | General Accounting Office |
| GC | gas chromatography |
| GC-TCD | gas chromatograph with a thermal conductivity detector |
| gpm | gallons per minute |
| GRAS | generally regarded as safe |
| HSE | health, safety, and environmental |
| HSWA | Hazardous and Solid Waste Amendments |
| HVAC | heating, ventilating, and air-conditioning |
| ICSC | International Chemical Safety Card |
| IDLH | Immediate Danger to Life and Health |
| IEAGHG | International Energy Agency Greenhouse Gas Programme |
| ILO | International Labour Organisation |
| IPCC | Intergovernmental Panel on Climate Change |
| IPCS | International Programme on Chemical Safety |
| IR | Infra-red |
| IRGA | Infra-Red Gas Analyzer |
| LDR | Land Disposal Restrictions |
| LEAF | Legal Environmental Assistance Foundation |
| LIDAR | light detection and range finding |
| LNG | Liquefied natural gas |
| Lpm | Liters per minute |
| MMTC/CE/$CO_2$ | Million Metric Tonnes Carbon/Carbon Equivalents/Carbon Dioxide |
| MPL | Maximum Permissible Limit |
| Mt | Million Tonnes (Metric) |
| Mya | million years ago |
| NAS | National Academy of Sciences |
| NASA | National Aeronautics and Space Administration |
| NCTR | National Center for Toxicological Research |
| NDIR | non-dispersive infra-red |
| NEA | Nuclear Energy Agency |
| NF | National Formulary |
| NFPA | National Fire Prevention Association |
| NIEHS | National Institute of Environmental Health Science |
| NIH | National Institutes of Health |
| NIOSH | National Institute of Occupational Safety and Health |
| NOAA | National Oceanic and Atmospheric Administration |
| NoD | Notices of Deficiency |
| NPDES | National Pollutant Discharge Elimination System |
| NRC | Nuclear Regulatory Commission |
| NTP | National Toxicology Program |
| OPS | Office of Pipeline Safety |
| ORIA | Office of Radiation and Indoor Air (EPA) |
| OSHA | Occupational Safety and Health Administration |
| PAVT | Performance assessment verification test |
| PEL | personal exposure limit |

| | |
|---|---|
| PHS | Public Health Service |
| psia | pounds per square inch area |
| R&D | research and development |
| RCRA | Resource Conservation and Recovery Act |
| RL | release limit |
| RTECS | Registry of Toxic Effects of Chemical Substances |
| SARA | Superfund Amendments and Reauthorization Act |
| SBA | supplied breathing air |
| SBS | Sick Building Syndrome |
| SCBA | self-contained breathing apparatus |
| SCUBA | self-contained underwater breathing apparatus |
| SDWA | Safe Drinking Water Act |
| SKI | Swedish Nuclear Power Inspectorate |
| SMV | storage, monitoring, and verification |
| STEL | short-term exposure limit |
| TCF | trillion cubic feet |
| TDS | total dissolved solids |
| TLV | threshold limit value |
| TNRCC | Texas Natural Resource Conservation Commission |
| Ton | 2000 pounds (lbs) |
| Tonne | 1000 kg |
| TRI | Toxic Release Inventory |
| Trillion | $10^{12}$ |
| TRU | transuranic |
| TSCA | Toxic Substances Control Act |
| TWA | time-weighted average |
| UIC | underground injection control |
| UNEP | United Nations Environmental Programme |
| UNFCCC | United Nations Framework Convention on Climate Change |
| UP | undisturbed performance |
| USDW | underground source of drinking water |
| USGCRP | United States Global Change Research Program |
| USP | United States Pharmacopeia |
| VOC | volatile organic compound |
| WHO | World Health Organisation |
| WIPP | Waste Isolation Pilot Plant |

# Executive Summary

The purpose of this study is to gather and interpret relevant information regarding the approaches used for assessing, managing and mitigating risks associated with the deep geologic storage of wastes, or useful products, which may provide guidance for the CCP's R&D program on geologic storage of $CO_2$. Three operations are currently underway in the U.S. that will provide useful insights for geologic storage of $CO_2$, namely, (1) deep well injection of industrial wastes, (2) natural gas storage, and (3) the development of a deep geologic repository for nuclear wastes. The study systematically evaluates the following for each of these three operations:

- History, status and scope of the activity,
- Risk assessment framework and methods, including key issues, performance specifications and performance assessment methods,
- Risk management approaches, including regulatory oversight and permitting, site characterization methods, monitoring and performance confirmation,
- Risk mitigation and remediation methods employed or planned in the event that performance specifications are not met or other unintended consequences arise, and
- Case studies documenting responses to historical accidents.

Ultimately, the health, safety, and environmental risk assessment for geologic storage will be driven by the hazards associated with exposure to elevated concentrations of $CO_2$. Therefore, in addition to reviewing the history and status of these activities, we first review information about human and ecological health risks from exposure to elevated levels of $CO_2$, information from natural analogues for $CO_2$ storage, industrial uses of $CO_2$ and monitoring technology for $CO_2$ detection.

As a first step in this study, we designed and participated in a CCP-sponsored workshop to gather as much information as possible that would be relevant to this investigation. This workshop was held in January 2001. Engineers, scientists and managers with practical experience in each of the above areas were invited to participate in a two-day workshop that was structured to provide information and guide the data gathering and evaluation phase of the project. Participants included individuals from the U.S., Canada and Europe. Following the workshop, we gathered and analyzed data from published literature, the Web and from discussions with noted experts in the field. The information is presented in six sections that are summarized below.

## Lessons Learned about Human Health and Ecosystem Response to Elevated $CO_2$

Carbon dioxide is generally regarded as safe and as a non-toxic, inert gas. It is an essential part of the fundamental biological processes of all living things. It does not cause cancer, affect development, or suppress the immune system in humans. Carbon dioxide is a physiologically active gas that is integral to both respiration and acid-base balance in all life. Exposure to elevated concentrations of $CO_2$ can lead to adverse consequences, including death. The effects of elevated $CO_2$ depend on the concentration and duration of exposure.

Ambient atmospheric concentrations of $CO_2$ are currently about 370 ppm. Humans can tolerate increased concentrations with no physiological effects for exposures up to 1% $CO_2$ (10,000 ppm). For concentrations of up to 3%, physiological adaptation occurs without adverse consequences. A significant effect on respiratory rate and some discomfort occurs at concentrations between 3 and 5%. Above 5%, physical and mental ability is impaired and loss of consciousness can occur. Severe symptoms, including rapid loss of consciousness, possible coma or death, result from prolonged exposure above 10%. Experiments conducted on a group exposed to up to 3% $CO_2$ for many weeks and short-term exposures to even higher concentrations have shown that all effects are reversible except for prolonged coma, the consequences of prolonged hypoxia (lack of oxygen), and death. Loss of consciousness occurs within several breaths and death is imminent at concentrations above 25 to 30%. Deaths from catastrophic releases of $CO_2$ are known from industrial accidents and natural disasters.

The potential for lethal or otherwise harmful exposure depends on the nature of the incident, rather than on the source concentration of $CO_2$ or the initial size of the release. In particular, since $CO_2$ is denser than air, hazardous situations arise when large amounts of $CO_2$ accumulate in low-lying, confined, or poorly ventilated spaces. Releases, even large ones, do not pose a hazard if they are quickly dissipated in the atmosphere, such as from tall industrial stacks or explosive volcanic events.

Evidence for the effects of exposure to elevated concentrations of $CO_2$ on natural resources and ecosystems comes from many sources, including volcanic releases, soda springs, comparative, respiratory and fundamental physiology, free-air $CO_2$ enrichment studies, food preservation literature, and space science research. Among the major classes of terrestrial vertebrates, respiratory physiology and mechanisms for acid-base balance (pH regulation) vary widely, so tolerance to $CO_2$ exposure varies as well. Tolerance for $CO_2$ also correlates to ecological niche suggesting evolutionary adaptation to environmental conditions. Plants, insects, and soil-dwelling organisms have higher tolerance to $CO_2$ than most other forms of life. In spite of these differences, all air-breathing animals including humans have similar respiratory physiology and therefore broadly similar tolerance to $CO_2$, and prolonged exposure to high $CO_2$ levels, above 20–30%, will kill virtually all forms of life except some microbes, invertebrates, fungi, and insects. Some microbes can survive in a pure $CO_2$ atmosphere as long as trace amounts of oxygen are available. However, the identity and physiology of microorganisms dwelling in deep geologic formations is largely unknown, so the effects of $CO_2$ on subsurface microbes are uncertain.

Ecosystem impacts from exposure to elevated concentrations of $CO_2$ are poorly understood. Plants in general are even more tolerant than invertebrates to elevated $CO_2$, so any small-scale, short-term gas leaks would have minimal impacts. Persistent leaks, in contrast, could suppress respiration in the root zone or result in soil acidification, and catastrophic releases could certainly kill vegetation as well as animals. Most of the controlled experiments have focused on the moderate increases in $CO_2$ concentrations that are expected to occur due to atmospheric buildup of $CO_2$ from the continued use of fossil fuels or that stimulate plant productivity in greenhouses. The studies have shown that moderate increases in $CO_2$ concentrations stimulate plant growth, while decreasing the loss of water through transpiration. At the other end of the scale, 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. Little information is available in the intermediate range of 2 to 30%. In addition, information on the tolerance of aquatic ecosystems to short-term, catastrophic releases was not found during this literature search and may need to be researched.

Carbon dioxide is used in a wide variety of industries: from chemical manufacture to beverage carbonation and brewing, from enhanced oil recovery to refrigeration, and from fire suppression to inert-atmosphere food preservation. Sources of $CO_2$ include natural reservoirs, separation from crude oil and natural gas, and as a waste product of industrial processes (chemical manufacture), combustion processes (energy production), and biological respiration (brewing). Because of its extensive use and production, the hazards of $CO_2$ are well known and routinely managed. Engineering and procedural controls are well established for dealing with the hazards of compressed and cryogenic $CO_2$. Nevertheless, the hazards of $CO_2$ are significant as fatalities from fire-suppression-system malfunctions and confined-space accidents attest.

Carbon dioxide is regulated by Federal and State authorities for many different purposes, including occupational safety and health, ventilation and indoor air quality, confined-space hazard and fire suppression, as a respiratory gas and food additive, for animal anesthesia and the humane slaughter of livestock, transportation and most recently as a greenhouse gas (UNFCCC). Federal occupational safety and health regulations set three limits:

- 0.5% or 5,000 ppm for an average 8-hour day or 40-hour week.
- 3% or 30,000 ppm for an average short-term 15-minute exposure limit.
- 4% or 40,000 ppm for the maximum instantaneous exposure limit above which is considered immediately dangerous to life and health.

Most industrial and safety regulations for $CO_2$ focus on engineering controls and specifications for transportation, storage containers, and pipelines.

Monitoring is a routine part of industrial use and production of $CO_2$. Both real-time monitors and air sampling are used to ensure that levels remain within the regulatory guidelines. In addition, $CO_2$ concentrations are routinely measured and used as a proxy for air quality in buildings. Virtually all real-time monitoring devices are based on infrared absorbance at 4.26 μm. Many instruments of this type are commercially available.

Ecosystem measurements of $CO_2$ and $CO_2$ fluxes have also been made using a combination of ground-based and airborne real-time monitoring and sampling. Most flux measurements are made using eddy-flux towers that combine meteorological parameters and $CO_2$ concentration measurements. Soil gas measurements of $CO_2$ concentrations have also been made as part of a number of research programs. The LI-COR monitor, again based on infrared absorbance of $CO_2$ at 4.26 μm, is most commonly used. For larger scale measurements that integrate over a longer path length, LIDAR, DIAL, long-path infrared, and the detection of vegetative stress are being investigated as remote-sensing techniques. We anticipate that remote sensing of all but very large $CO_2$ leaks from geologic formations will be difficult because $CO_2$ is a significant component of the atmosphere and varies naturally in space and time. Nevertheless, this is an important area of research that will help to ensure the safety of geologic $CO_2$ storage.

In addition to understanding when and how $CO_2$ is regulated for industrial and occupational settings, it is also important to know that $CO_2$ is not regulated, studied, or suspected as a toxic substance by the following federal agencies or regulations, including: Clean Air Act 1970, 1990, Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) 1972, Resource Conservation and Recovery Act (RCRA) 1976, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) 1980, Superfund Amendments and Reauthorization Act (SARA) 1986, National Toxicology Program, Agency for Toxic Substances and Disease Registry or the National Institute of Occupational Safety and Health within the Center for Disease Control and Prevention, National Institute of Environmental Health Science in the National Institutes of Health, and the National Center for Toxicological Research (NTCR) in the FDA. Only the inventory list for the Toxic Substances Control Act (TSCA) of 1976, the NIOSH confined space hazard classification system, and FEMA's hazardous materials guide treat $CO_2$ as a hazardous substance to the extent that any concentrated, pressurized or cryogenic gas poses a danger.

In conclusion, the key poorly understood health, safety and environmental concerns surrounding geologic sequestration of $CO_2$ relate to the potential for unanticipated leakage. Such releases could be associated with surface facilities, injection wells, or natural geological "containers" and may range from small-scale diffuse leaks to large catastrophic incidents. Long industrial experience with $CO_2$ and gases in general shows that the risks from industrial sequestration facilities are manageable using standard engineering controls and procedures. Serious 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. On the other hand, our understanding of and ability to predict $CO_2$ releases and their characteristics in any given geologic and geographic setting is far more challenging. Certainly there are many sites, such as oil and gas reservoirs where the probability of leakage is very low. However, brine formations, which generally are not well characterized and do not have caprocks or seals that have stood the test of time, will require significant effort to evaluate potential risks, and these risks must be taken seriously.

To date, the majority of the thought process regarding the risks of $CO_2$ geologic storage has revolved around human health risks. This study raises the issue that, if leakage occurs, ecosystem risks may also be significant, particularly for soil dwelling or ground hugging organisms. In addition, acidification of soils in the vicinity of surface leaks may also harm plants. Similarly, persistent low-level leakage could affect aquatic ecosystems by lowering the pH, especially in stagnant or stably stratified waters.

## Lessons Learned from Natural Analogues

Natural analogues for geologic storage of $CO_2$ provide information useful for demonstrating that long-term containment is possible and for characterizing the nature of potential risks from surface leakage, should it occur. Many studies are now underway to investigate natural $CO_2$ reservoirs and what they may tell us about the effectiveness of geologic sequestration. Less attention has been paid to $CO_2$ releases in this context. For this reason, most of this analysis was focused on reviewing the literature about natural releases of $CO_2$.

Carbon dioxide is contained in $CO_2$, natural gas, and oil reservoirs throughout the world. In locations where $CO_2$ concentrations exceed 10%, the origin is attributed, in part or primarily, to magmatic sources. Lower concentrations can be attributed to the decomposition of organic matter and the thermal decomposition of carbonate rocks. Effective containment of $CO_2$ occurs in the same types of geologic settings that trap hydrocarbons, mostly in sedimentary rocks overlain by low permeability strata. There is no evidence that $CO_2$ is stored underground any less effectively than other gases. Moreover, $CO_2$ accumulates underground as a gas, mixture of gases, supercritical fluid, and/or solute dissolved in oil or aqueous phase, thus providing confidence that storage will be possible for the range of conditions expected for intentional geologic storage by humans. Aside from the low-BTU (high $CO_2$) natural gas reservoirs, the best-known high $CO_2$ reservoirs are in the Four Corners and Colorado plateau regions of the western United States and in eastern China. No mention of natural catastrophic releases from conventional hydrocarbon or gas reservoirs was found during this literature review. Nevertheless, all hydrocarbon reservoirs, whether oil or gas, are thought to leak over geologic time. Vertically stacked $CO_2$ reservoirs are known and provide opportunities to study $CO_2$ migration, containment, and leakage over geologic timeframes of thousands to millions of years.

A comprehensive global review of $CO_2$ reservoirs and $CO_2$ in hydrocarbon reservoirs would be a valuable source of information to help determine whether or not geologic storage of $CO_2$ can be safe and effective. Assessing the seal integrity of known trapping systems like those in oil and gas reservoirs should be undertaken. A study of sealing mechanisms, caprock properties, leakage rates, and surface manifestations for hydrocarbon reservoirs would answer many of the questions currently being asked about long-term subsurface $CO_2$ storage and possible leakage. For large, brine-filled formations where the seal integrity has not been established, a more thorough site and regional characterization of containment structures and regional groundwater flow will be necessary. Also, the fate of brine displaced by the injected $CO_2$ remains a major uncertainty.

Examples of settings where $CO_2$ releases occur span the full range from the ubiquitous benign examples of diffuse off-gassing from soda springs to catastrophic examples from volcanic provenances. Diffuse $CO_2$ fluxes from the ground occur over most of the surface of the Earth and take place from bulk earth de-gassing, biological respiration, and organic matter decomposition. Most detectable leaks that lead locally to elevated atmospheric $CO_2$ concentrations and virtually all hazardous leaks occur in volcanic areas that are highly fractured and therefore unsuitable for sequestration. Large natural releases from these environments have had catastrophic consequences and continue to pose significant hazards. The most recent and publicized of these is the limnic eruption that occurred at Lake Nyos in Cameroon and killed over 1700 people and thousands of animals.

Note that the amounts of $CO_2$ involved at Lake Nyos and five other known $CO_2$-related natural disasters were small in comparison to the amounts to be injected annually for sequestration. On the other hand, the amount of $CO_2$ released in many volcanic eruptions is enormous but poses little or no direct hazard due to the force of release and subsequent dispersion high in the atmosphere. This apparent inconsistency leads to the conclusion that the level of hazard is defined more by the nature of the release and subsequent concentration versus dispersion of $CO_2$, rather than simplistically defined by the total volume released. These natural $CO_2$ leaks can be used to validate air dispersion models and/or coupled land surface-atmospheric models in assessing the potential hazards of various release scenarios.

A number of observations and research needs are apparent after reviewing natural analogues for geologic carbon sequestration. The analysis of known surface releases reveals that natural disasters involving $CO_2$ are unusual, yet when they occur, the associated hazards are significant. There are persistent risks of $CO_2$ accumulating in low lying or confined spaces near natural releases, even though most disperses harmlessly. Therefore, sequestration efforts must define and prove either that containment is completely effective or that the leakages are small enough and that dispersion is sufficient to prevent hazardous concentrations from accumulating.

The monitoring program at Mammoth Mountain reveals that we can detect significant leaks, and degassing Lakes Nyos and Monoun demonstrates that we can mitigate the potential hazard of limnic eruptions. Of greater importance is that all of the significant $CO_2$ hazards are associated with volcanism and not with any known $CO_2$ reservoirs or geologic settings that would be considered for sequestration. Diffuse emissions, cold soda and geothermal springs and associated travertine deposits are common and generally benign surface manifestations of $CO_2$, though accidents at geothermal plants and springs from pulses of $CO_2$ are known.

In conclusion, models for successful underground $CO_2$ storage exist but so do potential risks. To be deemed acceptably safe by the public, our understanding of geologic containment must improve. Natural reservoirs provide the opportunity to study many aspects of containment and surface releases by taking soil gas and flux measurements, testing remote sensing and monitoring techniques, assessing caprock seals, measuring gas composition to determine its origins, and analyzing cores of reservoir rock for diagenetic alteration and to gain a better understanding of the long-term chemical and physical interactions between the stored gas and the reservoir rocks. The risk-assessment process would be aided by finding, mapping, and quantifying any surface leaks and scouting for ecological effects above natural accumulations. The relationship of leakage rate and surface topography versus hazard potential must be assessed for natural manifestations of all types and tied to models of plume dispersion to understand adequately the human health and ecological risks of $CO_2$ releases from geologic carbon sequestration projects.

## Lessons Learned from Disposal of Industrial Waste in Deep Geologic Formations

The USEPA's Underground Injection Control Program recognizes 5 classes of injection wells, including:

- *Class I.* Wells used to inject hazardous, industrial or municipal waste beneath the lowermost formation containing an underground source of drinking water.
- *Class II.* Wells used to inject fluids related to the production of oil or natural gas.
- *Class III.* Wells used to inject for the extraction of minerals such as sulfur, salt, potash, or metals such as uranium by solution mining.
- *Class IV.* Wells used to dispose of hazardous or radioactive waste into or above a formation that contains a USDW or an exempted aquifer. These wells are now effectively prohibited.
- *Class V.* Injection wells not included in Classes I, II, III, or IV.

Class I and Class II wells are most relevant to geologic storage of $CO_2$, particularly with regard to the potential for contaminating drinking water aquifers. However, it is important to recognize that regulations regarding the health, safety and environmental effects of surface facilities and leakage of $CO_2$ back into the atmosphere are likely to be regulated through other programs. Confusion and inefficiencies from overlapping jurisdictions and requirements may create a regulatory morass. Early attention to this issue may prevent decades of frustration with an overly complicated and inefficient set of regulations.

Industrial liquid waste disposal by deep-well injection was initiated in 1939. Since that time the practice has expanded so that now, nine billion gallons per year of hazardous, industrial and municipal wastes are injected into 485 Class I wells. In 1987, the cost of liquid-hazardous-waste disposal ranged from $49 to $207/ton. Early performance was mixed, with many examples of well failures and contamination of drinking water aquifers. Failures were attributed to (1) poor characterization of the confining units; (2) improper well completion techniques; (3) use of well construction materials that were incompatible with the waste streams and, consequently, corroded; (4) inconsistent or inadequate monitoring; and (5) leakage through abandoned wells. Because of these problems and the inconsistent approach to oversight, progressively more stringent regulations were put in place to make the practice of industrial waste disposal by liquid injection safer. By 1988, the current set of regulations was put in place and since that time there have been no incidents where drinking-water contamination has been reported.

EPA has adopted the approach of stringent regulation of deep-well-injection operations, with the goal of ensuring that contamination does not occur in the first place. To obtain a permit for hazardous waste disposal by deep-well injection, the operator must demonstrate that “No Migration” of the waste will occur outside of the formation into which it is injected. The formation must contain over 10,000 parts-per-million of dissolved solids, be overlain by a suitable caprock and be separated from a drinking water aquifer by at least one other impermeable formation.

The regulations mandate stringent controls for the siting, operation, reporting and abandoning of injection wells. Experience has shown that leaks from injection and abandoned wells were the most frequent short-term failure mechanisms. Consequently, much of the current regulatory approach focuses on minimizing the possibility of such failures. Current well completion and rehabilitation techniques appear to be adequate to prevent leakage, although finding abandoned wells remains a significant challenge. As for contamination of drinking water aquifers distant from the wellbore, some efforts to detect transmissive faults between the injection zone and overlying aquifers are mandated, and if monitoring wells are already in place in overlying protective aquifers, EPA also requires that these must be monitored for contamination. The permitting process for hazardous waste injection wells is extensive, time consuming and expensive. According to USEPA (2001e), factoring in the costs for geologic testing and modeling, a “No-Migration” petition can cost in excess of $2,000,000.

When a facility is shut down, the EPA is particularly concerned that deep injection wells, especially those that have injected hazardous waste, are properly plugged and abandoned. Upon closure, a Class I hazardous waste well must be plugged with cement in a manner that will not allow the movement of fluids into or between drinking water aquifers. Class I hazardous waste well operators must also prepare and comply with a plan for post-closure care. The plan must include the predicted position of the waste front at closure, the status of any cleanups required, and the estimated cost of proposed post-closure care. In addition, the owner or operator must continue to conduct any required groundwater monitoring until pressure in the injection zone decays to the point that the well’s cone of influence no longer intersects the base of the lowermost drinking water aquifer. The owner or operator must demonstrate and maintain financial responsibility for post-closure care. This obligation survives the termination of a permit or the cessation of injection and is enforceable regardless of whether the requirement is a condition of the permit.

For deep well injection of liquid wastes, the density of the injected fluid is usually within ±5% of the surrounding formation fluids. In this case, the injected wastes tend to migrate away from the injection well with little buoyant force driving it up or down. For $CO_2$ storage in oil or water-filled geological formations, this will never be the case. Buoyancy forces will tend to drive $CO_2$ upward. A case study of municipal waste disposal in Florida demonstrates that under these conditions, containment can be more difficult and there is evidence that the less dense effluent is migrating in the opposite direction than originally anticipated based on regional hydrologic gradients. This is an important lesson for geologic storage of $CO_2$ and highlights the unique requirements for characterizing sites where the injected fluid will migrate under the action of gravity and not necessarily follow the migration path of or move at the same rate as regional groundwater.

Finally, experience has shown that opposition from communities near operating injection facilities can be strong, and in particular, facilities injecting wastes not generated on-site engender even more opposition. Issues cited include:

- Decrease in property values.
- Accidents associated with mixing wastes.
- Leaking surface impoundments.
- Air pollution.
- Transportation hazards.

In general, facilities far from population centers are subject to less local opposition.

## Lessons Learned From Natural Gas Storage Projects

Underground natural gas storage projects have been operated successfully in the U.S. for almost 90 years and today, 450 projects store approximately 139 million metric tonnes (MMT) of natural gas in 30 states. The majority of storage facilities are in depleted oil and gas reservoirs, but 51 are in brine-filled aquifers and 40 in salt caverns. Experience has shown that there are a number of factors critical to the success of these projects.

- First, it is important to have a site that is adequately characterized (i.e., permeability, thickness and extent of storage reservoir, caprock integrity, geologic structure, lithology, etc.).
- Second, the storage formation should be deep enough to allow sufficiently high gas pressures for the economic success of the operation.
- Third, injection/withdrawal wells must be properly designed, constructed, monitored and maintained.
- Fourth, overpressuring the storage reservoir should be avoided.
- Finally, abandoned wells in and near the project must be located and plugged.

While underground natural gas storage has been used safely and effectively, there have been a number of documented cases where leakage has occurred. In the vast majority of cases, leakage is caused by defective wells (poorly constructed or improperly plugged abandoned wells). Over time, as engineering practices have improved and regulatory oversight has grown more stringent, fewer accidents have occurred, and modern procedures have made underground natural gas storage a safe and effective operation.

One of USEPA's primary regulatory responsibilities is to protect drinking water aquifers from detrimental effects caused by underground gas storage. The USEPA has delegated authority to most of the states, which have effective regulations for permitting, operating, and monitoring underground gas storage fields. Regulations differ from state to state and are tailored to local concerns, such as in Pennsylvania where extra measures are taken to avoid leakage of gas into underground coalmines. In several states with abundant oil, gas, coal and/or mineral resources, a protection (or buffer) zone is established to avoid or reduce the risk of accidents caused by human intrusion.

Monitoring is an important part of the regulatory oversight of these projects. While regulations on monitoring and reporting vary among states, almost all monitoring requirements focus on assuring that the wells are not leaking (e.g., pressure measurements and down hole logs such as temperature, pressure, noise/sonic, and casing inspection logs). Observation wells installed and monitored for the purpose of verifying that gas has not leaked into shallower strata are rarely required; however, a few storage projects have over one hundred wells for this purpose. Geophysical techniques to monitor the operation are not required.

Depleted oil and gas reservoirs are easier to develop than are aquifer storage projects because the geologic structure and cap rock are usually well characterized from existing wells. Moreover, since the structure is known to have trapped and stored hydrocarbons over geologic time periods, it is likely to be effective for natural gas storage. Standard natural gas reservoir engineering practices are used during the permitting process and storage operations. For aquifer gas storage projects, extensive site characterization is required and well testing methods specifically for evaluating the permeability and continuity of the cap rock have been developed.

In the event that leakage occurs, remediation is possible by producing or venting the gas accumulated in shallower layers, and/or reducing reservoir pressure. In most cases, leakage is caused by the presence of leaking or abandoned wells which should be identified and plugged as soon as possible. Some projects, such as the Herscher storage project in Illinois, continue to operate even though leakage continues. Here shallow extraction wells are used to capture the gas that leaked from the storage interval.

When a natural gas storage site is shut down, as much of the gas as is practical is removed from the formation. The injection wells are then plugged and abandoned using prescribed procedures. No long-term monitoring is required after a project has been shut down.

## Lessons Learned From Nuclear Waste Storage

In reviewing the history, the regulatory requirements, and some key elements of performance assessment and monitoring planning of the WIPP project, we can identify a number of the lessons learned and methodologies used that could be applicable to $CO_2$ sequestration.

The first lesson is about involving the scientific community, local communities and the political system in advisory and decision making roles. For the WIPP project, it was very useful to involve national academies and the scientific community at large from the beginning. Thus the NAS was invited to give scientific consideration and guidance from WIPP's first conception. Consequently, all through the WIPP project up to its successful conclusion, NAS provided an objective peer-review function. Further, various ad hoc committees from the scientific community were organized to be peer reviewers for various aspects of the project. Along with this, WIPP was also consistently active in international cooperation, which gave credibility to the project. The public, state, tribes, and other interested groups were also encouraged to be involved early in the project history, to review and interact with the project. Though there were still conflicts that had to be decided in court, the open approach made the path forward possible. This is in contrast to the nuclear waste programs in certain countries, where the programs were stopped partly because of ineffective communication with interested parties, and partly because of the attitude of "trust us, we know best" that these programs were perceived to have. In addition, for a project of such large scale and such significant impact on the country, involvement of the Congress, the individual states, and the federal government is to be expected. Early contact with and considerations by responsible congressional and governmental staff was crucial to eventual project success.

The second lesson is about the role of simulation models, and how probabilistic approaches can be used to build confidence in simulations that extend well beyond the time period over which they have been tested. Like $CO_2$ storage, safe nuclear waste disposal requires understanding the complex, coupled physical-chemical-mechanical processes that will occur over periods of hundreds to thousands of years. Until geologic disposal of nuclear waste was proposed, models that could simulate such behavior were not available. Major effort was devoted to the development and testing of these models, and tremendous progress has been made in building this capability. Nevertheless, for nuclear waste disposal, significant uncertainties remain about the adequacy of such site characterization, the level of understanding of the complex processes involved, and the completeness of the important events included in our simulations. In light of the need to move forward, nuclear waste storage programs around the world have developed and adopted a disciplined approach for dealing with these uncertainties. The Features-Events-Processes (FEP) methodology for identifying and ranking the importance of various attributes of the site, containment approach, and human behavior may provide a useful framework for evaluating the geologic storage of $CO_2$. In addition, 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 $CO_2$ storage at a given site. The study and simulation of natural analogues, such as naturally occurring $CO_2$ reservoirs, are useful for demonstrating the ability of simulation models to predict the behavior of analogous systems on the time scales that are meaningful for $CO_2$ storage. Regulatory agencies and the general public are expected to require assurance about the reliability of the simulation models that are used to predict the safety and effectiveness of geologic storage of $CO_2$. Preparing for this requirement by having a documented track record of successful applications of these simulation models – to a wide range of relevant laboratory experiments and field sites – will be helpful in this regard.

Another important lesson to be learned from nuclear waste disposal is that safe and effective storage allows for the possibility that the primary containment structure might leak. In fact, nuclear waste disposal projects in the U.S. acknowledge leakage and are designed with the eventuality that when the waste container is breached, radionuclides move into the surrounding rocks and eventually, albeit very slowly, migrate to the accessible environment. A combination of three regulatory requirements is used to ensure human and environmental health under these conditions. First, there are performance requirements on elements of the engineered systems (e.g., canisters). Second, there are requirements on the integrated system (engineered plus geologic system) that limit the release of radionuclides from the repository. And finally, there are requirements that limit the dose to which an individual living at a specified distance from the site would be exposed. This hierarchy of performance requirements may provide a guide for regulating $CO_2$ storage sites where some leakage may also be acceptable. Performance requirements for leakage from $CO_2$-injection wells may be specified in a manner analogous to the engineered systems in a repository. Setting limits on the acceptable leakage rates from the primary storage structure is analogous to setting specifications for maximum permissible leakage from the repository. Also, the release of $CO_2$ to the atmosphere could be considered analogous to maximum dose limits for human exposure. Early consideration of this approach may create a helpful framework for HSE risk assessment for $CO_2$ storage in geologic formations.

Finally, similar to nuclear waste storage programs, a carefully designed monitoring effort is also needed for $CO_2$ storage. This includes the need for baseline measurements early on in the project, continued monitoring of critical parameters, predetermination of acceptable parameter ranges, and plans for actions if changes are beyond these acceptable ranges. Current plans for long term monitoring of nuclear waste disposal sites envision that monitoring can be stopped after the repository performance is confirmed to be within the expected range. For WIPP, this performance confirmation period is expected to last from 50 to 150 years. A similar concept may also be valuable for geologic storage of $CO_2$—that monitoring could be curtailed or stopped once the performance of the storage site is confirmed to be within an acceptable range. In light of the large mobility of $CO_2$ and the strong buoyancy forces acting on it in the underground environment, it may take a considerable length of time before monitoring data can confirm that the storage reservoir is performing as expected. However, this concept is important because of the long-term nature of $CO_2$ storage projects and ongoing costs associated with perpetual monitoring.

# CHAPTER 1. STUDY OBJECTIVES AND METHODS

## 1.1. Introduction

As part of the effort to mitigate the buildup of greenhouse gases in the atmosphere, research into carbon sequestration searches for methods to prevent carbon dioxide ($CO_2$) from being released into the atmosphere and to pull $CO_2$ out of the atmosphere into long-term sinks. Ultimately, the sinks for excess atmospheric $CO_2$ will be in the oceans (through long-term equilibration with the atmosphere), in terrestrial biomass, and in crustal rocks as carbonates or kerogen.[*] In the meantime, the most likely traps for initial sequestration efforts based on current technology and experience are geological reservoirs, including abandoned and producing oil and gas fields, unminable coal seams, and deep brine-filled sedimentary formations. Storing large amounts of $CO_2$ creates the potential hazard of accidental release, and exposure to high concentrations of $CO_2$ poses significant human or ecological risks, even though carbon dioxide is not a "toxic" substance. In this study we have gathered information that is useful for assessing risk scenarios for geological containment, including the possibility of persistent low-level leaks and catastrophic surface release.

## 1.2. Objectives

The purpose of this study is to gather and interpret relevant information regarding the approaches used in the United States for assessing, managing and mitigating risks associated with deep geologic storage of wastes or useful products, which may provide guidance for the CCP's R&D program on geologic storage of $CO_2$. Three operations are currently underway in the U.S. that will provide useful insights for geologic storage of $CO_2$, namely, deep well injection of industrial wastes, natural gas storage, and development of a deep geologic repository for nuclear wastes. The study systematically evaluates the following for each of these operations:

- History, status and scope of the activity,
- Risk assessment framework and methods, including key issues, performance specifications and performance assessment methods,
- Risk management approaches, including regulatory oversight and permitting, site characterization methods, monitoring and performance confirmation,
- Risk mitigation and remediation methods employed or planned in the event that performance specifications are not met or other unintended consequences arise, and
- Case studies documenting responses to historical accidents.

Ultimately, the health, safety and environmental risk assessment for geologic storage will be driven by the hazards associated with exposure to elevated concentrations of $CO_2$. Therefore, in addition to reviewing the history and status of these activities, we first review information about human and ecological health risks from exposure to elevated levels of $CO_2$, and information from natural analogues for $CO_2$ storage, industrial uses of $CO_2$ and ambient monitoring technology for detection of $CO_2$.

## 1.3. Approach

As a first step in this study we designed and participated in a CCP-sponsored workshop to gather as much relevant information as possible for this investigation. This workshop was held in January, 2001. Engineers, scientists and managers with practical experience in each of the above areas were invited to participate in a two-day workshop that was structured to provide information and guide the data gathering and evaluation phase of the project. Participants included individuals from the U.S., Canada and Europe. Following the workshop, we gathered data from published literature, the Web and from discussions with knowledgeable individuals.

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[*] a form of organic carbon

The information is presented in five chapters, including:

- Chapter 2. Human Health, Ecological and Industrial Risk Assessment of Carbon Dioxide Exposure;
- Chapter 3. Natural Analogs for Underground $CO_2$ Storage: Health, Safety, and Environmental Lessons Learned;
- Chapter 4. Disposal of Industrial Liquid Waste in Deep Geologic Formations;
- Chapter 5. Underground Natural Gas Storage; and
- Chapter 6. Nuclear Waste Disposal: Lessons Learned for $CO_2$ Sequestration.

We have organized each chapter to facilitate comparisons of risk assessment, management and mitigation approaches. Key issues and approaches relevant to the CCP have been identified, and compiled in the executive summary.

# CHAPTER 2. HUMAN HEALTH, ECOLOGICAL AND INDUSTRIAL RISK ASSESSMENT OF CARBON DIOXIDE EXPOSURE

## 2.1. Introduction

To begin a risk assessment of geologic sequestration, we must first understand both the context for evaluating $CO_2$ exposures as well as the human health and environmental impacts of exposure to elevated concentrations of $CO_2$. Fortunately, there is a large amount of information to draw on in this regard. Carbon dioxide was one of the first gases identified, and it remains widely used in industry. Regulations are well developed for using $CO_2$ in occupational and industrial settings and for storing and transporting it. Moreover, the central role that $CO_2$ plays in living systems and ecosystem processes has motivated the development of an enormous knowledge base from which to begin this assessment.

We begin this chapter by placing $CO_2$ sequestration in the context of the global carbon cycle. We then summarize what is known about the basic physiology of $CO_2$ and how exposure to elevated concentrations leads to human and ecological risks. A review of industrial sources, uses, and accidents follows, and finally, we summarize current regulations and monitoring approaches for occupational and industrial exposures to $CO_2$.

## 2.2. $CO_2$ Sequestration in the Context of the Global Carbon Cycle

Carbon dioxide is ubiquitous in the natural world. It undergoes an endless cycle of exchange among the atmosphere, living systems, soil, rocks, and water. Volcanic outgassing, the respiration of living things from humans to microbes, mineral weathering, and the combustion or decomposition of organic materials all release $CO_2$ into the atmosphere. Atmospheric $CO_2$ is then cycled back into plants, the oceans, and minerals through photosynthesis, dissolution, precipitation, and other chemical processes. Biotic and abiotic processes of the carbon cycle on land, in the atmosphere, and in the sea are connected through the atmospheric reservoir of $CO_2$.

Figure 2.1 illustrates the primary compartments of the global carbon cycle and the fluxes among them. The atmosphere contains approximately 755,000 Million Metric Tonnes of Carbon (MMTC), the terrestrial biosphere 1,960,000 MMTC and the oceans 38,100,000 MMTC. Carbon dioxide from the atmosphere is converted into biological matter by photosynthesis. The process, called primary production, converts approximately 60,000 MMTC (225,000 MMT $CO_2$) into biomass each year. This flux is balanced by a nearly equal flux of $CO_2$ back into the atmosphere, resulting from the respiration of living organisms and the decomposition of organic matter. Differences between these two competing fluxes determine whether the terrestrial biosphere is a net source or sink of $CO_2$. Carbon dioxide also dissolves in surface, ground, and ocean water, mostly as bicarbonate ($HCO_3^-$ ; $CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$), and in shallow tropical waters, it precipitates out as carbonate rocks such as limestone ($CaCO_3$; $2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + H_2O + CO_2$). Annually, approximately 90,000 MMTC are exchanged between the ocean and the atmosphere. These quantities provide a context for evaluating the 6,000 MMTC that is currently generated as $CO_2$ from fossil fuel emissions and the fraction of that amount that may be sequestered in geological formations in the future.

The quantities of $CO_2$ that might be sequestered may also be put in the context of other known carbon reservoirs, as well as industrial and natural emissions. Figures 2.2a and 2.2b tabulate many of the known carbon reservoirs and fluxes, and compare them to the carbon sequestration goals identified by the US DOE. The current US DOE target for global annual sequestration capacity by 2025 is 1,000 MMTC/yr (US DOE, 1999). As shown in Figure 2.2b, this is nearly equal to (for example) U.S. annual petroleum consumption or global annual natural gas consumption in 1998. The US DOE goal for global carbon

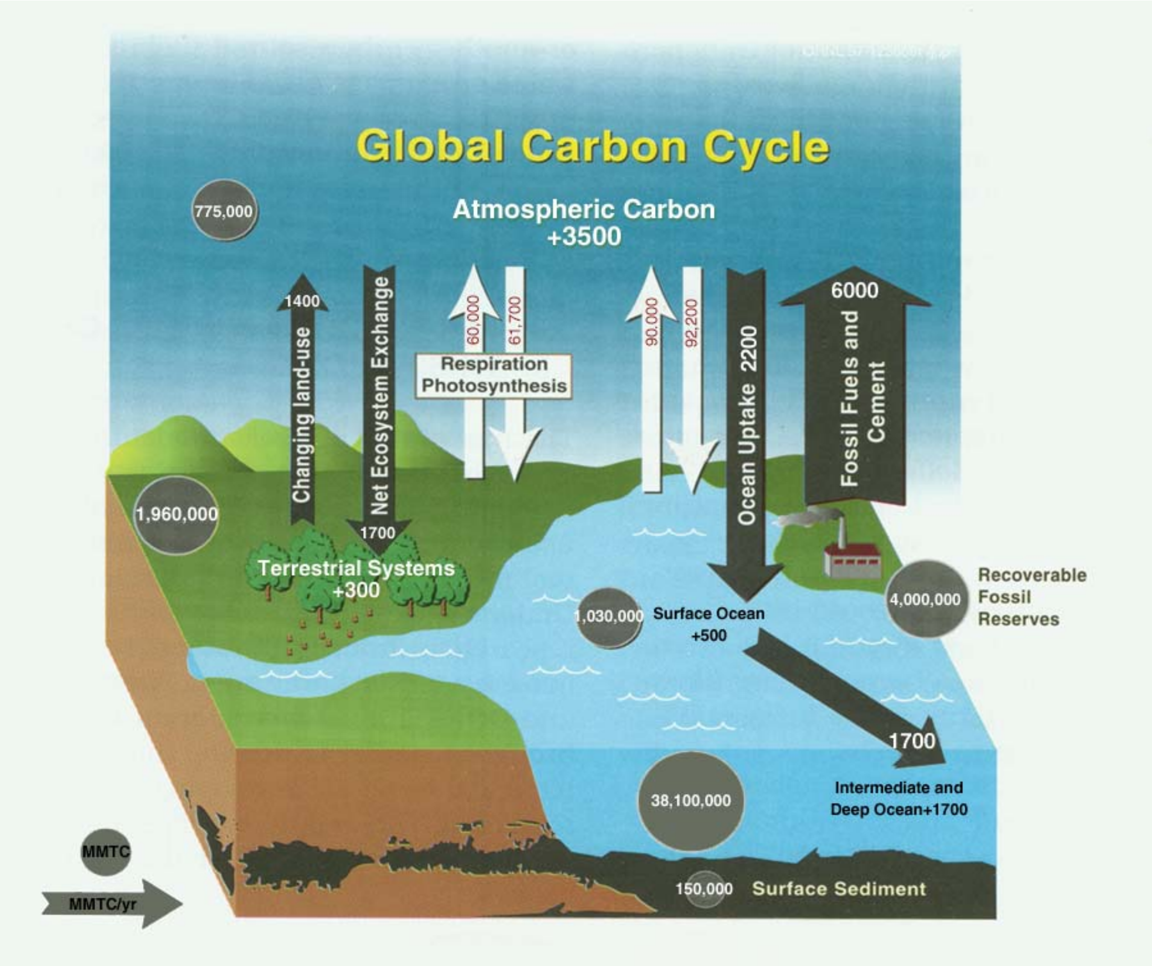


**Figure 2.1. Global biogeochemical carbon cycle. Includes human influence from fossil fuel combustion and changing land-use patterns. Black arrows indicate net fluxes and white arrows indicate gross fluxes. Annual net additions are shown as + numbers, and pool sizes (circles) are shown in gray. All quantities are in Million Metric Tonnes Carbon, MMTC, and all fluxes are in MMTC/yr (modified from US DOE, 1999).**

sequestration capacity in 2050 is 4,000 MMTC/yr, which is comparable to the total U.S. natural gas reserves as assessed in 1998. While these comparisons point to the very large quantities of $CO_2$ that may be sequestered, they are still small in comparison to the 90,000 MMTC/yr exchanged annually between the atmosphere and ocean and the 60,000 MMTC/yr exchanged between the atmosphere and the terrestrial biosphere. On the other hand, Figure 2.2b illustrates that the sequestration target is large compared to the global volcanic emissions of 42 MMTC/yr.

From a risk-assessment perspective, a more useful comparison may be the quantity of $CO_2$ associated with an individual sequestration project. Each facility is anticipated to sequester 0.25–10 MMTC/yr. For example, the Sleipner sequestration project in the North Sea currently pumps 1 MMT $CO_2$ or 0.27 MMTC (1 tonne carbon = 3.667 tonnes $CO_2$) into the Utsira Formation beneath the sea floor. While this is small in comparison to the reservoirs and fluxes mentioned thus far, it is twice the annual release of $CO_2$ at Mammoth Mountain in California between 1990 and 1995, where over 100 acres of trees were killed by

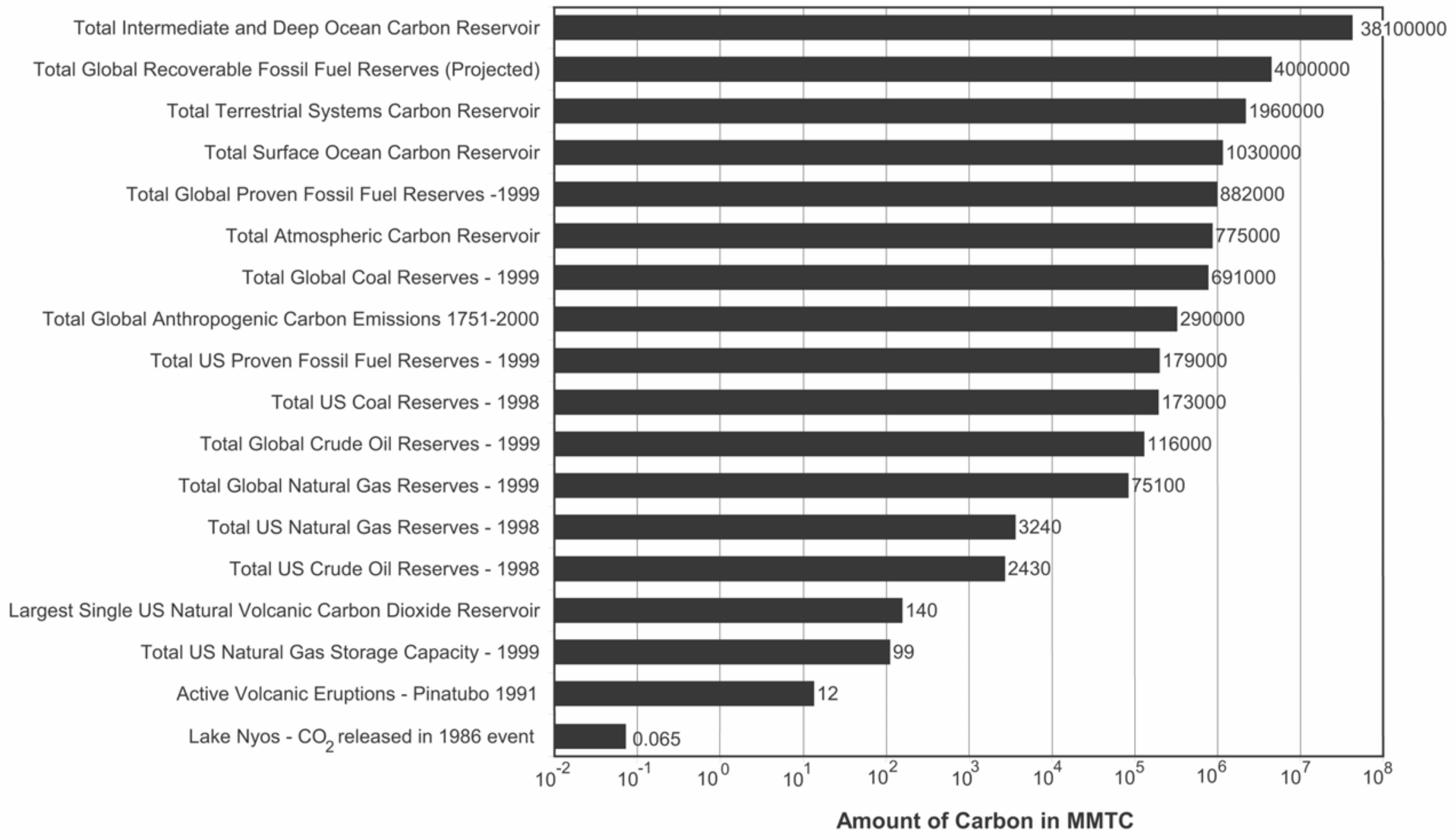


**Figure 2.2a. Comparison of carbon reservoirs and one-time events. Data tables, references, and conversions are attached as Appendices 1 and 3. Estimates are order of magnitude only and may include small conversion discrepancies due to independent rounding.**

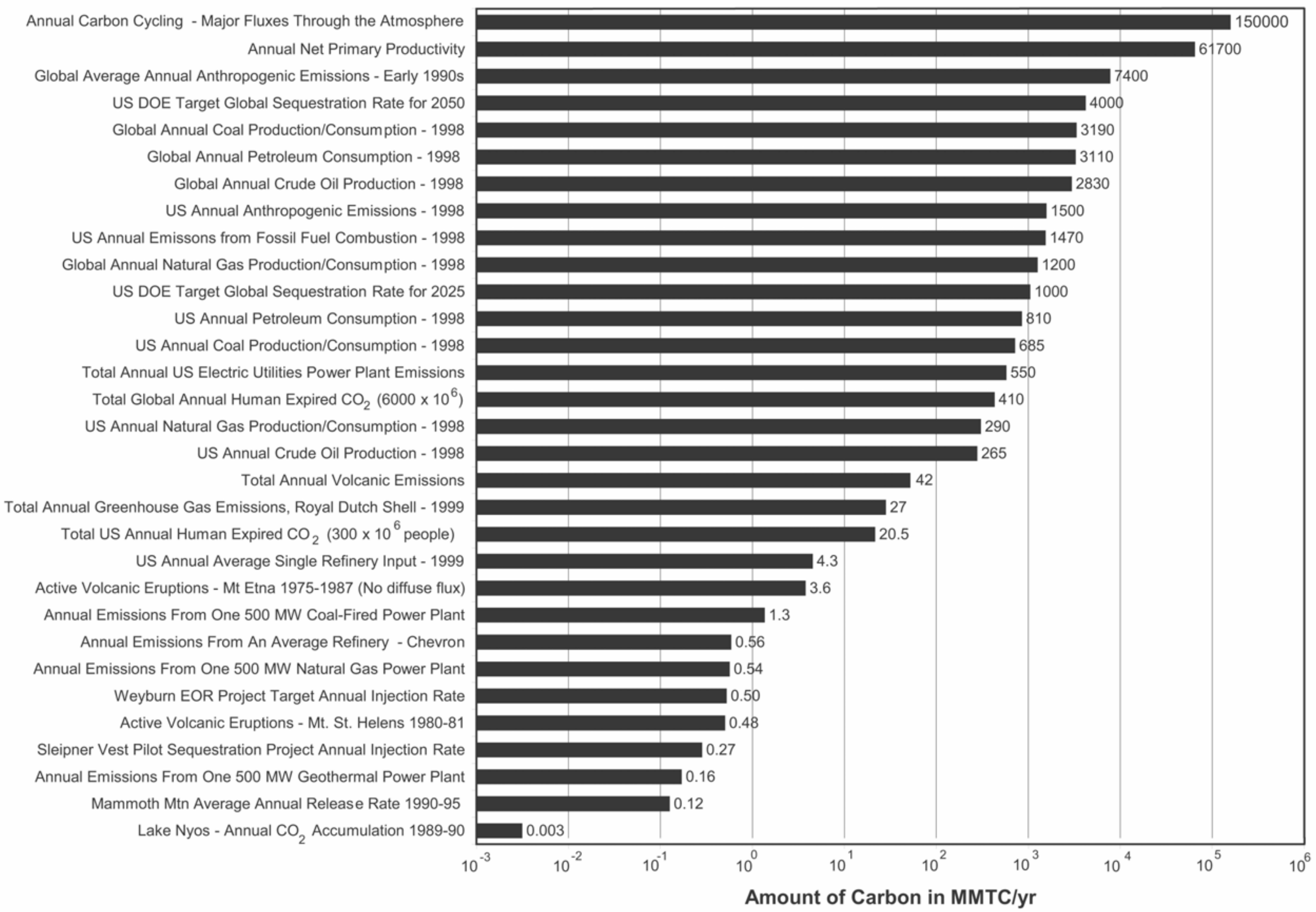


**Figure 2.2b. Comparison of carbon fluxes and target sequestration rates. Data tables, references, and conversions are included as Appendices 2 and 3. Estimates are order of magnitude only and may include small conversion discrepancies due to independent rounding.**

the natural release of magmatic $CO_2$. The 1986 Lake Nyos event in Cameroon released 0.24 MMT $CO_2$ (0.07 MMTC), approximately one quarter of the annual amount stored by Sleipner. This natural $CO_2$ release led to 1,746 people and many animals being killed, up to 14 km away and 24 hours after the initial event (see Chapter 3 from a more detailed discussion of this event). However, a significantly larger release in 1991 from an eruption at Mt. Pinatubo ejected 11.5 MMTC in one massive event, but the gas dispersed high in the atmosphere and did not pose a direct hazard.

In addition to providing a context for evaluating the magnitude of $CO_2$ that may be sequestered, these comparisons illustrate the important point that the risk associated with $CO_2$ sequestration depends much more on effective dispersion than the total quantity of $CO_2$. A small leak may pose significant risk to exposed humans, animals, or ecosystems if it becomes concentrated. Geologic containment, low-leakage rates, the characteristics of any surface manifestations, and effective dispersion or dilution are identified as the key elements of a risk assessment for the geologic carbon sequestration process.

## 2.3. General Physiology of Carbon Dioxide

Understanding the general physiology of $CO_2$ provides a context for evaluating the environmental health risks of $CO_2$ releases. Carbon dioxide is an important biological compound because it is the ultimate source of carbon for all life. Organic chemistry, the chemistry of biological compounds, is the study of carbon chemistry. Also, the biological cycling of carbon between photosynthesis and cellular respiration is a major portion of the global carbon cycle and is mediated through atmospheric $CO_2$ (Tolbert and Preiss, 1994).

Primary producers, such as plants and photosynthetic microbes, use energy from sunlight, water, and carbon dioxide absorbed from the atmosphere to generate all of their organic constituents. The primary product of carbon fixation or photosynthesis is the carbohydrate glucose. A simple empirical formula for carbohydrates is $CH_2O$. Photosynthesis uses energy (E), $CO_2$, and water ($H_2O$) to make carbohydrates ($CH_2O$) and oxygen ($O_2$). In the evolution of the biosphere, this process generated virtually all of the oxygen in the atmosphere and remains central to the world around us.

$$\text{Photosynthesis} = CO_2 + H_2O + E \rightarrow CH_2O + O_2$$
$$\text{Respiration} = CH_2O + O_2 \rightarrow CO_2 + H_2O + E\ ; \quad E \rightarrow ATP$$

Cellular respiration is the controlled reverse of photosynthesis, and the two together are integral to the flow of energy and carbon through the biosphere, as shown in Figure 2.3. Respiration, as depicted in Figure 2.4, is the combustion or oxidation of carbohydrates coupled to gas exchange and to reactions that produce ATP (adenosine tri-phosphate), the chemical energy currency of life. ATP is the primary form of energy used by most life for biosynthesis, metabolism, and movement. Some plants and microorganisms can produce every organic compound they need from glucose as a carbon skeleton starting material and energy source. The biosynthetic pathways retained in animals are relatively limited, so animals must consume organic material to obtain energy in the form of glucose and diverse raw starting materials. The processes of photosynthesis in primary producers and respiration, which is nearly universal among all forms of life, are of ancient origin and highly conserved through evolution. The few exceptions are chemoautotrophic bacteria. They survive on alternative abiotic energy sources and are typically thermophiles (heat-lovers), thiophiles (sulfur-lovers), or obligate anaerobes (oxygen-haters, e.g., methanogens) (Humphris et al., 1995).

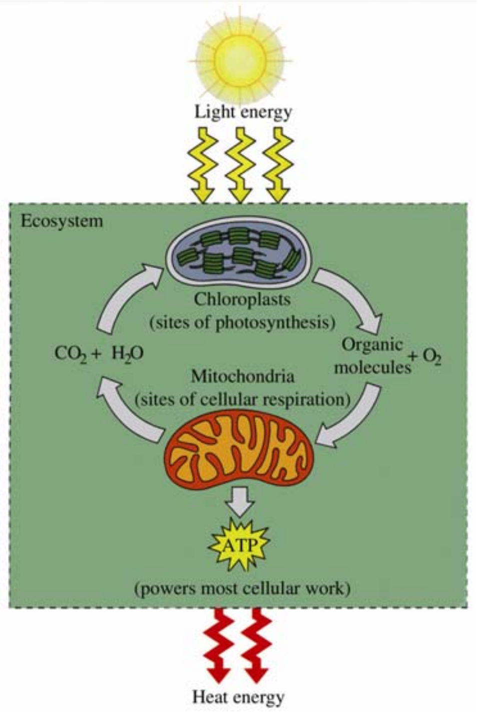


Figure 2.3. Fundamental biological carbon and energy cycles involving photosynthesis and respiration (Campbell et al., 1999).

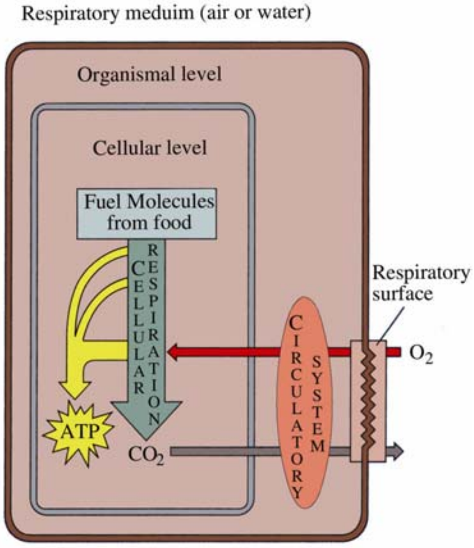


Figure 2.4. The role of gas exchange and respiration in bioenergetics. Illustration depicts the coupling of gas exchange and cellular respiration via the respiratory and circulatory systems (Campbell et al., 1999).

## 2.4. Human Physiology of Carbon Dioxide: Normal and Hazardous Exposure

### *2.4.1. Human Physiology of Carbon Dioxide*

In humans, like the vast majority of organisms, cellular respiration consumes $O_2$ and generates $CO_2$. Breathing is the process by which we obtain oxygen from the air and remove $CO_2$ from our bodies. Figure 2.5 illustrates how the coupling between the circulatory system and the respiratory systems transports $O_2$ to cells throughout our bodies and removes respired $CO_2$. Air breathed into the lungs contains 21% $O_2$ and 0.04% $CO_2$, and exhaled air is 16% $O_2$ and 3.5% $CO_2$ on average, though it can exceed 5% $CO_2$ during strenuous exercise.

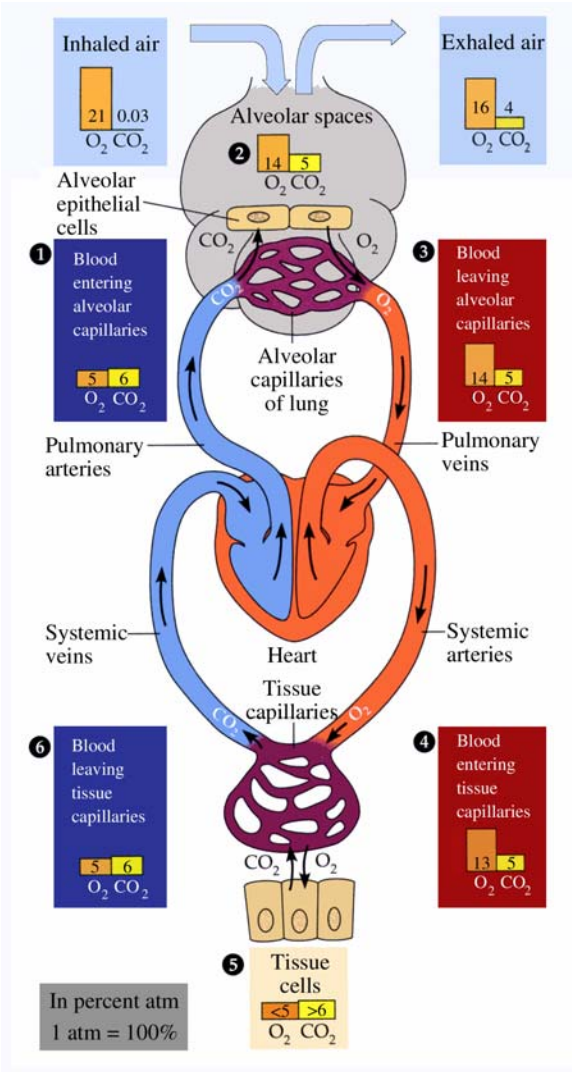


**Figure 2.5. Gas exchange and variation in respiratory gas concentration along the coupled respiratory and circulatory systems (modified from Campbell et al., 1999).**

Blood returns from the periphery through the right side of the heart to the lungs and contains 5% $O_2$ and 6% $CO_2$. Carbon dioxide diffuses out of the blood and into the lungs, and $O_2$ diffuses in the opposite direction, from the lungs to the blood. Blood leaving the lungs has 5% $CO_2$ and 14% $O_2$ and travels through the left side of the heart then on to the periphery. Oxygenated blood flows through capillaries surrounded by extracellular fluid. Oxygen is pulled out of the blood and into the cells because of its constant consumption by cellular respiration which maintains the low concentration within the cells, generally less than 5% $O_2$. The concentration of $CO_2$ in the blood, 5%, is lower than in the cells, where respiration produces $CO_2$, so $CO_2$ is absorbed into the blood and transported to the lungs (Campbell et al., 1999).

Carbon dioxide is involved in several physiological functions aside from cellular respiration and bioenergetics. It is the primary regulator of breathing in coordination with two regions of the brain, the pons and the medulla. Most $CO_2$ is transported in red blood cells in its dissolved, hydrated form of bicarbonate ($HCO_3^-$). ($CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$). When $CO_2$ dissolves in the blood, it increases H+ concentration or decreases pH, and humans are very sensitive to changes in pH. The concentrations of $CO_2$, electrolytes, and total weak acids determine blood pH (Kellum, 2000), which is normally 7.4, and Van de Ven et al. (2001) considered a pH drop of -0.04 to indicate acute metabolic acidosis. The relationship between $CO_2$ and pH is the most likely basis for $CO_2$ toxicity. The medulla monitors $CO_2$ levels in the blood by measuring subtle changes in pH, and lowered pH stimulates the need to breathe. Sensors in the aorta and carotid bodies detect blood oxygen, but oxygen levels only affect breathing when dangerously low, as at altitude. Via its role in acid-base and electrolyte balance, bicarbonate is involved in other processes including bone buffering and renal regulation (Jones, 1972; NIOSH, 1976; Hiesler, 1989; White, 1989).

Hyperventilation leads to hypocapnea or alkalosis, which is low blood $CO_2$ and high pH. Extreme stress and anxiety causes rapid breathing, which quickly lowers blood $CO_2$ levels and increases blood pH. The initial symptoms of hypoxia and feeling out-of-breath are indistinguishable from alkalosis. The breathing control center does not tell the body to breathe when blood pH is elevated, as long as there is sufficient oxygen. In a paradoxical, reinforcing reaction, one panics even more and continues taking rapid, deep breaths that keep blood pH elevated. One feels dizzy and out-of-breath, which further exacerbates the feelings of anxiety and panic. Taking slow, normal breaths or rebreathing exhaled air from a paper bag allows blood $CO_2$ levels to increase and return the control of breathing to the normal mechanism. This happens in any case after the person loses consciousness and the body's autonomic systems take over. At high altitude, hyperventilation is more serious because low $CO_2$ reduces the drive to breathe, while reduced partial pressures of oxygen require more vigorous breathing. For pilots to avoid losing consciousness, supplied oxygen is necessary and often contains added $CO_2$ to augment the physiological drive to breathe (NAMI, 1991; USAF, 2001).

Human exposure to elevated levels of carbon dioxide can be hazardous either by (1) reducing the oxygen content of the ambient air and causing hypoxia or (2) through direct carbon dioxide toxicity. For example, the National Institute of Occupational Safety and Health (NIOSH) confined-space-hazard classification system defines carbon dioxide as a nontoxic, inert gas that displaces oxygen. In most cases of hazardous $CO_2$ exposure, it is presumed to act as a simple asphyxiant, even though extensive research indicates that exposure to elevated concentrations of $CO_2$ has significant effects before oxygen dilution could be physiologically significant. Typically, the ambient oxygen concentration is 21%, and the normal range is from 19.5% to 23.5%. Below 17% $O_2$, hypoxia leads to weakened night vision, increased breathing rate and volume per breath, and increased heart rate. Declining muscle coordination, rapid fatigue, and intermittent respiration are observed between 14 and 16% $O_2$, in addition to increased volume per breath and accelerated heart rate. Nausea, vomiting, and unconsciousness occur between 6 and 10%. Below 6%, loss of consciousness is rapid, and death takes place within minutes (NIOSH, 1979).

### *2.4.2. Effects of Low-Level and Chronic Exposure to $CO_2$*

At exposure to slightly elevated concentrations of $CO_2$, such as in rebreathing masks on airplanes at high altitude, the effects of elevated $CO_2$ can be beneficial, but that changes rapidly when concentrations exceed a few percent. In the year 2000, the average concentration of $CO_2$ in the atmosphere was 370 ppm. Studies show the threshold for perceiving stale air is 800 ppm. Carbon dioxide is used to assess adequate ventilation in buildings, and standards are set to ensure indoor odor control and comfort. Sick building syndrome (SBS) is a broad suite of health problems and complaints associated with inadequately ventilated buildings. Research shows that $CO_2$ is a good proxy for SBS and sufficient ventilation. Carbon dioxide builds up in enclosed spaces where occupants respire it, but no causal connection between SBS and $CO_2$ is known at this time. No physiological compensation or adverse health effects have been noted at or below 1% $CO_2$, though no controlled studies of exposure to such low levels have been done yet for longer than six weeks. Most studies involved healthy young male subjects, especially in controlled atmospheres such as submarines. Carbon dioxide tolerance in highly susceptible subgroups such as children, the elderly, or people with respiratory deficiency has not been studied—except for some work on chronic acidosis resulting from respiratory impairments and the observation of decreased ventilatory response to $CO_2$ in infants who were developmentally exposed to cocaine (NIOSH, 1976; NRC, 1986; US EPA, 1991, 1994; Gingras et al., 1994; OSHA, 1994; NIOSH, 1997a; ASHRAE, 1999).

Carbon dioxide acts as a respiratory stimulant above 1%, and chronic exposure to 1.5 to 3% $CO_2$ results in physiological adaptation without adverse consequences. The only lingering effects are increased alveolar dead space (alveoli are the microscopic air sacs in the lungs where gas exchange takes place) and decreased sensitivity to increased concentrations of carbon dioxide as measured by respiratory stimulation. Exposure to 1.5 to 3.0% $CO_2$ leads to hypercapnea (elevated levels of blood $CO_2$). Because of the direct relationship between dissolved blood $CO_2$ and pH, hypercapnea is synonymous with decreased blood pH or acidosis. The immediate reaction is increased breathing rate and depth (respiratory compensation). In response to chronic acidosis, the body compensates by altering the electrolyte balance in the blood and through bone buffering and renal regulation. Increased urine production aids in excreting excess hydrogen ions ($H^+$) and bicarbonate. Calcium deposition may increase transiently, but the body eventually attains homeostatic compensation as long as the chronic level of $CO_2$ exposure does not exceed 3%.

Elevated $CO_2$ levels in the air or blood limit the capacity for exercise and require increased respiration and long-term metabolic compensation. Below 3%, no adverse effects appear aside from the awareness of increased breathing rate and effort, mild headache, and sweating. No deleterious long-term consequences have been observed for chronic exposure to 3% $CO_2$ or less, and all symptoms of short-term exposure to such levels have proven to be short-lived and reversible (NIOSH, 1976, 1981; ACGIH, 1994).

### *2.4.3. Acute Exposure to Elevated Concentrations of $CO_2$*

The most striking effect of carbon dioxide levels over 3% is the exponential increase in minute volume, the average volume breathed during one minute. Minute volume increases from 7 liters/minute at 0.03% $CO_2$ to 8 liters/minute at 1%, 9 liters/minute at 2%, 11 liters/minute at 3%, 26 liters/minute at 5%, and 77 liters/minute at 10.4%. Volume per breath increases from 440 to 2500 ml during exposure to 10.4% $CO_2$.

Hearing loss and visual disturbances occur above 3% $CO_2$. Carbon dioxide also acts as a local vasodilator and a potent cerebral vasodilator. This may explain many of the symptoms associated with carbon dioxide toxicity, including narcosis, headache, and dizziness. Healthy young adults exposed to more than 3% $CO_2$ during exercise experience adverse symptoms, including labored breathing, headache, impaired vision, and mental confusion.

Exposure to 4–5% $CO_2$ for a few minutes leads to headache, dizziness, increased blood pressure, and uncomfortable dyspnea (difficulty breathing). Suppressed shivering is observed at 7.5% $CO_2$ for 15 min in 5ºC. Seven to ten percent $CO_2$ for several minutes to an hour results in headache, increased heart rate, shortness of breath, dizziness, sweating, rapid breathing, and near or full unconsciousness. (The lowest published lethal concentration for humans, reported in 1933, was 9% $CO_2$ for 5 minutes—Vermont SIRI, 2001.) Eye flickering, psychomotor excitation, myoclonic twitching, headache, dizziness, dyspnea, sweating, restlessness, and "fullness in head" were observed at 10% carbon dioxide. Dizziness, drowsiness, severe muscle twitching, and unconsciousness occur after one to several minutes exposure to 10–15% $CO_2$. Above 15%, loss of consciousness occurs in less than one minute. Narcosis, respiratory arrest, convulsions, coma and death due to depression of the central nervous system can take place rapidly with continued exposure. Death occurs within minutes at 30% $CO_2$ (NIOSH, 1976, 1981; ACGIH, 1994). An interesting aside to the discussion of hazardous $CO_2$ exposure is the routine use of a single breath of 20–35% $CO_2$ to diagnose and treat panic disorder (Coryell, 1997; Forsyth et al., 2000; Coryell et al., 2001; Koszycki and Bradwejn, 2001).

Figure 2.6 summarizes information about natural occurrences of carbon dioxide compared with physiologically relevant concentrations and thresholds at which human health effects become noticeable or significant (see section 2.7.1 for a discussion of regulatory limits for occupational $CO_2$ exposure). Clearly, $CO_2$ is not toxic at parts per million or even low percentage levels, but someone enveloped in a cloud of highly concentrated $CO_2$ is in imminent danger. The risk of exposure to dangerous levels whenever $CO_2$ is concentrated in large amounts or under pressure must be considered in the context of geologic carbon sequestration for both surface facilities and leakage from geological formations. Fortunately, industry has long experience with $CO_2$ and routinely controls this hazard in settings such as breweries, beverage carbonation facilities, and enhanced oil recovery (EOR) operations—through engineering and procedural controls and monitoring (as reviewed in Sections 2.6 and 2.8). Although individual susceptibility to $CO_2$ is variable, general guidelines are straightforward and useful, especially in light of the precautionary principle used in setting occupational exposure limits.

## 2.5. Ecological and Environmental Impacts of $CO_2$ Releases

### *2.5.1. Introduction*

The environmental impacts of $CO_2$ releases are not well understood, despite numerous natural and man-made examples and extensive physiological research. Nevertheless, a summary of the existing literature that is qualitatively relevant to the potential risks of geologic carbon sequestration is helpful. Respiratory physiology and pH control are the primary physiological bases for the responses of different forms of life to hazardous $CO_2$ exposures. Information on the response of animals and vegetation to elevated $CO_2$ and low levels of $O_2$ can be found in diverse locations, including physiology, respiratory physiology, comparative physiology, plant physiology, botany, food preservation, and aerospace literature. Human responses are useful models for other mammals, and for all air breathers and large terrestrial animals, because of the universal nature of respiration. The death of animals and people in similar areas from the plume of natural $CO_2$ released from Lake Nyos, Cameroon in 1986 supports this observation. Plants usually have a higher tolerance for $CO_2$ than mammals, as evinced by the lack of broad vegetation die-off at Lake Nyos. A standard amount used to preserve food from insects, microbes, and fungi is 40% $CO_2$; at this amount, insects are incapacitated or killed and microbes and fungi either die or experience severely retarded growth rates. Comparative physiology reveals that gas exchange mechanisms and organs, respiratory medium, and pH and osmotic homeostatic regulation vary among organisms and according to the ecological niche inhabited. These factors determine tolerance to elevated $CO_2$. The physiological basis of $CO_2$ tolerance and ecosystem response will be reviewed by looking at respiration and gas exchange in simple organisms, animals, and plants.

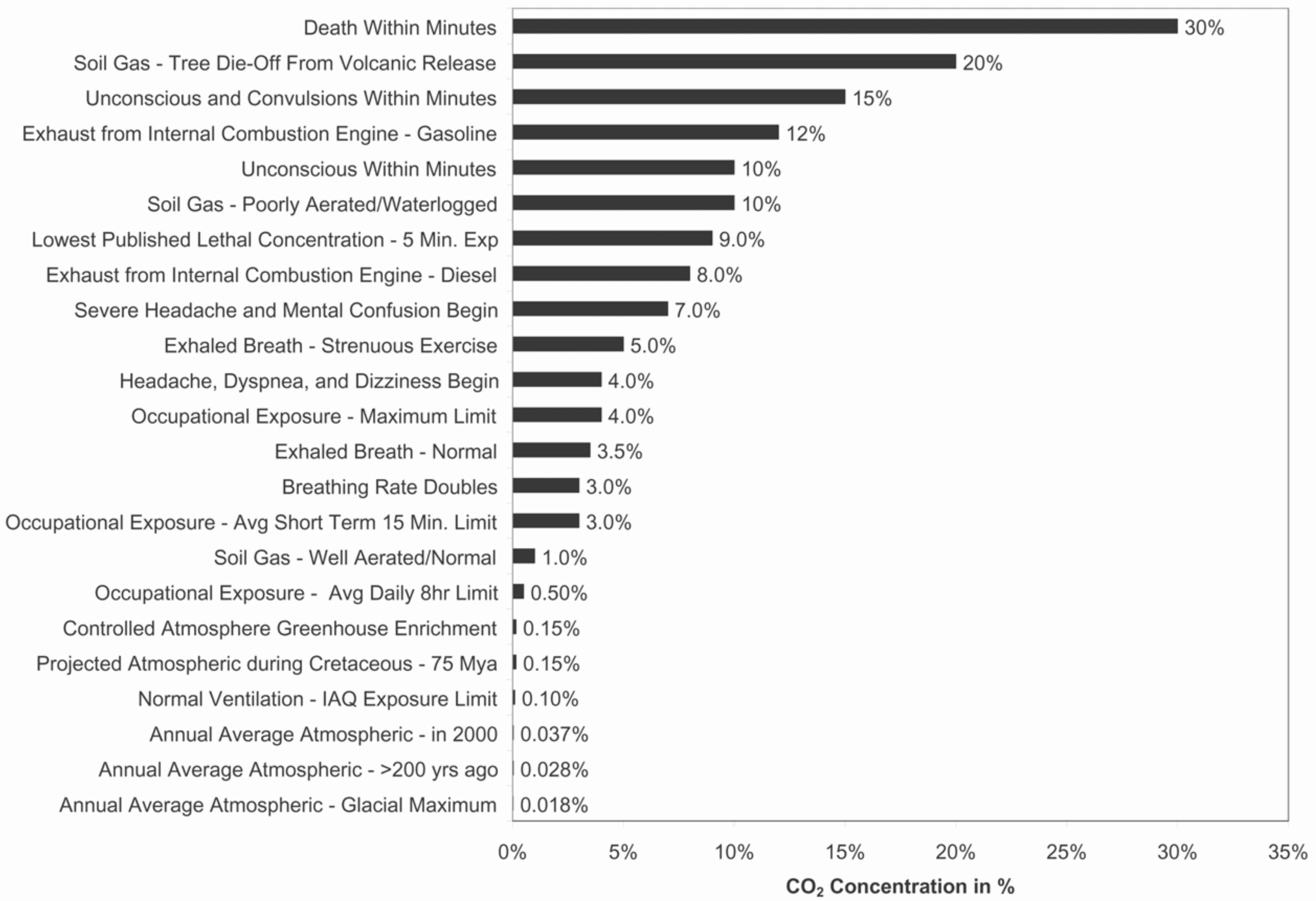


**Figure 2.6. Comparison of ambient concentrations of $CO_2$ and risks of exposure. Data Tables with references attached as Appendix 4.**

### *2.5.2. Simple Organisms: Cellular Respiration, Homeostasis, Diffusion, and Increasing Complexity*

Cellular respiration, especially the preliminary step called glycolysis, which does not require oxygen, is almost universal among organisms from the most simple to the most complex. Photosynthetic organisms store solar energy as the chemical energy of organic compounds by converting water and $CO_2$ to simple carbohydrates and oxygen. This provides the organic material consumed by all heterotrophic organisms. Oxidative respiration is the reverse—the harnessing of chemical energy via the breakdown of carbohydrates back to $CO_2$ and water. As a result, $CO_2$ is the primary metabolic waste product of all oxygen-consuming organisms. Respiration requires regular gas exchange between an organism and its environment. Oxygen is required as the terminal electron acceptor in oxidative respiration, and $CO_2$ must be eliminated. All single-celled organisms maintain some level of homeostasis, especially osmotic and pH, by controlling what passes through their cell membranes; but in the case of respiratory gases, diffusion is usually the operative, uncontrolled process. Microbes have adapted to virtually every environment that exists on Earth, and they use biochemical mechanisms to adjust to variable environmental conditions. Some microbes can survive in virtually 100% $CO_2$ as long as trace amounts of $O_2$ are available. The suspension of metabolism under extreme desiccating conditions is an analogous survival mechanism. As a result of variation in environmental conditions and such adaptive capabilities, only a qualitative generalization is useful about the level of $CO_2$ that is toxic to microbes or bacteria. Although the range is broad and $CO_2$ concentrations below 10% kill some simple organisms, in general 50% $CO_2$ has a significant inhibitory if not lethal effect (McIntyre and McNeil, 1997; Bennik et al., 1998). The distribution and physiology of microbes in the subsurface is not well known, so a projection of their response to elevated $CO_2$ is not yet possible (Fredrickson and Onstott, 1996). A survey of the range of known responses to $CO_2$ by a representative cross section of single-celled and colonial organisms would be useful.

Fungi are not simple organisms from an evolutionary perspective, but their respiratory gas exchange is controlled by diffusion as opposed to more complex, specialized systems. As with insects and microbes, the majority of information on the tolerance of fungus to elevated $CO_2$ comes from food-preservation literature. This source biases our understanding toward the amount and duration of exposure at which virtually nothing survives as opposed to defining the minimum level at which the most sensitive are harmed. Temperature, relative humidity, oxygen concentration, and $CO_2$ concentration all have significant effects on the growth of fungi. Significant inhibition of growth and the germination of spores was observed at 15–25% $CO_2$ for two types of fungi. At 30% $CO_2$, no measurable growth was observed, and 50% $CO_2$ prevented the germination of spores (Haasum and Nielsen, 1996; Tian et al., 2001).

Simple organisms only have biochemical methods available for adaptation and cell membranes or cell walls as barriers to the outside environment, so they remain biochemically flexible. In contrast, most "advanced" organisms maintain strict control of internal conditions and possess significant barriers to the external environment. Larger multicellular organisms have simplified biochemistry but complex systems. Humans are a good example. Our skin can tolerate a broad range of temperature and pH, but we cannot survive if our internal environment changes from optimum by a few degrees Centigrade or a few hundredths to tenths of pH. We have no barrier to $CO_2$, so elevated $CO_2$ in the air immediately equilibrates with our blood. If the amount of $CO_2$ overwhelms our various mechanisms for maintaining blood pH and it drops much below 7.4, then we would succumb, whereas many other forms of life would survive.

### *2.5.3. Animals: Comparative Physiology and Active Bulk Gas Exchange in Water and Air*

To summarize the effects of elevated $CO_2$ on animals, a brief review of respiration in complex organisms is required. The transition from water to air as the respiratory medium, the transition to terrestrial habitation, and increasing metabolic rates that could ultimately support flight dominate the evolutionary history of respiration. Aqueous, soil, terrestrial, and aerial environments offer distinct respiratory challenges. Also, respiration encompasses two interrelated yet distinct processes, the procurement of $O_2$ and the elimination of $CO_2$.

The oldest form of respiration is simple diffusion in water. Water is relatively dense and viscous compared to air, so gas exchange using water is inherently less efficient because of the energy required to move it. Oxygen is more difficult to obtain because it is poorly soluble, and $CO_2$ is relatively easy to eliminate because it is highly soluble. Paleoclimatic evidence suggests that before 70 million years ago, previous climates were typically much warmer, biological productivity was much higher, and consequently tropical swamps were widespread. These conditions are thought to be one of the main driving forces behind the evolution of air breathing because such waters have little $O_2$ and very high levels of $CO_2$. The end product of organic matter decay in such reducing environments is predominantly methane, with 60% methane, 30% $CO_2$, and 10% hydrogen, carbon monoxide and ethylene typical of carbohydrate-rich decomposition (refer to references in Maina, 1998). Studies of the physiology of inhabitants of high $CO_2$ aquatic or marine environments such as Lake Nyos were not found, but the preponderance of lungfish in the Amazon Basin is suggestive of the relationship between swampy conditions and air breathing (Pierre, 1989; White, 1989; Hamilton et al., 1995; Maina, 1998).

Terrestrial habitation requires two major adaptations. The first is to minimize water loss, and the second is to increase metabolism to meet the demands of terrestrial mobility. Supporting and moving the entire body-weight without the buoyancy of water is energy intensive. Fortunately, air is a much more efficient medium for delivering $O_2$, in contrast to aqueous breathing, but $CO_2$ disposal becomes difficult. The $CO_2$ carrying capacity of water is high, especially when bicarbonate is included. The limiting factor, then, is the exchange rate at the respiratory interface. Developing or co-opting the enzyme carbonic anhydrase solves this problem, because it catalyzes the bi-directional conversion of $CO_2$ to bicarbonate and back again, and accelerates the reaction rate in the range of a million fold (Maina, 1998; Campbell et al., 1999).

Ambient $O_2$, $CO_2$ and pH are determining factors for what types of organisms inhabit a given environment. A rapid or significant change in any of these conditions would cause biological stress, and the type of respiratory organ tells us much about an organism's normal environment and its ability to adapt or survive. Aquatic and marine animals use skin diffusive respiration, the gill, the water lung, or the placenta. The transport of respiratory gases in the circulatory system, the diffusion of gases between the blood and the cells, and the placenta *in utero* are the connection of humans with water as a respiratory medium. Gills are considered either simple or complex, and they are involved in many different processes, including respiration, feeding, ammonia excretion, locomotion, and the regulation of osmotic pressure, acid-base balance, and some hormones. Because of the extensive buffering capacity of the oceans, pH varies little in marine environments, but the concentrations of $O_2$ and $CO_2$ can be dynamic. This is especially true in enclosed or stagnant bodies of water where mixing is not thorough. Lakes that are stably stratified by salinity or temperature contrasts are particularly susceptible to variations in respiratory gas concentrations. In contrast, freshwater does not have much buffering capacity, so $CO_2$ released into freshwater could change pH significantly. The dearth of macrofauna in or near geothermal efflux or soda springs suggests that $CO_2$ leakage may have significant localized impacts. The effects of such change would depend upon the natural variability of pH in that specific environment and an organism's physiological ability to adapt.

Typically, a change in pH of a few tenths would be a significant stressor, if not fatal. However, the impact of $CO_2$ released into a body of water depends upon the amount and rate of release, the water body's buffering capacity, and its mixing dynamics. Studies of the natural $CO_2$ release at Mammoth Mountain, California, indicated that large amounts of $CO_2$ were dispersed through the groundwater system and released quickly upon exposure to the atmosphere. In fact, no evidence of a high $CO_2$ flux remained in the water even a few hundred meters downstream of the source (Kennedy, 2001, personal communication). Evidence from fish kills and swamps suggests that $O_2$ is the key respiratory gas among aquatic and marine organisms instead of $CO_2$, except to the extent that $CO_2$ could affect environmental pH (Hamilton et al., 1995; Maina, 1998). An interesting caveat to $CO_2$ in oceans is that at pressures and temperatures common in the deep oceans below approximately 500–800 m, $CO_2$ becomes denser than the surrounding water. Recent experiments have shown that below the critical depth, concentrated $CO_2$ will sink en masse instead of rising toward the surface (Brewer, 2001).

The transition from water to air breathing and from aquatic to terrestrial habitat involved bimodal breathing – the combination of an air-breathing lung with remnant gills or skin diffusive respiration. Some current bimodal breathers are exclusively aquatic (e.g., lungfish), some are primarily terrestrial (e.g., land crabs), and some live in both worlds (e.g., amphibians). Most bimodal breathers are amphibians, gastropod mollusks, crustaceans, or lungfish. Such animals obtain most of their oxygen via their lungs and eliminate most $CO_2$ through the skin or gills, effectively separating these processes; but they often have multiple modes of breathing available, depending upon the respiratory medium and medium of immersion. No studies were found that specifically addressed the tolerance of bimodal breathers to elevated $CO_2$ concentrations.

The retention of water, the elimination of $CO_2$ and its integral relationship with acid-base balance became the primary respiratory challenges for air breathers and terrestrial creatures. The transition was first notable in the swim bladder and the lungfish, and it was continued in the true diffusive or convective air-breathing organs. Passive diffusion can be effective only over short distances, so it is used in small, relatively immobile, low-metabolism organisms. Some gastropods use diffusion lungs, and terrestrial arthropods use a diffusive tracheal system, essentially an invaginating network of tubes. The insect tracheal system is unique in being both diffusive and convective. The tracheae distribute air directly to the tissues so that direct diffusion is effective, and the system allows for some of the highest aerobic rates ever measured. Arachnids possess the archaic book lung, trachea, or both, but their trachea exchange gas with hemolymph, analogous to blood. Oxygen is then transported throughout the body by a hemoglobin analog, hemocyanin, within the hemolymph.

Food preservation research has shown that insects have much higher tolerance to $CO_2$ than vertebrates. Mortality data for the rusty grain beetle compiled by Mann et al. (1999) varies from 15% $CO_2$ for 42 days to 100% $CO_2$ for 2 days. Table 2.1 shows a subset of recommended $CO_2$ concentrations and exposure time. Even after hours to days of exposure to high $CO_2$, many insects can recover. Other insects tolerances have been measured, and 35% $CO_2$ is the minimum concentration needed for effective control of all but a few unusually $CO_2$-tolerant species (Annis and Morton, 1997). Another common trend is decreasing mortality with increasing $CO_2$ concentrations above 85% (Leong and Ho, 1995; Mbata and Reichmuth, 1996). Zhou et al. (2000, 2001) are investigating the precise mechanisms of elevated $CO_2$ effects on insects.

**Table 2.1. Concentrations of $CO_2$ and the duration required for effective control of the rusty grain beetle (virtually 100% killed) (Mann et al., 1999).**

| $CO_2$ concentration (%) | Exposure time (days) |
|---|---|
| 15+ | 42 |
| 40 | 8-13 |
| 60 | 3-4 |
| 80 | 3 |
| 100 | 2 |

Information on $CO_2$ tolerance was not compiled for each type of animal, but some further studies on burrowing animals and soil invertebrates were found.

Fossorial animals, more commonly called burrowers, live within soils where environmental conditions are extremely variable. Even though soils are extremely heterogeneous, $CO_2$ in soil air (gas-phase occupying soil pore-space) normally increases with depth along a diffusion gradient. Diffusion is the primary transport mechanism for $O_2$ into the soil air and for $CO_2$ out to the atmosphere, and diffusion limits respiration in the soil environment because respiration itself is a constant source of $CO_2$. In well-aerated soils, the $CO_2$ concentration can remain below 1% at 1-meter depth; but in poorly aerated, waterlogged soils, $CO_2$ levels can exceed 10%. In fact, the major controls on $O_2$ and $CO_2$ levels in soils are the amount of respiration, the moisture level, and the specific soil chemistry (Amundson and Davidson, 1990; Holter, 1994; Pinol et al., 1995; Maina, 1998).

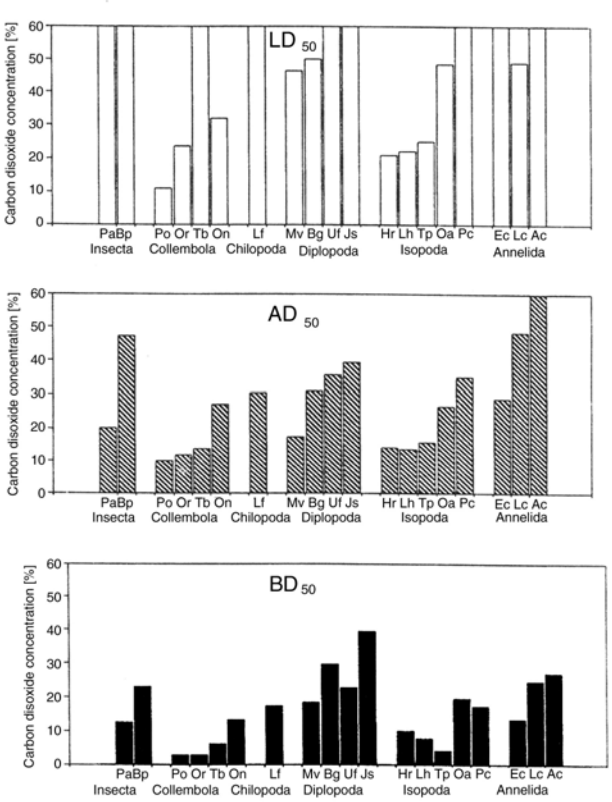


**Figure 2.7. Response of 19 species of soil invertebrate to elevated levels of $CO_2$. The concentrations of $CO_2$ at which behavioral reactions (BD50), constant paralysis (AD50), or mortality (LD50) appeared in 50% of animals. Species abbreviations are shown in Table 2.2. LD50 was higher than 60% $CO_2$ for some species, but the range in this figure is limited to 60% (Sustr and Simek, 1996).**

The response of soil invertebrates to $CO_2$ shows inter- and intra-species variation and depends upon their ecomorphological niche. The results of the study by Sustr and Simek (1996) are shown in Figure 2.7. Behavioral changes in half of the observed individuals for a given species occurred between 2 and 39% $CO_2$ in the ambient soil air, with the majority of species affected by 20%. Paralysis in half of observed individuals was apparent between 10 and 59% $CO_2$. Half of the species were paralyzed by 30%, and all but one were paralyzed by 50%. Carbon dioxide levels from 11% to 50% were lethal for half of the species investigated. The effects of $CO_2$ depend upon temperature, humidity, and oxygen concentration, but (according to previous research) the dilution of oxygen in soil environments at high $CO_2$ levels is not significant. Breathing mechanism had an obvious effect, with gills and skin-diffusive respiration being more sensitive to $CO_2$ levels than tracheal and pseudotracheal respiratory mechanisms or skin breathing earthworms with closed circulatory systems. Biochemical mechanisms also appeared significant based upon the range in sensitivity of springtails (Collembola), a group using skin diffusive respiration (Sustr and Simek, 1996).

**Table 2.2. Species abbreviations and descriptions modified from Sustr and Simek (1996).**

| Species | | Abbreviation | Notes on age, habitat, and ecomorphological type |
|---|---|---|---|
| Insecta (Insects) | *Pyrrhocoris apterus* | Pa | adults, soil surface |
| | *Bibio pomonae* | Bp | larvae, litter |
| Collembola (Springtails) | *Pogonognatellus flavescens* | | epigeic (surface) species |
| | *Orchesella flavescens* | Or | atmobiotic species |
| | *Tetrodontophora bielanensis* | Tb | hemiedaphic species (part-time soil dweller) |
| | *Onychiurus cf. ambulans* | On | euedaphic species (soil dweller) |
| Chilopoda (Centipedes) | *Lithobius forficatus* | Lf | litter |
| Diplopoda (Millipedes) | *Melogona voigti* | Mv | litter |
| | *Blaniulus guttulatus* | Bg | litter |
| | *Unciger foetidus* | Uf | litter |
| | *Julus scandinavius* | Js | litter |
| Isopoda (Pill bugs) | *Hyloniscus riparius* | Hr | litter, hygrophilous (water/moisture loving) |
| | *Trichoniscus pussillus* | Tp | litter, hygrophilous |
| | *Oniscus asellus* | Oa | litter, hygrophilous |
| | *Porcellium collicolla* | Pc | litter |
| Enchytraeidae (Potworms) | *Enchytraeus crypticus* | Ec | litter |
| Lumbricidae (Earthworms) | *Lumbricus castaneus* | Lc | epigeic species |
| | *Aporrectodea caliginosa* | Ac | endogeic (subsurface) species |

Another group of insects analogous to soil dwellers are beetles and fly larvae that are specially adapted to living in dung pats. Microbial activity in fresh pats is substantial, so the dung air may have $O_2$ concentrations below 1%, $CO_2$ concentrations from 20-30%, and methane concentrations from 30–50%. The dung insects generally could adapt to 20% $CO_2$, and some larvae remained visibly unaffected up to 43% $CO_2$. Yet tolerance varies greatly, and some surface-dwelling insects are paralyzed by 8% $CO_2$ (Holter, 1994).

Burrowers have the highest $CO_2$ tolerance among vertebrates because soil air often contains high levels of $CO_2$. Most burrowers inhabit open tunnels and spend only part of their time underground. Such animals include gophers, many rodents, and some birds. The $CO_2$ content of their respective burrows have been measured as high as 4%, 2%, and 9%. Concentrations of $CO_2$ as high as 13.5% have been found in the dens of hibernating mammals (see references in Maina, 1998).

Among the major classes of terrestrial vertebrates—reptilia, mammalia, and aves—the lung takes on several forms. Reptilian lungs are morphologically the most diverse, but they are also the least efficient. Aerobic capacity in reptiles is a fraction of that in mammals. In contrast, anaerobic capacity and tolerance for hypoxia is greater. As a result, reptiles are probably more tolerant to elevated $CO_2$ than mammals. Turtles are specially adapted to hypoxia via depressed metabolism. They can withstand complete anoxia for days or even months and a decrease in brain pH to 6.4. The diaphragm affects the complete functional separation of the thoracic and abdominal cavities in mammals and is a unique characteristic. The homogeneity of form and function of the mammalian lung is another striking feature: all are tidally (rhythmically) ventilated, dead-end sacs. The lungs of bats are proportionally much larger in order to sustain flight and increased aerobic capacity, yet bats are aerobically inefficient relative to birds. The lung-airsac system of birds is closest to the multicameral reptilian lung. There is remarkable morphological and functional homogeneity among bird lungs, as with mammals, but the lung airsac is a highly efficient gas exchanger. The airsac changes volume by only 1–2% per breath, but it allows a constant unidirectional flow of air through the lungs. Along with several other structural and functional characteristics (including countercurrent exchange), the avian lung is unquestionably the most efficient vertebrate gas exchange system known. Birds can sustain increases in aerobic capacity by a factor of 20-30, while elite human athletes can manage similar increases for a few minutes at most. Birds are uniquely tolerant to low-pressure oxygen deficiency and low $CO_2$ from flying at altitude and sustaining high-energy output. Specific references for the tolerance of birds to elevated $CO_2$ were not found and may represent an important research gap (Maina, 1998).

### *2.5.4. Effects of Elevated $CO_2$ Concentrations on Plants*

At slightly enriched levels (500–800 ppm) over atmospheric background (370 ppm), carbon dioxide usually stimulates growth in plants, depending on the mechanism of introducing $CO_2$ into the photosynthetic or Calvin cycle—C3, C4, or CAM (crassulacean acid metabolism). The majority of plants are C3, like trees, and first make a three-carbon acid when fixing $CO_2$. As part of adapting to arid conditions, the need to minimize water loss during hot, dry days, and perhaps low levels of $CO_2$, C4 and CAM plants such as grasses and succulents first make four-carbon acids. C4 plants separate $CO_2$ uptake and fixation spatially by segregating the processes in different cell types, and CAM plants separate uptake and fixation temporally by absorbing $CO_2$ at night and fixing it during the day (Mohr, 1995). The experimental increase of ambient $CO_2$, called free air $CO_2$ enrichment (FACE), initially causes proportional increased growth in C3 plants, followed by a tapering down to slightly elevated growth rates above unenriched levels. It also increases water-use efficiency and changes carbon allocation among tissue types. The growth rate of C4 and CAM plants is not limited by $CO_2$ availability as it is for C3 plants. As a result, the response of C4 and CAM plants is usually more complex and of lesser magnitude, so no simple generalization can be made about the effects of FACE (Orcutt and Nilsen, 2000). Enhanced growth of plants in controlled-atmosphere greenhouses with enriched $CO_2$, optimally between 1000 and 2000 ppm, is the result of elevated $CO_2$ in conjunction with elevated temperature, plentiful water, and intensive fertilization (Mastalerz, 1977). Individual plants adapt easily to small changes in ambient $CO_2$, perhaps changing the allocation of biomass among roots, stems, and leaves, but over decades to centuries, plant-species composition may change at the ecosystem level, generally in favor of C3 plants, with a consequent change in ecosystem composition and type. Enormous amounts of climate change research are underway that investigate the response of all aspects of ecology and the environment to elevated $CO_2$, projected temperature increases, and alterations to the hydrologic cycle. (See articles in Press et al., 1999; IPCC, 1996, 2001; Jones and Curtis, 2000; Orcutt and Nilsen, 2000; CDIAC 2001a, 2001b.)

The range and effects of high levels of $CO_2$ on plants, between FACE and lethal levels, are not clearly delineated. The precise mechanisms of tree kill in events like the outgassing from Mammoth Mountain, California, are poorly understood. The most likely cause is suppression of root-zone respiration via hypoxia, hypercapnia, or acidification of the soil environment. Long-term exposure over weeks or months to 20% or more $CO_2$ in soil gas led to dead zones where no macroscopic flora survived. The distribution of effects relative to $CO_2$ concentration suggests that 20–30% is a critical threshold for plants and ecosystems in general. Although some plants will die quickly from severe hypoxia, the lack of vegetation killed by the natural release of $CO_2$ at Lake Nyos indicates that plants generally have a much higher tolerance than animals to extremely high, short-lived exposures.

### *2.5.5. Concluding Remarks Regarding Ecosystem Exposure to Elevated Levels of $CO_2$*

In the future, a more thorough review of comparative, plant, and ecosystem physiology relating to hypoxia, hypercapnea, pH tolerance, and biochemical mechanisms of homeostasis may prove fruitful. In fact, modeling of ecosystem response to various scenarios of $CO_2$ release will require rigorous, quantitatively defined thresholds or probability distributions correlating $CO_2$ concentrations with specific impacts. Human tolerance provides a convenient rule of thumb for environmental $CO_2$ exposure limits, based on this review of physiology. Some organisms may be more sensitive than humans to elevated $CO_2$, but precautionary limits render it unlikely that there would be any surprise devastating ecological impacts. The poorly understood physiological tolerance of birds to elevated $CO_2$ and response of aquatic organisms to catastrophic $CO_2$ release requires a more extensive review of comparative physiology literature and additional research.

With regard to geologic sequestration, subsurface $CO_2$ storage and leakage may lead to the dissolution of minerals, the mobilization of metals in the aqueous phase, and the potential concentration of organic compounds in supercritical $CO_2$ due to its solvent properties (Hyatt, 1984; Pawliszyn and Alexandrou, 1989; Spall and Laintz, 1998). The rates, likelihood, and potential significance of these processes (if any) are not well known. The risks associated with these types of processes are not addressed here.

Carbon dioxide outgassing near geothermal vents, fumaroles, and soda springs may provide an opportunity for research on the environmental effects of a range of concentrations and duration of exposure. The scarcity of macrofauna in such high $CO_2$ environments may be indicative of the physiological stress caused by elevated $CO_2$. However, the presence of other gases such as $H_2S$ in some cases may make it difficult to draw quantitative conclusions about the effects of elevated $CO_2$ concentrations from such an evaluation.

More importantly, while there has been a great deal of research about the ecological effects of slightly elevated concentrations of $CO_2$ and on the high concentrations that are known to create a lethal response, there is little research about short or long-term exposure to intermediate concentrations of $CO_2$. (For example, what would be the ecological consequence of prolonged exposure to 3–5% $CO_2$?) Soil gas and biological surveys near natural $CO_2$ surface releases and above underground reservoirs would be useful to address issues such as these.

## 2.6. Industrial Sources and Uses of $CO_2$

The risk-assessment process for $CO_2$ can also be informed by a review of industrial sources and uses, safety issues and procedures, and accidents. Carbon dioxide was one of the first chemicals identified, and it has diverse uses. Table 2.3 is a summary of U.S. emissions and sinks of $CO_2$ in 1998. Fossil fuel combustion generated 1468.2 million metric tonnes of carbon equivalents (MMTCE). All other industrial processes utilized and ultimately emitted 18.4 MMTCE. In addition to being a by-product of fossil fuel combustion, $CO_2$ is a by-product of pH control/acid neutralization, cement manufacture, and the chemical production of lime, ammonia, ethyl alcohol, hydrogen, ethylene oxide, and synthetic natural gas.

Yet $CO_2$ is also a commodity with diverse applications. The main sources of $CO_2$ for industrial use are natural reservoirs, the by-product of chemical manufacture, and separation from crude oil or natural gas. Manufacturing carbonates, urea, and methanol uses $CO_2$ as a reactant. Carbon dioxide is used to carbonate beverages, and when produced by yeast, it is the leavening agent in baking and the by-product of fermentation in the manufacture of alcoholic beverages. We use it to preserve food and extinguish fires. Under regulations for the humane slaughter of livestock, we anesthetize and kill animals with it. The oil industry, in a process called enhanced oil recovery (EOR), pumps $CO_2$ into hydrocarbon reservoirs to aid in the secondary and tertiary recovery of oil and gas. In EOR, $CO_2$ can form an immiscible mixture with the reservoir oil, thus making it easier to extract from the reservoir. When $CO_2$ dissolves in the crude oil or preferentially acts as a solvent for the lighter hydrocarbons, it causes a decrease in bulk fluid viscosity and density. This drive to increase volume maintains reservoir pressure and increases the proportion of original-oil-in-place recovered. Enriched levels of $CO_2$ in greenhouses enhance the growth of plants, and dry ice and liquid $CO_2$ are used as refrigerants. Carbon dioxide is also used as a pressurizing agent and a supercritical solvent. A list of applications from Airgas, a company that sells $CO_2$, is included as Appendix 5 (NIOSH, 1976; IEAGHG, 1995; CGA, 1997; Airgas, 2000; US EPA, 2000b).

**Table 2.3. U.S. sources of $CO_2$ in 1998. Emissions and sinks in MMTC (US EPA, 2000b).**

| Source | Amount in 1998 |
|---|---|
| Fossil Fuel Combustion | 1468.2 |
| Industrial Processes | 18.4 |
| Cement Manufacture | 10.7 |
| Lime Manufacture | 3.7 |
| Limestone and Dolomite Use | 2.4 |
| Soda Ash Manufacture and Consumption | 1.2 |
| Carbon Dioxide Consumption* | 0.4 |
| Iron and Steel Production** | 23.9 |
| Ammonia Manufacture** | 6.3 |
| Ferroalloy Production** | 0.5 |
| Aluminum Production** | 1.6 |
| Natural Gas Flaring | 3.9 |
| Waste Combustion | 3.5 |
| Land Use Change and Forestry (Sink) | (210.8) |
| International Bunker Fuels | 31.3 |
| Total Emissions | 1494.0 |
| Net Emissions (Sources and Sinks) | 1283.2 |

* Includes food processing, chemical production, carbonating beverages, and EOR. Primary sources include natural reservoirs,chemical manufacture, and separation from crude oil and natural gas.

** Emissions from these processes are primarily due to energy consumption and are included in the total for fossil fuel combustion.

For 1999, an industry research group called Freedonia reported the shipment of 1.81 MMTC of liquid carbon dioxide (1 MMTC = 3.67 million metric tonnes of $CO_2$) through the merchant market and 1.87 MMTC (6.86 MMT $CO_2$) total production, including on-site captive consumption. Another Freedonia $CO_2$ industry study from 1991 estimated that 20% of $CO_2$ sold on the merchant market came from natural reservoirs and 80% from captured emissions. The EPA's emissions estimate of 0.4 MMTC comes from assigning 80% of the 1.87 MMTC to emissions accounted for elsewhere and only the 20% derived from natural reservoirs uniquely to $CO_2$ consumption. Total EOR demand in 1999 according to Freedonia was 1.79 MMTC (6.56 MMT $CO_2$), of which 5.3% or 0.09 MMTC (0.35 MMT $CO_2$) was supplied by the merchant market. The remaining 1.70 MMTC (6.21 MMT $CO_2$) was supplied via pipeline from natural reservoirs, separated from crude oil or natural gas, or recycled in existing EOR projects. Figure 2.8 shows the distribution of some major $CO_2$ sources, pipelines, and EOR projects in the U.S. Combining Freedonia's estimates for liquid $CO_2$ sold on the merchant market with the EOR estimates yields a total of 3.56 MMTC (13.1 MMT $CO_2$) utilized in 1999. The summary report on industrial gases for 1999 from the Department of Commerce (DOC) estimates total production of 3.25 MMTC (11.9 MMT $CO_2$). The difference of 0.31 MMTC (1.2 MMT $CO_2$) between the numbers from Freedonia and the DOC can be ascribed to uncertainty in the estimates of $CO_2$ separated from crude oil and natural gas or recycled within existing EOR projects. The proportion of $CO_2$ that comes from natural reservoirs versus recycled or separated from crude oil and natural gas has not been compiled (Freedonia, 1991, 2000; US DOC, 1999; US EPA, 2000b).

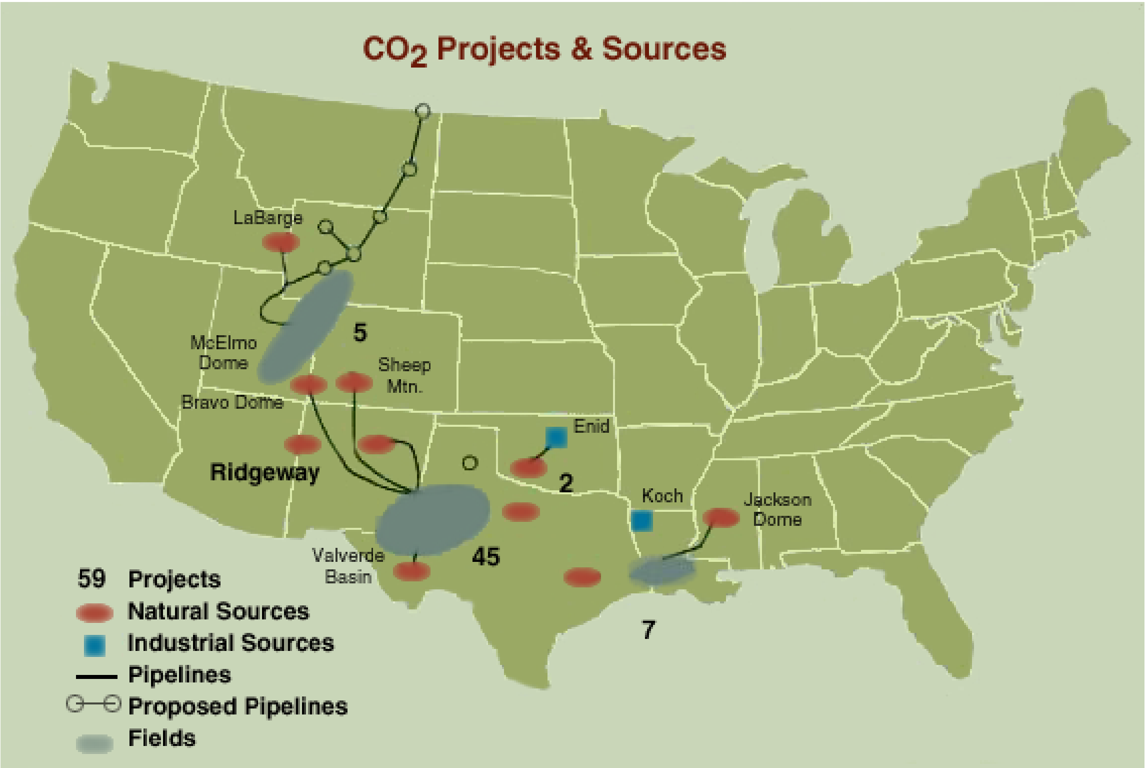


**Figure 2.8. Major U.S. natural $CO_2$ reservoirs, pipelines, and proximity to EOR projects (Ridgeway, 1998).**

Industry experience with $CO_2$ also provides insights into the safety concerns of any geologic sequestration project. Refineries process large quantities of hydrocarbons, on average 4.3 MMTCE per refinery in the U.S. during 1999. According to the Texas Natural Resources Conservation Commission, one large refinery in Harris County, Texas, vented 1.47 MMTC or 5.4 MMT $CO_2$ in 1998 (TNRCC, 2001), yet that $CO_2$ posed no immediate human health or environmental hazard because it dispersed from high smokestacks. Chevron Research and Technology Corporation's Health, Environment and Safety Group estimates that an average refinery emits 5600 tonnes $CO_2$/day or 2 million tonnes $CO_2$/year (2.0 MMT $CO_2$/yr or 0.545 MMTC/yr) (Chevron, 2001, personal communication). Shell, one of the largest international energy companies, estimated their total annual global emissions in 1999 to be 90 MMT of $CO_2$ alone or 27 MMTCE including other greenhouse gases (Shell, 2000). Carbon dioxide pipelines are mostly associated with EOR, and their accident record is available through the Office of Pipeline Safety (OPS) in the Department of Transportation (DOT). Eight accidents are on record for $CO_2$ pipelines from 1968 to 2000: three in 1994, one in 1995, three in 1996, and one in 1997. There were no injuries and no fatalities. A failed weld caused one, and corrosion caused another. Three were failures of control or relief equipment, and two more resulted from other failed components. Outside force caused the other one (US DOE, 2000; US DOT, 2000).

Catastrophic pipeline failures are considered unlikely and the environmental consequences of a massive $CO_2$ pipeline rupture are expected to be minimal because of engineering controls. One attempt to model the impacts of rupture was reported by Kruse and Tekiela (1996). Typically, the main procedural controls are maintenance routines and visual inspections via plane, truck, or walking the line. If odorants and colorants are used, they render small leaks easier to detect. Vegetation that has been killed or that is visibly under stress is used to locate leaks in natural gas pipelines, especially where they are underground. In addition to manufacturing standards for the pipeline materials, automatic pressure control valves are placed regularly along the length of pipelines in case of catastrophic ruptures. The safety control valves shut down the flow of gas if the pressure in the pipeline exits a preset range. The pressure drop of a large leak or rupture would trip the shut-off valves, so only the gas between two safety control valves could vent to the atmosphere. The spacing of such control devices is set according to regulations and safety considerations depending upon proximity to human residences (US DOT, 2000).

The EPA published a review of the risks of $CO_2$ as a fire suppressant. Carbon dioxide is used in 20% of fire protection applications, and it is common in large industrial systems. The EPA report included a summary of 51 incidents that occurred between 1975 and 2000. These involved a total of 72 deaths and 145 injuries. In a characteristic incident at Idaho National Engineering and Environmental Laboratory, an accidental release during the maintenance of an electrical system resulted in one fatality and 12 injuries. The sudden discharge filled an enclosed space with 2.5 tonnes of $CO_2$ and created an atmosphere with approximately 50% $CO_2$ and 10.5% $O_2$.

Engineering controls and procedures set by the DOT, National Fire Protection Association (NFPA), American National Standards Institute (ANSI), Compressed Gas Association (CGA), American Society of Mechanical Engineers (ASME), and Occupational Safety and Health Administration (OSHA) are used to ensure the safety of refineries, pipelines, fire suppression systems, and any transportation of $CO_2$ whether it is pressurized, cryogenic, solid, liquid, or gas (US DOE, 1998; US DOT, 2000; US EPA, 2000a; US GPO, 2000).

The cumulative experience of industry suggests two conclusions. First, $CO_2$ is a familiar and integral part of our everyday lives that is generally regarded as safe; and second, concentrated $CO_2$ in confined spaces poses a significant but well-known hazard that falls within standard industry practice, engineering controls, and safety procedures. The environmental consequences of $CO_2$ separation facilities and pipelines are the same as such facilities used for other purposes. Geologic carbon sequestration does not pose any new or uncertain hazards in its surface facilities. One major change from the existing $CO_2$ industry would be scaling up sequestration to a projected 1,000 MMTC in 2025 versus the 3.5 MMTC used in industry in 1999. This reinforces the need for carefully reviewed, publicly accepted safety standards. Injection wells are intermediate between surface facilities and geologic containment, and (along with plugged and abandoned wells) they pose the greatest risk for loss of containment. The integrity, safety, and regulations regarding new well construction and known and unknown plugged and abandoned wells are discussed thoroughly in Chapters 4, 5, and 6. The more poorly understood potential hazards of geologic sequestration are associated with geologic storage over the long-term. To address this aspect of risk assessment, we turn to natural manifestations of $CO_2$ in the following chapter, but first we review regulations and measurement techniques for $CO_2$.

## 2.7. Carbon Dioxide Regulations

Regulations for $CO_2$ have been promulgated by a number of organizations for a variety of purposes. These guidelines roughly reflect our collective experience with, understanding of, and attitude toward $CO_2$ and provide further context for risk assessment. We discuss the regulations briefly and summarize them in Tables 2.5 and 2.6.

### *2.7.1. Occupational Health Standards for Carbon Dioxide*

The Occupational Health and Safety Administration (OSHA) in the Department of Labor (DOL) sets the most directly relevant regulations regarding $CO_2$. The National Institute of Occupational Safety and Health (NIOSH) in the Center for Disease Control and Prevention (CDC) is part of the Public Health Service (PHS) in the Department of Health and Human Services (DHHS) and recommends exposure limits. These agencies regulate $CO_2$ as an occupational air contaminant. The general personal exposure limit (PEL) set by OSHA is a time-weighted average (TWA) of 5,000 parts per million by volume (ppm)

(0.5%) for an 8-hour workday and a 40-hour workweek. The NIOSH recommended exposure limit (REL) is a 10-hour/day and 40-hour/week TWA of 5,000 ppm, a 15-minute TWA short-term exposure limit (STEL) of 30,000 ppm (3%), and 40,000 ppm (4%) as the level immediately dangerous to life and health (IDLH). All IDLH atmospheres require the use of respiratory protection equipment. The *Occupational Health Guideline for Carbon Dioxide*, published jointly by OSHA and NIOSH, is included as Appendix 7, and the NIOSH *Pocket Guide to Chemical Hazards* entry for $CO_2$ is attached as Appendix 8 (NIOSH, 1976, 1981, 1994a, 1997b; US GPO, 2000).

The American Conference of Governmental Industrial Hygienists (ACGIH) is the source of OSHA standards for construction and recommends a 5,000 ppm TWA threshold limit value (TLV) and a 30,000 ppm TWA-STEL. ACGIH and NIOSH criteria documents are the core sources of occupational exposure limits through their own research and references to primary literature. The limit for $CO_2$ in surface and underground metal and nonmetal mines set by the Mine Safety and Health Administration (MSHA) in DOL is referenced to the ACGIH as well (NIOSH, 1976; ACGIH, 1994; US GPO, 2000).

The Department of Transportation (DOT) regulates $CO_2$ through the Federal Aviation Administration (FAA) as an air contaminant and as a surrogate for adequate ventilation in cabin air (5,000 ppm $CO_2$) (NRC, 1986; US GPO, 2000).

### *2.7.2. Ventilation and Indoor Air Quality*

The FAA uses the criteria for occupational exposure to $CO_2$ to set its ventilation rates, but that is unusual. General building ventilation and indoor air-quality requirements are set by ANSI (American National Standards Institute)/ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) Standard 62-1999 at 700 ppm above ambient outdoor $CO_2$ levels, or about 1,000 ppm $CO_2$ for HVAC (Heating, Ventilating and Air-Conditioning) industrial ventilation systems. This standard was set using comfort and odor control criteria. HVAC systems often monitor $CO_2$ concentration as a general proxy for indoor air quality because it is the primary contaminant produced by occupants. Ventilation rates that keep $CO_2$ levels below 1,000 ppm are proven to reduce Sick Building Syndrome, complaints such as irritated eyes, nose, and throat; headache, coughing, nausea, and dizziness (US EPA, 1991; OSHA, 1994; NIOSH, 1997a; ASHRAE, 1999).

### *2.7.3. Confined Space Hazard and Fire Suppressant*

NIOSH is the single best source of information on confined space hazards, and OSHA is the regulatory body with oversight responsibility. OSHA establishes labeling, warning, and training requirements for confined space hazards like $CO_2$. In occupational settings such as silos, manure pits, breweries, and ship holds, $CO_2$ is recognized as a serious inert gas danger that creates oxygen-deficient atmospheres. Other OSHA regulations control the use of $CO_2$ as a fire suppressant and require a discharge alarm, time to exit before discharge, and employee training about the hazards associated with the use of $CO_2$ to fight fires. Many of the OSHA rules regarding fire protection come from the National Fire Prevention Association (NFPA) (NIOSH, 1979, 1994c, 1997b; CGA, 1992a, 1992b, 1998; US EPA, 2000a; US GPO, 2000). The Emergency Management Institute of the Federal Emergency Management Agency (FEMA), professional and academic emergency management programs, and underground utilities organizations are additional sources of regulations, information, and training regarding confined space hazards.

### *2.7.4. Breathing Gas, Respiratory Protection, and Controlled, Self-Contained Atmospheres*

Academic medical researchers and governmental aviation and aerospace organizations such as NASA and the US Naval Medical Research Institute have investigated the physiology of $CO_2$ and the engineering controls needed to sustain humans in controlled and self-contained environments. The compressed-breathing-gas $CO_2$ limit for OSHA/CGA Grade D breathing air used in respiratory protection and Self

Contained Underwater Breathing Apparatus (SCUBA) equipment is 1,000 ppm. Through the Coast Guard, the DOT establishes a limit for $CO_2$ at 1000 ppm in SCUBA breathing gas for commercial diving.

NIOSH and PHS also regulate the $CO_2$ content of breathing gas for self-contained breathing apparatus (SCBA) and supplied air respirators. These limits are the same CGA standard of 1000 ppm, but also mandate maximum inspired $CO_2$ content for rebreathed air while using an SCBA (as shown in Table 2.4). Because humans at rest exhale 3.5% $CO_2$ on average, some exhaled air in the mask of an SCBA is rebreathed. The equipment design must ensure that the average $CO_2$ content of inhaled air does not exceed the tolerances listed in the following table (CGA, 1990, 1997a; US GPO, 2000).

**Table 2.4. Maximum allowed percentage of $CO_2$ in mixed supplied/rebreathed air from SCBA apparatus (US GPO, 2000–42 CFR 84.97).**

| Service Time in hours | Maximum allowed $CO_2$ content in % |
|---|---|
| <1/2 | 2.5% |
| 1 | 2.0% |
| 2 | 1.5% |
| 3 | 1.0% |
| 4 | 1.0% |

### *2.7.5. Food Additive and Medical Gas*

The DHHS sets rules for or defines uses of $CO_2$ as a general food additive, a leavening agent, a diagnostic indicator of severe disorders associated with changes in body acid-base balance, and as a medical gas. As long as $CO_2$ is manufactured in accordance with current good manufacturing practices (CGMP) as defined in 21 CFR sections 210-211, it is generally recognized as safe (GRAS) as a food additive. The $CO_2$ limit for medical gas is 500 ppm, as set by the CGA, United States Pharmacopeia (USP), and the National Formulary (NF).

### *2.7.6. Chemical Safety, Hazard Communication, and Hazard Response*

Information on the hazards of $CO_2$ and recommended responses to its release are available through the OSHA-mandated Material Safety Data Sheets (MSDS) produced by manufacturers. MSDS for $CO_2$ from Airgas (Appendix 11) and from the CGA (Appendix 12) are included. Other sources include FEMA's Hazardous Material Guide (Appendix 8), the DOT's Emergency Response Guide (Appendix 9), toxicological information from the Registry of Toxic Effects of Chemical Substances (RTECS), and the International Chemical Safety Card (ICSC) (Appendix 10). The International Programme on Chemical Safety that produces the ICSCs is a joint project of the United Nations Environmental Programme (UNEP), the World Health Organization (WHO), and the International Labour Office (ILO).

The response to $CO_2$ releases or hazards is the same as for any IDLH atmosphere. First, rescuers must wear respiratory protection. Victims are removed to a well-ventilated area and provided with supplementary oxygen if available. Aggressive ventilation and release to the atmosphere disperse the $CO_2$.

### *2.7.7. Transportation*

Most regulations regarding $CO_2$ by the DOT refer to engineering controls on equipment used to transport $CO_2$ (such as tanks and pipelines) and include the Office of Pipeline Safety. The CGA, ANSI, ASME, and NFPA are other good sources of information and regulations pertaining to the transport of $CO_2$ by various means.

### *2.7.8. Toxic and Hazardous Substances: Where $CO_2$ Is Not Regulated*

The regulations that do not include $CO_2$ are equally interesting. As with any substance, the dose makes the poison. Even $O_2$ is toxic at high concentrations, so while $CO_2$ is a physiologically active gas and lethal above 15% to 30%, it is not regarded as a toxic substance because it has no known toxicological effects (such as causing cancer, impairing the immune system, or causing birth defects). The EPA enforces the Clean Air Act by regulating ambient outdoor air-quality contaminants, and $CO_2$ is not included. The EPA does not set a limit for the amount of $CO_2$ allowed in food, as it does for other pesticides. Carbon dioxide is not suspected of any harmful effects in small concentrations (ppm), so the National Toxicology Program (NTP) has not studied it yet. None of the following organizations lists or studies $CO_2$ as a toxic substance: the Agency for Toxic Substances and Disease Registry (ATSDR) or NIOSH in the CDC, the National Institute of Environmental Health Science (NIEHS) in the National Institutes of Health (NIH), or the National Center for Toxicological Research (NCTR) in the FDA. Nor do the following regulations identify or regulate $CO_2$ as a toxic or hazardous material: the Federal Insecticide, Fungicide, and Rodenticide Act of 1972 (FIFRA), the Resource Conservation and Recovery Act of 1976 (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund), and the Superfund Amendments and Reauthorization Act of 1986 (SARA). Only the inventory list for the Toxic Substances Control Act of 1976 (TSCA), the NIOSH confined-space hazard classification system, and FEMA's hazardous materials guide treat $CO_2$ as a hazardous substance to the extent that any concentrated or pressurized gas poses a danger. In all cases, it is included in the least hazardous category.

### *2.7.9. Summary of Regulations Related to $CO_2$*

Table 2.5 is a summary of established exposure limits, and Table 2.6 is a list of the majority of regulations from the Code of Federal Regulations that pertain to $CO_2$.

**Table 2.5. Summary of information regulatory limits for exposure to carbon dioxide.**

| Organization | Regulation Type | Regulation Limit |
|---|---|---|
| OSHA | Occupational | 5,000 ppm TWA PEL; 30,000 ppm TWA STEL |
| NIOSH | Occupational | 5,000 ppm TWA REL; 30,000 ppm TWA STEL;<br>40,000 ppm IDLH |
| ACGIH | Occupational | 5,000 ppm TWA TLV; 30,000 ppm TWA STEL |
| ASHRAE | Ventilation | 1,000 ppm |
| OSHA/NIOSH/ CGA/USP/NF | Compressed Breathing Gas for Respiratory Protection SCBA and SBA | 1,000 ppm |
| OSHA/CGA/ Coast Guard | SCUBA Breathing Gas | 1,000 ppm |
| FDA/CGA/USP/ NF | Medical Gas | 500 ppm |

**Table 2.6. Code of federal regulations (CFRs) relating to carbon dioxide.**

| CFR | Government Branch | Regulated As | Description | Regulation (limit/max) |
|---|---|---|---|---|
| 9 CFR 313.5 | FSIS, DOA | Anaesthetic and Asphyxiant | Humane Slaughter of Livestock | XX |
| 14 CFR 25.831 | FAA, DOT | Ventilation Air Contaminant | In Airplane Cabins | 5,000 ppm (0.5%) by volume |
| 21 CFR 137.180, 137.185, 137.270 | FDA, DHHS | Leavening Agent | In Self-Rising Cereal Flours | Must exceed 5,000 (0.5%) |
| 21 CFR 184.1240 | FDA, DHHS | Direct Food Substance | GRAS – Generally Recognized as Safe | GRAS |
| 21 CFR 201.161 | FDA, DHHS | Medical Drug | Exempt from Labeling Requirements of 21 CFR 201.100 | Exempt from Labeling |
| 21 CFR 210-211 | FDA, DHHS | Medical Gas | Current Good Manufacturing Practices (CGMP) | CGMP |
| 21 CFR 582.1240 | FDA, DHHS | General Purpose Food Additive | GRAS – Generally Recognized as Safe | GRAS |
| 21 CFR 862.1160 | FDA, DHHS | Clinical Chemistry Test System | Diagnostic of Blood Acid-Base Imbalance | XX |
| 29 CFR 1910.134 | OSHA, DOL | Compressed Breathing Gas | In Respiratory Protection Equipment CGA and USP | CGA breathing air Grade D – 1,000 ppm (0.1%) |
| 29 CFR 1910.146 | OSHA, DOL | Confined Space Hazard | General Environmental Controls | Permit required to enter |
| 29 CFR 1910.155-1910.165<br>Subpart L | OSHA, DOL | Fire Suppressant and Confined Space Hazard | Required engineering controls on fire- fighting systems and equipment, employee training, and respiratory protection. NFPA | XX |
| 29 CFR 1910.430 | OSHA, DOL | Compressed Breathing Gas | Commercial Diving Operations – SCUBA | 1,000 ppm (0.1%) |
| 29 CFR 1910.1000 Table Z-1 | OSHA, DOL | Air Contaminant | General Occupational Exposure Limits | 5,000 ppm (0.5%) TWA PEL |
| 29 CFR 1915.1000 Table Z | OSHA, DOL | Air Contaminant | Exposure Limits for Shipyard Employment | 5,000 ppm (0.5%) TWA PEL |
| 29 CFR 1926.55 | OSHA, DOL | Air Contaminant | Exposure Limits for Construction | ACGIH: 5,000 ppm (0.5%) TWA TLV |
| 30 CFR 56.5001 | MSHA, DOL | Air Contaminant | Exposure Limits for Surface Mines | ACGIH: 5,000 ppm (0.5%) TWA TLV |
| 30 CFR 57.5001 | MSHA, DOL | Air Contaminant | Exposure Limits for Underground Mines | ACGIH: 5,000 ppm (0.5%) TWA TLV |
| 40 CFR 180.1049 | EPA | Pesticide, Insecticide | Tolerance for Pesticide Chemical in Food | Exempt from Tolerance |
| 42 CFR 84.79 | NIOSH, PHS, DHHS | Compressed Breathing Gas | SCBA | USP/NF, CGA: 1,000 ppm (0.1%) |
| 42 CFR 84.97 | NIOSH, PHS, DHHS | Inspired Air from SCBA | Test of Inspired Air in SCBA – control of rebreathing | >30 min./2.5%; 1hr/ 2.0%; 2hr/1.5%; 3hr/1.0%; 4 hr/1.0% |
| 42 CFR 84.141 | NIOSH, PHS, DHHS | Compressed Breathing Gas | Supplied Air Respirators | CGA: 1,000 ppm (0.1%) |
| 46 CFR 197.340 | Coast Guard, DOT | Compressed Breathing Gas | Commercial Diving Operations – SCUBA | 1,000 ppm (0.1%) |
| 49 CFR 100-180 | DOT | Transportation Material | General Transportation Requirements | |
| 49 CFR 190-199 | OPS, DOT | Gas or Hazardous Liquid | Engineering Safety Controls on Pipelines | |

## 2.8. Monitoring and Measurement Systems for Carbon Dioxide

Safety concerns surrounding geologic carbon sequestration require an effective method for monitoring $CO_2$. Small infrared (IR) detectors are available for occupational monitoring, and similar systems are used for soil gas surveys and large-footprint ecosystem-scale eddy-flux measurements for investigating the carbon cycle. Remote sensing through air and earth are also possible, but both have significant limitations. In this section, we review monitoring techniques for enforcing these regulations, industrial safety, and potentially detecting surface leaks. We focus on the detection of $CO_2$ in air. Geophysical techniques, such as seismic or electromagnetic methods, are the subject of many sequestration and EOR studies currently underway.

For occupational exposure, the federal government mandates in CFR 1900–2000 that companies comply with OSHA regulations and that they are subject to inspections. OSHA regulation CFR 1910.1000 requires administrative and engineering controls that are appropriate to specific toxic and hazardous air contaminants and that are subject to approval by industrial hygienists. Carbon dioxide levels in most buildings are not of great concern and therefore are controlled by ventilation. NIOSH, OSHA, and the EPA use gas sampling bags and gas chromatography for occasionally measuring $CO_2$ concentrations (EMC, 2001; EPA, 2000c; NIOSH, 1994b; OSHA, 2001, 2000). Gas chromatographs with thermal conductivity detectors (GC-TCD) are more rugged than IR detectors and are commonly used for long-term monitoring in the field. Mass spectrometry is the most accurate method for measuring $CO_2$ concentration, but it is also the least portable. Electrochemical solid-state $CO_2$ detectors exist, but they are not cost-effective at this time (Freifeld, 2000; Tamura et al., 2001; Torn, 2001, personal communication).

Continuous monitoring sensors are used in $CO_2$ demand-controlled HVAC systems, greenhouses, combustion emissions measurement, and the monitoring of environments in which $CO_2$ is a significant hazard (such as breweries). Such devices rely on IR detection principles and are referred to as infrared gas analyzers (IRGA). IRGAs are small and portable and commonly used in occupational settings. Most use nondispersive infrared (NDIR) or Fourier Transform infrared (FTIR) detectors. Both methods depend upon light attenuation by $CO_2$ at a specific wavelength, usually 4.26 μm. The attenuation or Beer's Law, $I = I_o e^{kc}$, is the basis for this method, where the measured intensity, I, is a function of the light source intensity, $I_o$, a proportionality constant, k, and the $CO_2$ concentration, c. Transmittance = I/Io, and absorbance = log(1/T) = log(Io/I) = ecL, where e is the molar extinction coefficient (proportion of light intensity blocked or absorbed versus the concentration of the substance, c, through which light is traveling) and L is the path length. With fixed light source intensity and fixed path length, the only remaining variable is $CO_2$ concentration (Hanst, unspecified). The list of companies that make $CO_2$ detectors from the *Sensors Magazine Buyer's Guide 2001* is included as Appendix 13 (Freifeld, 2000).

Common field applications in environmental science include the measurement of $CO_2$ concentrations in soil air, flux from soils, and ecosystem-scale carbon dynamics. Diffuse soil flux measurements are made using simple IR analyzers (Oskarsson et al., 1999). The USGS measures $CO_2$ flux on Mammoth Mountain using LI-COR detectors, named after the company that makes them (LI-COR, 2001; Sorey et al., 1996; USGS, 1999, 2001). Biogeochemists studying ecosystem scale carbon cycling use $CO_2$ detectors on 2–5 meter-tall towers in concert with wind and temperature data to reconstruct average $CO_2$ flux over large areas. These eddy flux correlation measurements (ECOR) assume thorough atmospheric mixing.

Remote sensing by satellites of $CO_2$ releases to the atmosphere is another complicated issue, because of the long path length through the atmosphere and because of the inherent variability of atmospheric $CO_2$. The total amount of $CO_2$ integrated by a satellite through the depth of the entire atmosphere is large. Infrared detectors measure average $CO_2$ concentration over a given path length, so a diffuse or low-level surface leak viewed through the atmosphere by satellite would be undetectable. In contrast, $SO_2$ and integrated total atmospheric $CO_2$ are routinely measured (Lopez-Puertas and Taylor, 1989). Geologists use a method called COSPEC (correlation spectroscopy) to measure the amount of $SO_2$ in eruption plumes, but it is not directly relevant to monitoring for surface leaks of $CO_2$ over large areas. A plane carries a spectrometer through the plume and measures the attenuation of solar ultraviolet light relative to an internal standard. Carbon dioxide is measured either directly in the plume by a separate IR detector, or calculated from $SO_2$ measurements and direct ground sampling of the $SO_2/CO_2$ ratio for a given volcano or event (Hobbs et al., 1991; Mori and Notsu, 1997; USGS, 2001). Remote-sensing techniques currently under investigation for $CO_2$ detection are LIDAR (light detection and range-finding) – a scanning airborne laser, DIAL (differential absorption LIDAR) - which looks at reflections from multiple lasers at different frequencies, and the detection of vegetative stress (Hobbs et al., 1991; Menzies et al., 2001).

In summary, occupational monitoring of $CO_2$ is well established. On the other hand, while some promising technologies are under development for environmental monitoring and leak detection, $CO_2$ measurement and monitoring approaches on the temporal and spatial scales that are relevant to geologic sequestration remain a key area for further research.

## 2.9. Summary Conclusions and Remarks

Carbon dioxide is generally regarded as safe and as a non-toxic, inert gas. It is an essential part of the fundamental biological processes of all living things. It does not cause cancer, affect development, or suppress the immune system in humans. Carbon dioxide is a physiologically active gas that is integral to both respiration and acid-base balance in all life. Exposure to elevated concentrations of $CO_2$ can lead to adverse consequences, including death. The effects of exposure to $CO_2$ depend on the concentration and duration of exposure.

Ambient atmospheric concentrations of $CO_2$ are currently about 370 ppm. Humans can tolerate increased concentrations with virtually no physiological effects for exposures that are up to 1% $CO_2$ (10,000 ppm). For concentrations of up to 3%, physiological adaptation occurs without adverse consequences. A significant effect on respiratory rate and some discomfort occurs at concentrations between 3 and 5%. Above 5%, physical and mental ability is impaired and loss of consciousness can occur. Severe symptoms, including rapid loss of consciousness, possible coma or death, result from prolonged exposure above 10%. Experiments conducted on a submarine crew exposed to up to 3% $CO_2$ for many weeks and short-term exposures to even higher concentrations have shown that all effects are reversible except for prolonged coma, consequences of prolonged hypoxia (lack of oxygen), and death. Loss of consciousness occurs within several breaths and death is imminent at concentrations above 25 to 30%. Deaths from catastrophic releases of $CO_2$ are known from industrial accidents and natural disasters.

The potential for lethal or otherwise harmful exposure depends more on the nature of the release than on the concentration of $CO_2$ or the size of the release. In particular, since $CO_2$ is denser than air, hazardous situations arise when large amounts of $CO_2$ accumulate in low-lying, confined, or poorly ventilated spaces. Releases, even large ones, do not pose a hazard if they are quickly dissipated in the atmosphere, such as from tall industrial stacks or explosive volcanic events.

Evidence for the effects of exposure to elevated concentrations of $CO_2$ on natural resources and ecosystems comes from many sources, including volcanic releases, soda springs, comparative, respiratory and fundamental physiology, free-air $CO_2$ enrichment studies, food preservation literature, and space science research. Among the major classes of terrestrial vertebrates, respiratory physiology and mechanisms for acid-base balance (pH regulation) vary widely, so tolerance to $CO_2$ exposure varies as well. Tolerance for $CO_2$ also correlates to ecological niche suggesting evolutionary adaptation to environmental conditions. Plants, insects, and soil-dwelling organisms have higher tolerance to $CO_2$ than most other forms of life. In spite of these differences, all air-breathing animals including humans have similar respiratory physiology and therefore broadly similar tolerance to $CO_2$, and prolonged exposure to high $CO_2$ levels, above 20–30%, will kill virtually all forms of life except some microbes, invertebrates, fungi, and insects. Some microbes can survive in a pure $CO_2$ atmosphere as long as trace amounts of oxygen are available. However, the identity and physiology of microorganisms dwelling in deep geologic formations is largely unknown, so the effects of $CO_2$ on subsurface microbes are uncertain.

Ecosystem impacts from exposure to elevated concentrations of $CO_2$ are poorly understood. Plants in general are even more tolerant than invertebrates to elevated $CO_2$, so any small-scale, short-term gas leaks would have minimal impacts. Persistent leaks, in contrast, could suppress respiration in the root zone or result in soil acidification, and catastrophic releases could certainly kill vegetation as well as animals. Most of the controlled experiments have focused on the moderate increases in $CO_2$ concentrations that are expected to occur due to atmospheric buildup of $CO_2$ from the continued use of fossil fuels or that stimulate plant productivity in greenhouses. The studies have shown that moderate increases in $CO_2$ concentrations stimulate plant growth, while decreasing the loss of water through transpiration. At the other end of the scale, 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. Little information is available in the intermediate range of 2 to 30%. In addition, information on the tolerance of aquatic ecosystems to short-term, catastrophic releases was not found during this literature search and may need to be researched.

Carbon dioxide is used in a wide variety of industries: from chemical manufacture to beverage carbonation and brewing, from enhanced oil recovery to refrigeration, and from fire suppression to inert-atmosphere food preservation. Sources of $CO_2$ include natural reservoirs, separation from crude oil and natural gas, and as a waste product of industrial processes (chemical manufacture), combustion processes (energy production), and biological respiration (brewing). Because of its extensive use and production, the hazards of $CO_2$ are well known and routinely managed. Engineering and procedural controls are well established for dealing with the hazards of compressed and cryogenic $CO_2$. Nevertheless, the hazards of $CO_2$ are significant as fatalities from fire-suppression-system malfunctions and confined-space accidents attest.

Carbon dioxide is regulated by Federal and State authorities for many different purposes, including occupational safety and health, ventilation and indoor air quality, confined-space hazard and fire suppression, as a respiratory gas and food additive, for animal anethesia and the humane slaughter of livestock, transportation and most recently, as a greenhouse gas (UNFCCC). Federal occupational safety and health regulations set three limits:

- 0.5% or 5,000 ppm for an average 8-hour day or 40-hour week.
- 3% or 30,000 ppm for an average short-term 15-minute exposure limit.
- 4% or 40,000 ppm for the maximum instantaneous exposure limit above which is considered immediately dangerous to life and health.

Most industrial and safety regulations for $CO_2$ focus on engineering controls and specifications for transportation, storage containers, and pipelines.

Monitoring is a routine part of industrial use and production of $CO_2$. Both real-time monitors and air sampling are used to ensure that levels remain within the regulatory guidelines. In addition, $CO_2$ concentrations are routinely measured and used as a proxy for air quality in buildings. Virtually all real-time monitoring devices are based on infrared absorbance at 4.26 μm. Many instruments of this type are commercially available.

Ecosystem measurements of $CO_2$ and $CO_2$ fluxes have also been made using a combination of ground-based and airborne real-time monitoring and sampling. Most flux measurements are made using eddy-flux towers that combine meteorological parameters and $CO_2$ concentration measurements. Soil gas measurements of $CO_2$ concentrations have also be made as part of a number of research programs. The

LI-COR monitor, again based on infrared absorbance of $CO_2$ at 4.26 μm, is most commonly used. For larger scale measurements that integrate over a longer path length, LIDAR, DIAL, long-path infrared, and the detection of vegetative stress are being investigated as remote-sensing techniques. We anticipate that remote sensing of all but very large $CO_2$ leaks from geologic formations will be difficult because $CO_2$ is a significant component of the atmosphere and varies naturally in space and time. Nevertheless, this is an important area of research that will help to ensure the safety of geologic $CO_2$ storage.

In addition to understanding when and how $CO_2$ is regulated for industrial and occupational settings, it is also important to know that $CO_2$ is not regulated, studied, or suspected as a toxic substance by the following federal agencies or regulations, including: Clean Air Act 1970, 1990, Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) 1972, Resource Conservation and Recovery Act (RCRA) 1976, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) 1980, Superfund Amendments and Reauthorization Act (SARA) 1986, National Toxicology Program, Agency for Toxic Substances and Disease Registry or the National Institute of Occupational Safety and Health within the Center for Disease Control and Prevention, National Institute of Environmental Health Science in the National Institutes of Health, and the National Center for Toxicological Research (NTCR) in the FDA. Only the inventory list for the Toxic Substances Control Act (TSCA) of 1976, the NIOSH confined space hazard classification system, and FEMA’s hazardous materials guide treat $CO_2$ as a hazardous substance to the extent that any concentrated or pressurized gas poses a danger.

In conclusion, the key poorly understood health, safety and environmental concerns surrounding geologic sequestration of $CO_2$ relate to the potential for unanticipated leakage. Such releases could be associated with surface facilities, injection wells, or natural, geological “containers” and may be small-scale diffuse leaks or large catastrophic incidents. Long industrial experience with $CO_2$ and gases in general shows that the risks from industrial sequestration facilities are manageable using standard engineering controls and procedures. Serious 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. On the other hand, our understanding of and ability to predict $CO_2$ releases and their characteristics in any given geologic and geographic setting is far more challenging. Certainly there are many sites, such as oil and gas reservoirs where the probability of leakage is very low. However, brine formations, which generally are not well characterized and do not have caprocks or seals that have stood the test of time, will require significant effort to evaluate potential risks, and these risks must be taken seriously.

To date, the majority of the thought process regarding the risks of $CO_2$ geologic storage has revolved around human health risks. This study raises the issue that, if leakage occurs, ecosystem risks may also be significant, particularly for soil-dwelling or ground-hugging organisms. In addition, acidification of soils in the vicinity of surface leaks may also harm plants. Similarly, persistent low-level leakage could affect aquatic ecosystems by lowering the pH, especially in stagnant or stably stratified waters.

# CHAPTER 3. NATURAL ANALOGUES FOR UNDERGROUND $CO_2$ STORAGE: HEALTH, SAFETY AND ENVIRONMENTAL LESSONS LEARNED

## 3.1. Introduction

Having reviewed the human health and environmental impacts of carbon dioxide ($CO_2$) and its industrial sources and uses, we now turn to natural occurrences of $CO_2$ as analogues and precedents to inform the development of risk-assessment procedures for the underground storage of $CO_2$. For geologic sequestration, there are three types of potential reservoirs: abandoned and producing oil and gas reservoirs, deep brine-filled formations, and unminable coal seams. All of these reservoirs or deposits occur in sedimentary settings of one type or another. Natural analogues exist for both structural containment and surface releases, and a number of articles addressing risk assessment and natural analogues have been published (IEAGHG, 1994; Pearce et al., 1996; Holloway, 1997; Koide et al., 1997; Lindeberg, 1997; Johston et al., 1999; Allis et al., 2001; Baines and Worden, 2001; Stevens et al., 2001). Sequestering $CO_2$ in coal seams is studied under the rubric of the technological feasibility of enhanced coalbed methane recovery (ECBMR) and will not be specifically treated further. No direct natural analogues for sequestration in coal are known, but two ECBMR pilot projects currently underway in the San Juan Basin of New Mexico may provide information related to HSE risk assessment, if they are monitored with the goal of addressing these issues.

Natural analogues can be important sources of information about two aspects related to health, safety and environmental risk assessment. First, they provide evidence for the feasibility of geologic containment over the long-term. Second, looking at surface releases elucidates potential consequences, hazards, and worst-case scenarios in the event that leakage occurs.

The fundamental concept behind geologic sequestration is the use of natural materials as pressure vessels for the containment of supercritical or gaseous $CO_2$. This raises a series of questions. First, will the gas be contained or not? To answer this, we must know the physical properties of the caprock or geologic barrier. We must also know the physical and geochemical processes that will take place in the reservoir and in interaction with the seal, and we must know where the $CO_2$ would migrate as long as it stays below the seal. Second, if the storage structure leaks, how much will it leak and on what time scale, where would the $CO_2$ go, and how and when would it manifest at the surface? Finally, what is the likelihood of a catastrophic failure, event, or surface release? Catastrophic failures of natural containment systems are considered unlikely because of the broad distribution of diffuse $CO_2$ degassing and subsurface $CO_2$ reservoirs and the relative scarcity of analogous disasters, but this risk has not been quantified yet.

We will set the context of this analysis within the global carbon cycle, the origins of subsurface $CO_2$, and volcanic hazards, then look at all possible abiotic natural manifestations of $CO_2$, which include diffuse hydrothermal degassing, volcanic eruptions, and focused venting from fissures. Understanding the sources of surface manifestations of $CO_2$ is not always straightforward, but knowing the distinctive isotope and trace-element characteristics of sources and emissions allows us to address this problem. The vast majority of high $CO_2$ concentrations in nature are related to volcanism, tectonic activity, and magmatic degassing. All natural disasters involving $CO_2$ have been correlated similarly.

Carbon dioxide only poses a hazard under specific conditions of release, surface topography, and weather. Recent media attention to the 1986 Lake Nyos disaster has piqued public concern about the risks associated with $CO_2$ (Brown, 2000; Holloway, 2000, 2001; Pickrell, 2001), so all five recent $CO_2$ related natural disasters (Dieng in Java, Indonesia, Lakes Nyos and Monoun in Cameroon, Mammoth Mountain in California, and Rabaul in Papua New Guinea) will be discussed. Known natural subsurface $CO_2$ reservoirs are examples of successful containment over geologic time and suggest a continuum of processes relating to the geodynamic cycling of carbon (Barnes et al., 1984a, 1984b; Chivas et al., 1987; Berner and Lasaga, 1989; Giggenbach et al., 1990, 1991; Sorey et al., 1998, 1999). We will look at geologic containers within the context of their formation processes, and finally, we will assess the relevance of various surface manifestations of $CO_2$ to the risks of geologic carbon sequestration.

## 3.2. The Global Carbon Cycle, Origins of Subsurface $CO_2$, and Volcanic Hazards

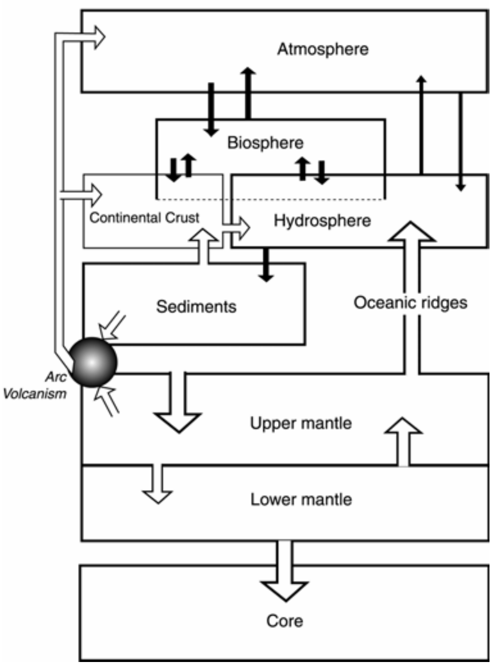
### *3.2.1. Global Carbon Cycle*

The global carbon cycle involves processes that take place over a broad hierarchy of scales of space and time (Walker, 1993; Sarmiento and Wofsy, 1999). Human impacts on climate affect daily, yearly, and millennia scale processes, many of which are biologically mediated. In Chapter 2, Figure 2.1 shows the global biogeochemical carbon cycle as we conceive of it in the context of climate change with its focus on daily to millennia scale processes involving the oceans, atmosphere, and biosphere, collectively referred to as the exosphere. Figure 3.1 shows the global geochemical carbon cycle or geodynamic carbon cycle, which is composed of reservoirs with residence times measured in millions of years. The geodynamic carbon cycle focuses on the fluxes between the solid earth and the exosphere as a whole. There are many links between the two cycles, as together they comprise the entire global carbon cycle, but they can be separated for ease of analysis.

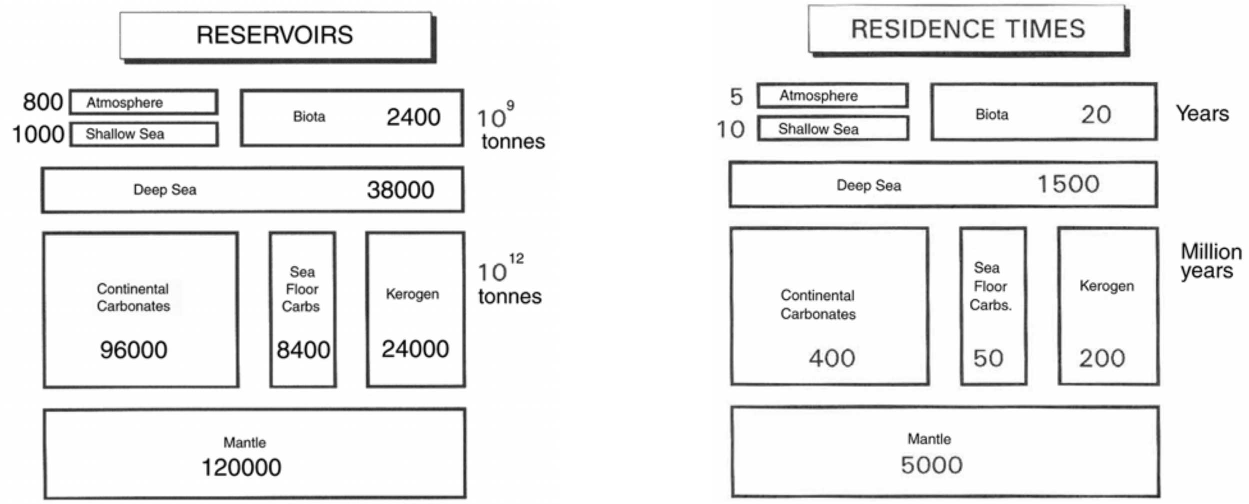
One of the more enlightening comparisons is that the annual biotic cycling of net primary productivity (NPP) and respiration at 60,000 million metric tonnes carbon (MMTC)/yr and annual anthropogenic emissions of 7,100 million metric tonnes carbon equivalents (MMTCE)/yr (as defined by IPCC, 1996a; US DOE, 1999; US EPA, 2000) dwarf the abiotic cycle estimated at 70-130 MMTCE/yr (See Table 3.1) (Berner and Lasaga, 1989; Gerlach, 1992; Brantley and Koepenick, 1995; IPCC, 1996a; Marty and Tostikhin, 1998; Sarmiento and Wofsy, 1999; US DOE, 1999). Although the geodynamic cycle is significantly smaller than even the annual variability in NPP, abiotic, geodynamic, volcanic sources of $CO_2$ are responsible for the vast majority of natural hazardous concentrations. The correlations among tectonic zones, seismic activity, volcanism, and high $CO_2$ discharge (>90% $CO_2$ gas by volume or >1g/L $HCO_3^-$ but excluding formation waters from oil and gas fields) are well established (Irwin and Barnes, 1980; Barnes et al., 1984a; 1984b; SI, 2001). Figure 3.2 shows the worldwide correlation among volcanic, tectonic, and seismic activity, and Figure 3.3 shows the worldwide distribution of high $CO_2$ springs. Figure 3.4 depicts the distribution of high $CO_2$ springs in the U.S.

Our conceptual understanding of the geodynamic carbon cycle is robust, but specific mass flux estimates are not well constrained. In particular, $CO_2$ emissions from volcanoes, magmatic and mantle degassing, metamorphic decarbonation, and diffuse hydrothermal emissions are poorly known. However, some flux estimates have been measured or calculated for active erupting volcanic $CO_2$, passive release from subaerial volcanism, submarine seafloor spreading centers, back-arc basins, hot spots, and diffuse hydrothermal fluxes in high heat flow regions (Harris et al., 1980; Berner, 1990; Casadevall et al., 1990; Gerlach, 1991a, 1992; Williams et al., 1992; Giggenback et al., 1993; Nojiri et al., 1993; McGee and Casadevall, 1994; Brantley and Koepenick, 1995; Chiodini et al., 1995, 1999; Dando et al., 1995; Farrar et al., 1995; Kerrick et al., 1995; Webster, 1995; Aeschbach-Hertig et al., 1996; Sano and Williams, 1996; Seward and Kerrick, 1996; Allard, 1997; D'Allessandro et al., 1997; Fischer et al., 1998; Gerlach et al., 1998; Kerrick and Caldeira, 1998; Marty and Tolstikhin, 1998; Sorey et al., 1998, 1999; Cruz et al., 1999; Favara et al., 2001). Table 3.1 provides a compilation of representative fluxes. Emissions from nonvolcanic mid-plate geothermal sources remain unknown to within a factor of 10. All abiotic $CO_2$ fluxes come from magmatic sources, metamorphic decarbonation, or calcite dissolution. Volcanic sources are thought to be 130–230 $MMTCO_2$ per year (35–63 MMTC/yr) (Gerlach, 1992; Williams et al., 1992; Brantley and Koepenick, 1995; Marty and Tostikhin, 1998) and the total Earth degassing estimate is 260–

480 MMTCO$_2$ (70-130 MMTCE) (Berner and Lasaga, 1989; Gerlach, 1991a, 1992; Brantley and Koepenick, 1995; Marty and Tostikhin, 1998).



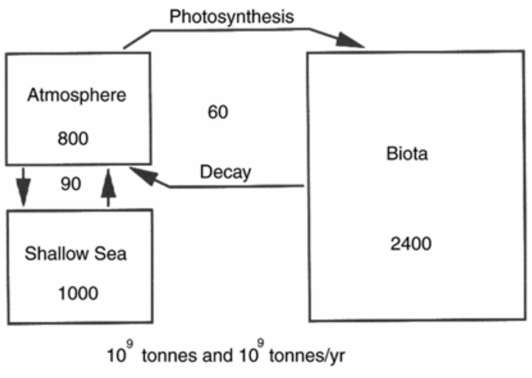
**a) Overview of global carbon cycle reservoirs and interactions including geochemical components (Javoy et al., 1982).**



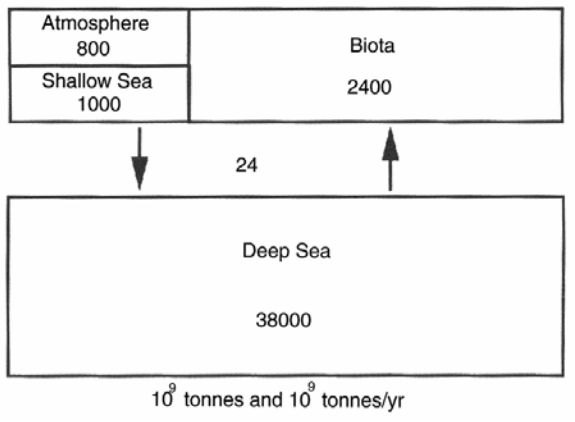
**b.) Carbon reservoirs in metric tonnes of carbon (Walker, 1993).**

**c) Residence time for carbon reservoirs (Walker, 1993).**

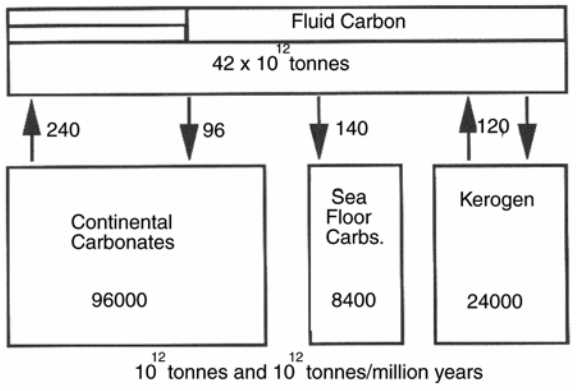
**Figure 3.1. Schematics of the global carbon cycle.**



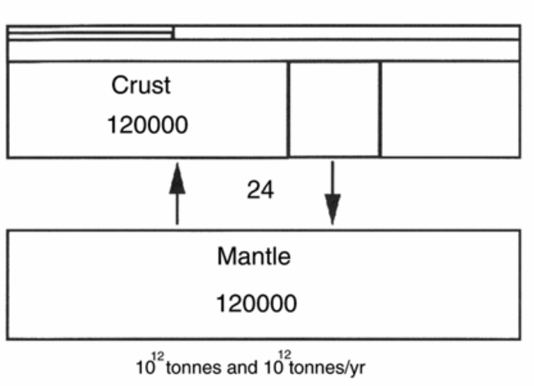
**d) Fluxes among surface reservoirs of carbon (Walker, 1993).**



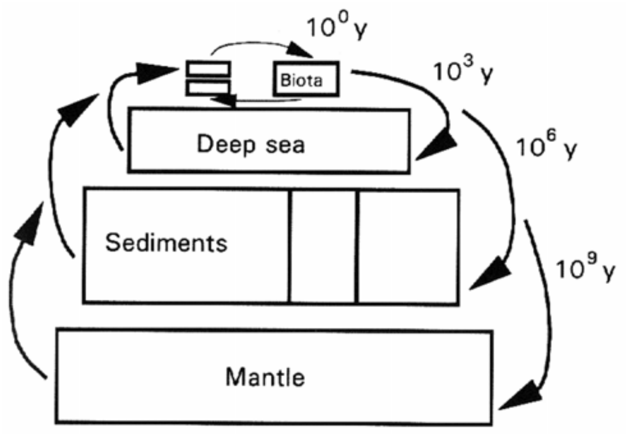
**e) Fluxes within the exosphere between surface reservoirs and the deep sea (Walker, 1993).**



**f) Fluxes between the exosphere and crustal carbon reservoirs (Walker, 1993).**



**g) Fluxes between the crust and mantle (Walker, 1993).**



**h) Hierarchy of time scales (Walker, 1993).**

**Figure 3.1 (cont.)**

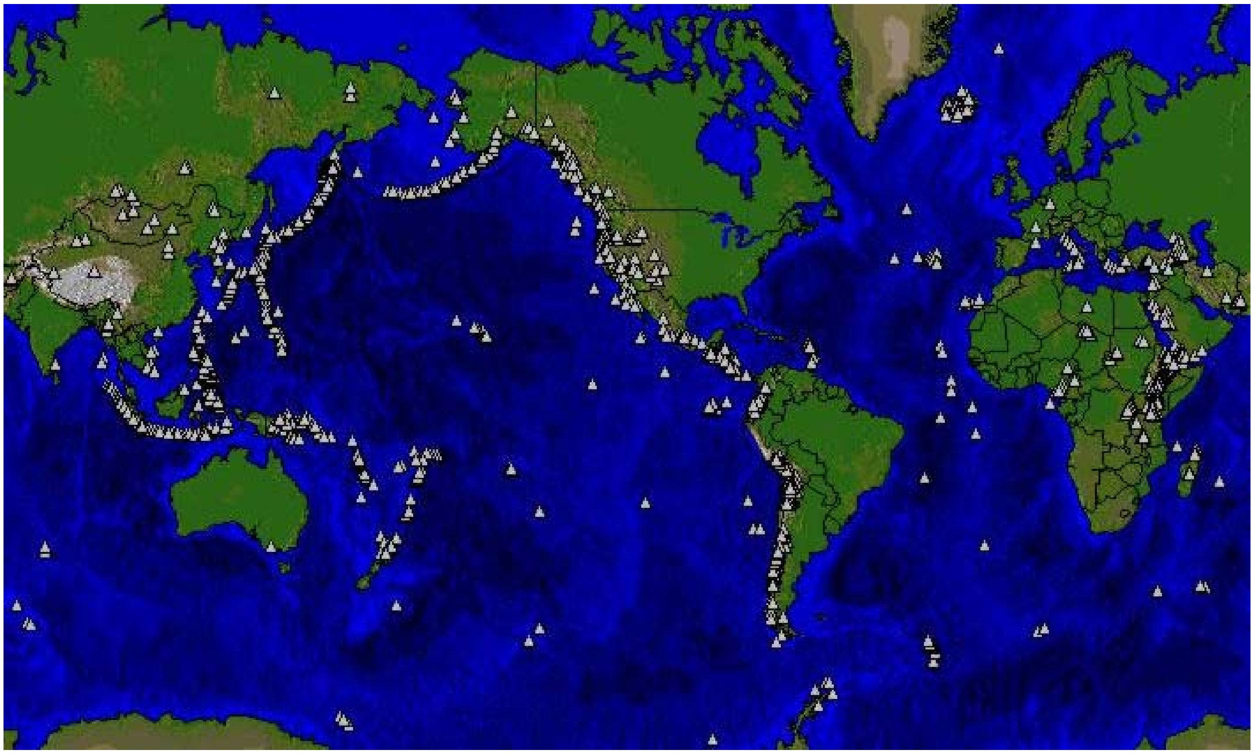


**Figure 3.2. Worldwide distribution of volcanism, tectonics, and seismicity (SI, 2001).**

For further information on the carbon cycle and climate change science, refer to the IPCC Climate Change Science report 2001, published by Cambridge University Press. Other references for carbon cycle assessments, syntheses, and programs include Javoy et al. (1982), Berner et al. (1983), Trabalka (1985), Marty and Jambon (1987), Berner and Lasaga (1989), Heimann (1993), Oremland (1993), IPPC (1996a), Franck et al. (1999), Sarmiento and Wofsy (1999), Wigley and Schimel (2000), CDIAC (2001a), and NOAA (2001a). Some references specific to the geochemical carbon cycle are: Berner (1991, 1994), Godderis and Francois (1995), Francois and Godderis (1998), Tajika (1998), Ludwig et al. (1999), and the papers cited for degassing and flux estimates in Table 3.1. For examples of discussions of paleoclimates and the historical role of atmospheric $CO_2$ in climate, refer to: Sundquist and Broeker (1985), Cerling (1991), Mora et al. (1991), Andrews et al. (1995), Godderis and Francois (1995), Nesbitt et al. (1995), IPCC (1996a), Francois and Godderis (1998), Barnes (1999), Beerling (2000), Oeschger (2000), Ozima and Igarashi (2000), Starkel (2000), Crowley and Berner (2001), NOAA (2001c).

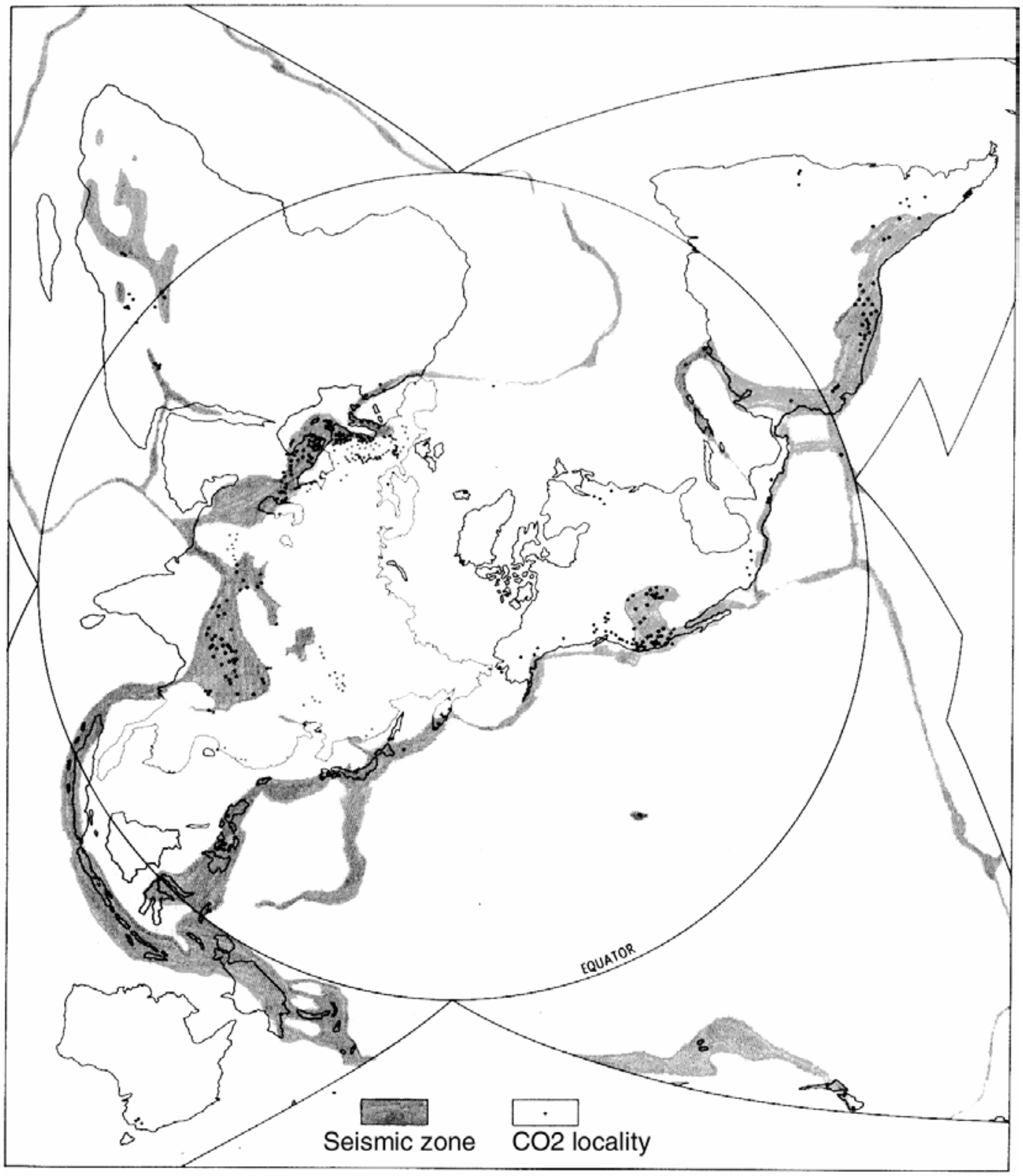


**Figure 3.3. Worldwide correlation of high $CO_2$ discharge springs and areas of seismicity (modified from Irwin and Barnes, 1980).**

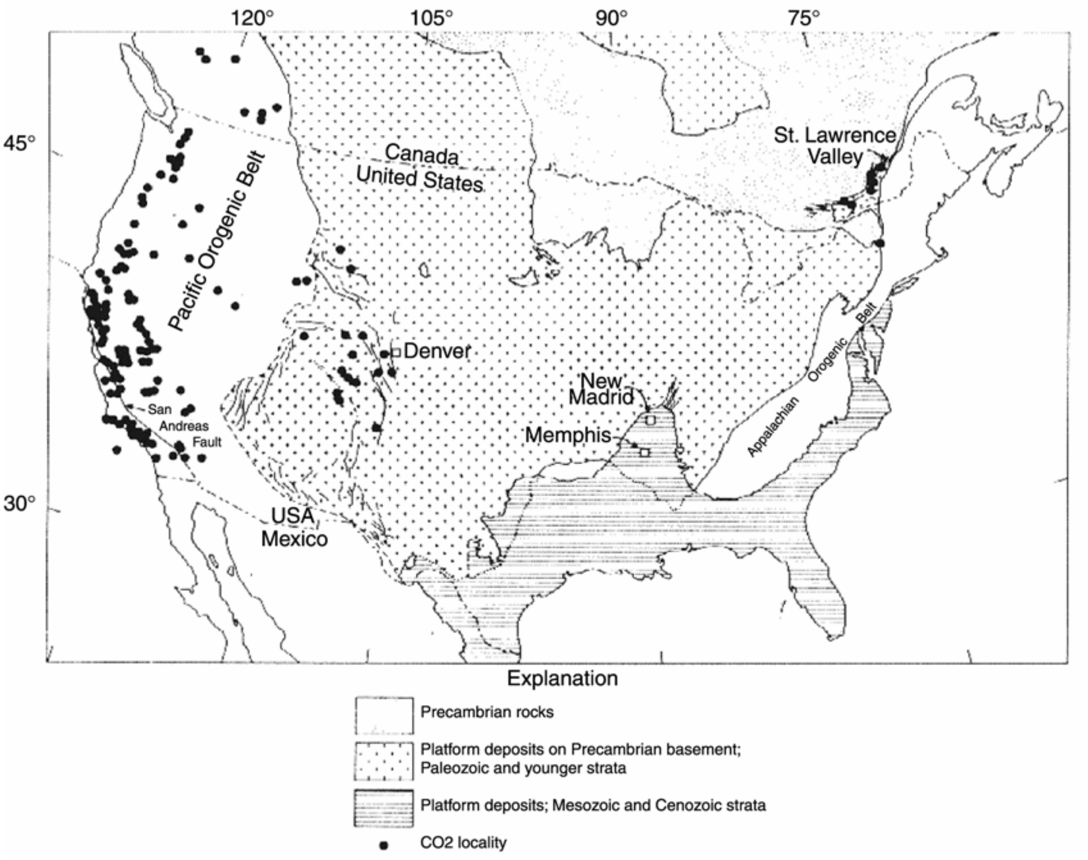


**Figure 3.4. Distribution of high $CO_2$ discharge springs in the United States (Irwin and Barnes, 1980).**

**Table 3.1. Average annual flux rates of $CO_2$ for various volcanic and hydrothermal processes and events.**

| Volcano, Process or Area | Periods Observed | Rate in MMT $CO_2$/yr | Reference | Notes |
|---|---|---|---|---|
| Estimated total global volcanic and magmatic degassing | | 260-480 | Berner et al. (1983), Berner (1990), Brantley and Koepenick (1995), Marty and Tolstikhin (1998) | |
| Estimated total global volcanic degassing | | 130-170 | Berner and Lasaga (1989), Gerlach (1992), Brantley and Koepenick (1995) | |
| Plumes | | 132 | Marty and Tolstikhin (1998) | +/- factor of 2<br>(66-264 MMT $CO_2$) |

**Table 3.1 continued**

| | | | | |
|---|---|---|---|---|
| Convergent margins/ island arcs/ subduction zones | | 110 | Marty and Tolstikhin (1998) | +/- factor of 2; mostly exogenic, recycled carbonate |
| Mid-ocean ridges | | 98 | Marty and Tolstikhin (1998) | +/- factor of 2 |
| Global Hydrothermal | | 44 | Kerrick et al. (1995) | Hydrothermal |
| Mount Pinatubo, Philippines | 6/1991 | 42* | Gerlach et al. (1996) | * Amount emitted in single eruptive event |
| Nonerupting volcanoes | | 34 | Williams et al. (1992) | |
| Noncontinuously erupting volcanoes | | 23 | Williams et al. (1992) | |
| Mount Etna, Italy | 9/1984, 6/1985 | 13/23 | Allard et al. (1991) | Summit crater only/ total incl. diffuse emissions from volc. pile |
| Continuously erupting volcanoes | | 7.8 | Williams et al. (1992) | |
| Total hydrothermal flux in central Italy | | 5.7 | Derived from Chiodini et al. (1999) | [(9×$10^6$ mol/km$^2$/yr×14000 km$^2$) + (4×$10^5$mol/km$^2$/yr× 7500km$^2$)]×[4.4x$10^{-5}$ tonnes/mol] |
| Oldoinyo Lengai, Tanzania | 6/1994 | 2.6 | Brantley and Koepenick (1995) | During quiescent phase |
| Augustine, AK | 4/1986 | 2.2 | Symonds et al. (1992) | During explosive event |
| Mount St. Helens, WA | 7/1980-9/1981 | 1.8 | Harris et al. (1981), McGee and Casadevall (1994) | During eruptive phase |
| Kilauea, HI | 12/1983 | 1.4 | Greenland et al. (1985) | During noneruptive phase, from summit plume |
| White Island, NZ | 11/1983 | 1.3 | Rose et al. (1986) in Brantley and Koepenick (1995) | |
| Milos, Helenic Volcanic Arc | 3,6/1992 | 0.75-3.7 | Dando et al. (1995) | Submarine hydrothermal |
| Redoubt, AK | 6/1990 | 0.66 | Casadevall et al. (1990) | |
| Mammoth Mountain, CA | 1989-1995 | 0.13-0.44 | Farrar et al. (1995), Sorey et al. (1999) | Diffuse emissions following deep seismic activity |
| Pantelleria Island, Italy | 9/1998 | 0.39 | Favara et al. (1998) | Diffuse emissions during quiescent phase |
| Taupo Volcanic Zone, NZ | | 0.35 | Kerrick et al. (1995), Seward and Kerrick (1996) | Hydrothermal |
| Grimsvotn, Iceland | 3/1992 | 0.13 | Brantley et al. (1993) | |

**Table 3.1 continued**

| | | | | |
|---|---|---|---|---|
| Vulcano Island, Italy | 9/84,<br>9-10/1988 | 0.066/ 0.077 | Baubron (1990) | Summit crater only/ total including diffuse emissions from volcanic pile |
| Salton Trough, CA | | 0.044 | Kerrick et al. (1995) | Hydrothermal |
| Kudryavy, Russia | | 0.019 | Fischer et al. (1998) | |
| Lake Nyos, Cameroon | | 0.010 | Evans et al. (1993) | Geothermal recharge into lake bottom |
| Furnas Volcano, Sao Miguel, Azores | 5/1991-7/1994 | 0.0094 | Cruz et al. (1999) | Diffuse geothermal emissions from inactive volcano |
| Laacher See, Germany | 5-9/1991 | 0.0048 | Aeschbach-Hertig et al. (1996) | Maar field above mantle plume |

### *3.2.2. The Origins of Subsurface $CO_2$*

Most of the $CO_2$ emitted to the atmosphere from bulk earth degassing is derived from volcanic and magmatic sources, but there are other sources relevant to understanding how and why natural manifestations of $CO_2$ pose a danger and how $CO_2$ accumulations form. Volcanic, geothermal, carbon cycle, and oil industry research are primarily responsible for our current understanding of $CO_2$ sources. Carbon stable isotope composition and the relative abundance of noble gases allow us to distinguish among source reservoirs and processes. Noble gases are chemically inert, so their abundances typically reflect their original source composition. The carbon isotopic composition ($\delta^{13}C$) of the upper mantle varies from -2 to -10 per mil (per mil = difference in parts per thousand versus a standard, percent = difference in parts per hundred). Carbonate is usually around 0 ± 2 per mil, and biogenic carbon is -15 to -40 per mil. $^3He$ in the mantle is significantly enriched over atmospheric levels, and radiogenic decay in the crust produces $^4He$. The $^3He/^4He$ isotopic ratios of mantle and crustal sources versus atmospheric composition, R/Ra, are distinctive at 8 and 0.02 respectively. As a result, $^3He$ is a direct indicator of a mantle component. The use of C/He isotope systematics to trace and calculate multicomponent mixing in $CO_2$ reservoirs and emanations is widespread and thoroughly documented, even though the correlation does not prove that the carbon and noble gases in a given reservoir were co-genetic (Marty and Jambon, 1987; Sorey et al.,1993, 1998, 1999; Trull et al., 1993; Rose et al., 1996; Sherwood-Lollar et al., 1997; Kaneoka, 1998; Nishio et al., 1998; USGS, 1999a; Ballentine et al., 2000; Battani et al., 2000; Hulston et al., 2001).

Some confusion results from variable components of magma. Magma can have significant fractions of crustal material, either carbonate or organic carbon from buried sediments. The origins of magma in subduction zones, back arc basins, and hot spots are more complex than at mid-ocean spreading centers, where an exclusive mantle source is assumed (Giggenbach et al., 1993; Kerrick and Caldeira, 1998; Marty and Jambon, 1987; Marty and Tostikhin, 1998; Minissale et al., 1997; Moreira and Sarda, 2000; Nishio et al., 1998; Sano and Marty, 1995; Sano and Williams, 1996; Trull et al., 1993).

Carbon dioxide emanations from springs and subsurface reservoirs have sources even more diverse than magma, especially in sedimentary basins. Possible sources include volcanic and magmatic degassing, metamorphic decarbonation, diagenesis, and the decomposition of organic carbon in buried sediments. A representative box model system for mixing is shown in Figure 3.5. Carbon dioxide is often a significant component in hydrocarbon reservoirs, but it rarely exceeds 10% by volume outside of tectonically and often volcanically active, highly faulted areas. At low-levels, the $CO_2$ can usually be traced to organic sources, but when $CO_2$ content is between 10% and 25%, a combination of sources is most likely.

Hydrocarbon production and maturity, and metamorphism are correlated with tectonic activity via high geothermal gradients. When $CO_2$ exceeds 25% by volume in hydrocarbon reservoirs, isotopic analysis typically shows a significant mantle component (Pankina et al., 1978; Rigby and Smith, 1981; Clayton et al., 1990; Giggenbach et al., 1990, 1993; Cappa and Rice, 1995; Dai et al., 1995; Giggenbach, 1995; Xu et al., 1995, 1997; Hao et al., 1996; Wycherley et al., 1999; Ballentine et al., 2000).

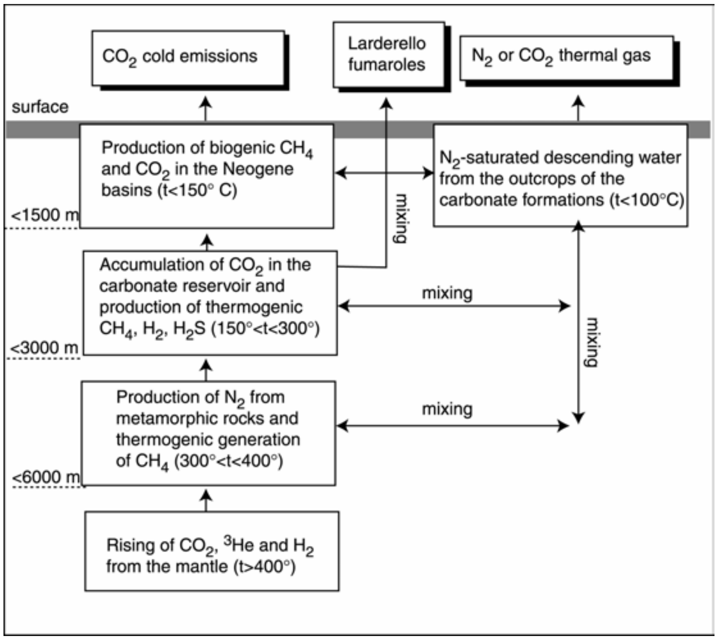


**Figure 3.5. Block diagram of mixing processes among diverse sources of hydrothermal gases (Minissale et al., 1997).**

For further discussion of noble gas and isotope systematics as mantle tracers refer to: Dunai and Baur (1995), Xu et al. (1995), Ballentine et al. (1996), Ballentine (1997), Kambio et al. (1998), Kaneoka (1998), Osenbruch et al. (1998), Pedroni et al. (1999), Moreira and Sarda (2000), and Ozima and Igarashi (2000).

### *3.2.3. Volcanic Hazards*

As mentioned above, the occurrence of $CO_2$ in nature is strongly correlated with tectonic activity and volcanism. Most $CO_2$ comes from volcanoes and mantle degassing, but when assessing volcanic gas hazards, $CO_2$ is generally ignored. Other major volcanic gases are $H_2O$, $H_2S$, $H_2$, CO, HCl, and HF. Water and $CO_2$ are generally considered benign, aside from the role they play in the eruptive process and heat transfer, but the sulfur compounds and halogens are highly reactive and toxic. Yet even the toxic gases play a small role in overall volcanic hazards. Famine and tsunamis cause most of the deaths and suffering from volcanic disasters, followed by pyroclastic flows, mud and debris flows, falling debris, hot ash, and other physical as opposed to chemical causes (Baxter, 1990; Simkin and Siebert, 1994; Bacon et al., 1997; Myers et al., 1997; Sherrod et al., 1997; USGS, 1997, 2000a, 2001e). However, ignoring $CO_2$ may be misguided because sudden deaths caused by $CO_2$ in volcanic areas appear to be common. The record of these hazards has been poorly documented to date, though it appears to be common knowledge among those who live close to volcanoes. Many caves in Italy, Indonesia, Germany, and other volcanic areas are called 'dog's caves' because small animals are often killed in them by $CO_2$. Visible mists of mostly $CO_2$ gas are occasionally seen flowing down hillsides as described at Vulcano and Etna in Italy,

**Table 3.2. Compilation of some known natural disasters (possibly) caused by $CO_2$. This list is representative only, not comprehensive (Simkin and Siebert, 1994; SI, 2001).**

| Date | Location | Event | Fatalities/Consequences |
|---|---|---|---|
| 1989-present | Mammoth Mtn, CA | Diffuse $CO_2$ emissions | 1 person, 100 to 170+ acres of tree-kill area[1] |
| 1990 | Tavurvur, Rabaul, Papua New Guinea | $CO_2$ release from volcanic vent | 6 people |
| 1980-1989 | Vulcano Island, Italy | Accumulation of diffuse $CO_2$ emissions | 2 children and many animals including rabbits and goats[2] |
| 1988 | Dieng, Java, Indonesia | Pulse of $CO_2$ from geothermal well | 4 workers died[2] |
| 1986 | Lake Nyos, Cameroon | Limnic eruption of $CO_2$ | 1746 people, 3000+ cattle, and many other animals[3] |
| 1984 | Lake Monoun, Cameroon | Limnic eruption of $CO_2$ | 37 people[4] |
| 1979 | Dieng, Java, Indonesia | $CO_2$ released from vent during phreatic/ pneumatic eruption | 149 people, some livestock, and many fish[2] |
| 1973 | Vestmannaeyjar (Heimaey), Iceland | $CO_2$ from eruption accumulated in basement | 1 person |
| 1955 | Carran Maar, Los Carran Venados, Chile | Gas release—probably $CO_2$ | 2 people |
| 1923 | Tangkubanparahu, Java, Indonesia | Venting volcanic gas during non-eruptive phase, $CO_2$ and $H_2S$ | 3 boys |
| 1903 | Karthala, Indian Ocean | Venting volcanic gas of unknown composition | 17 people |
| 1902 | Santa Maria, Guatemala | Large eruption included volcanic gas of unknown composition | 1500 people killed in eruption, 350 in one village from deadly fumes |
| 1873 | Vesuvius | Venting volcanic gas of unknown composition | 7 people |
| 1872 | Vesuvius | Venting volcanic $CO_2$ | Unknown number |
| 1794 | Vesuvius | Large eruption | 400 people killed in eruption, several from $CO_2$. |
| 1677 | La Palma, Canary Islands | Venting volcanic gas of unknown composition | 1 person and many animals |
| 1.3-2.3 Mya | Seneze Maar, France | $CO_2$ releases in or near a maar lake | Many animals of all types[5] |

[1] Farrar et al., 1995; Sorey et al., 1998; Hunt, 2000.

[2] Le Guern et al., 1982; Allard et al., 1989; Baubron et al., 1990.

[3] Freeth and Kay, 1987; Kling et al., 1987; Baxter and Kapila, 1989; Holloway, 2000; SI, 2001.

[4] Sigurdsson et al., 1987; SI, 2001.

[5] Couthures, 1989.

Lake Nyos in Cameroon, Kituro of Nyamuragira in eastern Africa, and Tangkuban Prahu Volcano near Bandung, Java, Indonesia. These mists are locally known to kill children and animals periodically (Le Guern et al., 1982; Allard et al., 1989; Stupfel and Le Guern, 1989; Baubron et al., 1990; Simkin and Siebert, 1994; Baxter et al., 1999; USGS, 2000a, 2001e). Table 3.2 summarizes the major recorded consequences and fatalities from volcanic disasters ascribed to $CO_2$. In light of these hazards and the broader context described previously, we next consider natural manifestations of $CO_2$.

## 3.3. Natural Manifestations of Carbon Dioxide: Surface-Release Analogues

The Earth is enveloped in an atmosphere containing 0.04% $CO_2$. Our cells are steeped in a medium containing 5-6% $CO_2$ by weight, and we exhale 3.5% $CO_2$ with every breath. Every living thing respires $CO_2$ into the atmosphere as its primary metabolic waste product. Primary producers such as plants take up and fix atmospheric $CO_2$ into the organic compounds that animals and plants use for food and reconvert to $CO_2$. There is a constant flux of $CO_2$ from any ground covered by organic matter due to the break down of detrital material and respiration by bacteria, fungi, and other decomposers; and $CO_2$ is routinely off-gassed from water that passes through the root zone in soils. Surface emanations of groundwater usually contain some $CO_2$ from dissolved carbonate, decomposing organic matter in buried sediments, and soil or root zone respiration. Only in specific areas with regional metamorphism, active volcanism, or magmatic degassing do $CO_2$ fluxes become significant. However, it is this geological, volcanic subset of natural sources that elucidates the potential hazards of $CO_2$ surface releases. As shown in Figures 3.6a and 3.6b, volcanic manifestations include a variety of types of eruptions, vents and fissures, and diffuse hydrothermal degassing. The five recent major natural disasters caused by $CO_2$ are the only ones well documented and will be discussed according to the type of manifestation.

### *3.3.1. Volcanic Eruptions*

Normal Continuous. Carbon dioxide plays a variable role in volcanic eruptions, depending on the type of eruption, and poses variable hazards. Normal continuous eruptions, such as Kilauea at the Hawaiian hot spot, emit significant quantities of $CO_2$ (1.4 $MMTCO_2$/yr), but the eruptive process is not primarily gas driven. In fact, the lava flowing from Kilauea is often highly depleted in $CO_2$ due to off-gassing while the magma resides in the summit reservoir. Steam plays a greater role, but continuous eruptions are generally low pressure, non-explosive events. The $CO_2$ flux is low enough, with sufficient heat and atmospheric mixing, that it poses minimal hazard. Water is the dominant gas at approximately 80%, and although the more toxic trace gases of $H_2S$ and halogens can cause acid rain and crop damage from long-term persistent venting, the only significant danger is immediately downwind of a vent before the gases have been diluted in the atmosphere. In continuous eruptions, the hazards from volcanic gases are relatively minor outside of the immediate vicinity of release (Greenland et al., 1985; USGS, 1997).

Normal Episodic. Normal episodic or catastrophic eruptions, such as Mt. St. Helens, WA in 1980 and Mt. Pinatubo, The Philippines in 1991, emit enormous amounts of $CO_2$ (1.8 and 42 $MMTCO_2$ respectively), which plays a significant role in driving the eruptions. Because so much kinetic energy is released in the explosions, the $CO_2$ is ejected high into the atmosphere where it mixes and disperses. Conventional volcanic hazards such as flows and debris are associated with catastrophic eruptions, but the volcanic gases pose relatively little immediate health threat (Harris et al., 1981; Baxter, 1990; McGee and Casadeveall, 1994; Simkin and Siebert, 1994; Gerlach et al., 1996; SI, 2001; USGS, 2001e).

Phreatic and Pneumatic. Phreatic and pneumatic eruptions are violent, explosive eruptions driven by steam or other gases. The most extreme involve diatremes erupting kimberlites that derive from deep in the upper mantle, 100–200 km below the surface. As the deep magma ascends along fractures, large amounts of $CO_2$ begin to exsolve. The separating $CO_2$-rich fluid phase forces its way along the fractures,

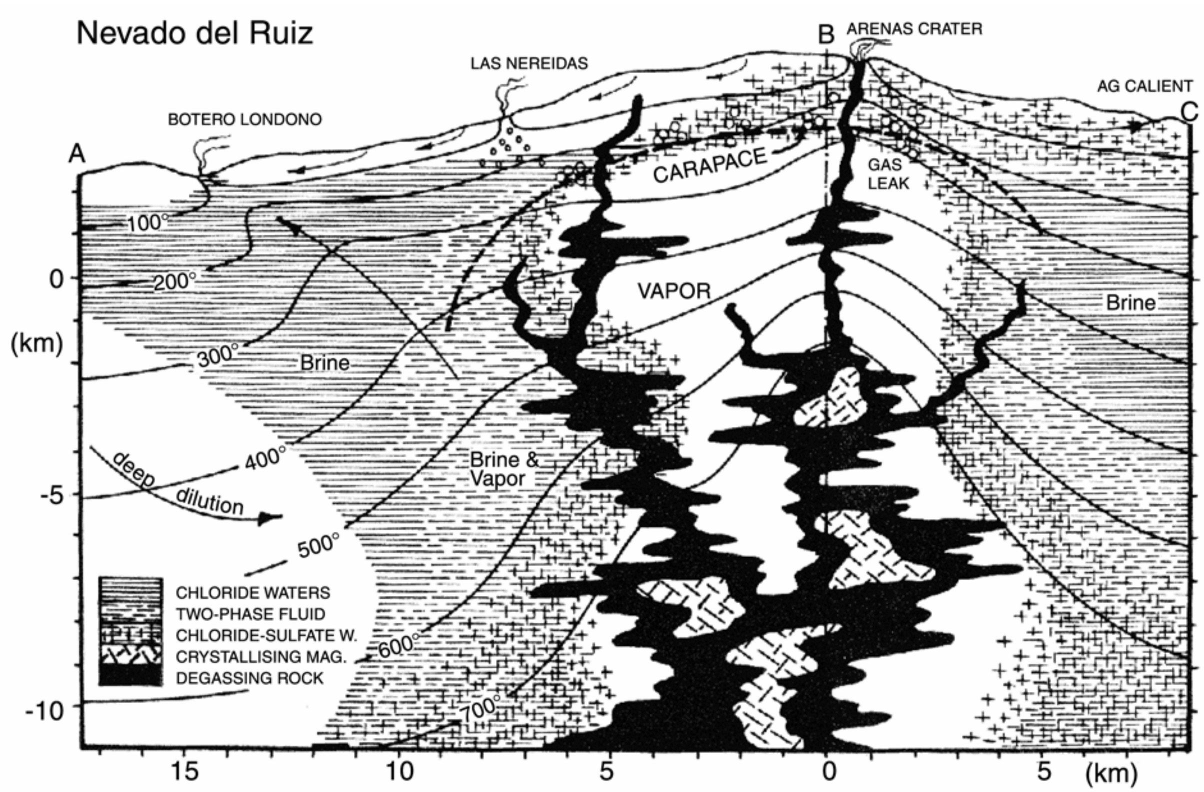


**Figure 3.6a. Tentative cross section through Nevado del Ruiz, Colombia volcanic structure showing active volcanic releases of $CO_2$. Heavy dashed line indicates likely position of chemically sealed carapace (from Giggenbach et al., 1990).**

creating a fast-path to the surface and resulting in what are thought to be spectacular catastrophic explosions. Kimberlitic magmas are typical of diatremes, which are volcanic pipes resulting from the release of explosive, gas-charged magma. Maars are the surface craters left above diatremes after the explosions and can be formed by steam or gas. In volcanic areas, when magma comes into contact with groundwaters, steam pressure builds, and the result is often an explosion at the surface. Most volcanic explosions were assumed to be steam-driven, but in recent decades accumulating evidence shows that some such explosions are pneumatic (gas-driven) as opposed to phreatic (steam-driven) (Lorenz, 1973; Chivas et al., 1987; Giggenbach et al., 1991; Neri et al., 1999; USGS, 1999b; Gevrek and Kazanci, 2000). The formation of the Ukinrek maars in Alaska in 1977 is one example of $CO_2$-driven maar formation (Barnes and McCoy, 1979; Keinle et al., 1980; Self et al., 1980). Other examples exist in the Eifel maar district of Germany, which is an area of high $CO_2$ flux above a magmatic plume (Dunai and Baur, 1995; Aeschbach-Hertig et al., 1996; Giggenbach et al., 1996; Ritter et al., 2001). The 1979 eruption at Dieng in Java, Indonesia was probably a pneumatic, largely $CO_2$-driven eruption, and Lake Nyos fills a diatreme vent (Le Guern et al., 1982; Chivas et al., 1987; Allard et al., 1989; Lockwood and Rubin, 1989; Freeth and Rex, 2000). The Lake Monoun and Lake Nyos disasters will be discussed next, under limnic eruptions, and the natural disaster that occurred at Dieng will be discussed in detail under vents and fissures.

*Limnic.* The limnic eruption is a new type of eruption that was entirely unknown before 1984. (Sigurdsson et al., 1987) Deep tropical crater lakes can become supersaturated with $CO_2$ at depth through the input of $CO_2$ to the lake bottom. The $CO_2$ presumably comes from the continual degassing magma of

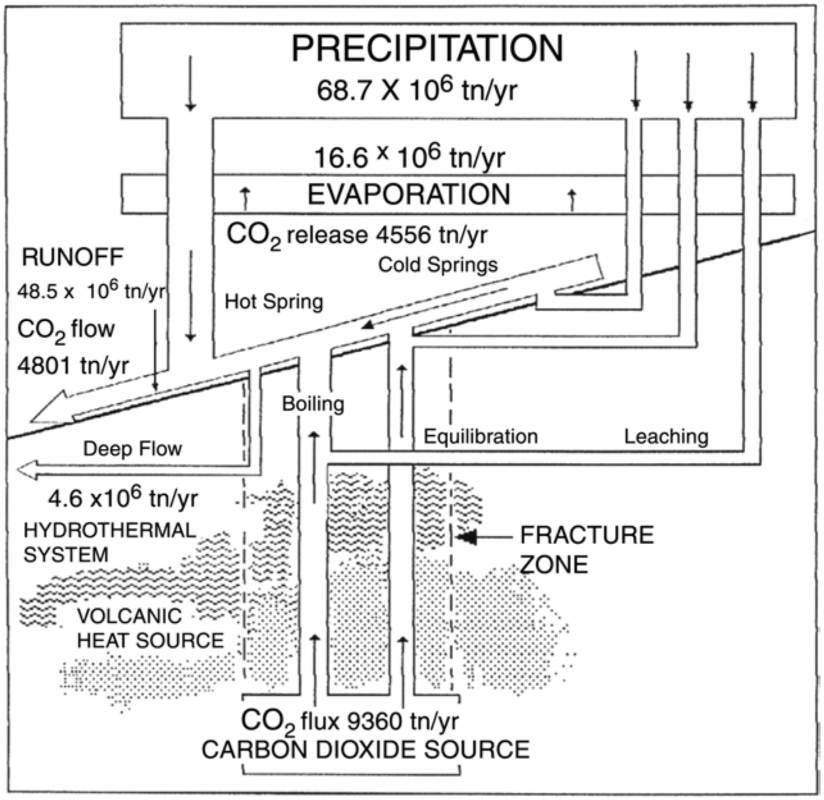


**Figure 3.6b. Passive geothermal release of $CO_2$ at Furnas volcano, Sao Miguel, Azores, including precipitation, evaporation, and groundwater flow rates and $CO_2$ flux from springs and in runoff (Cruz et al., 1997). (tn = tonne).**

the diatreme, which formed the crater in the first place. Normally such $CO_2$ would reach the surface dissolved in groundwater or geothermal fluids and off-gas harmlessly to the atmosphere. At any latitude outside of the tropics, seasonal temperature variations drive the annual turnover of all but extremely deep or large lakes. Cold surface water sinks and forces the bottom water to the surface, so any build-up of $CO_2$ would off-gas harmlessly from the lake waters. When $CO_2$ migrates into the bottom of a deep lake, it dissolves and increases the bulk density of the bottom layer. Large amounts of $CO_2$ can build up over many years because of the high hydrostatic pressure and modest temperature at depth. The result of the density relationship and lack of seasonal turnover in the tropics is a stably stratified lake. This situation remains unremarkable until there is a significant disturbance such as an earthquake, landslide, strong wind, or descending packet of cold rain-water. Alternatively, the bottom waters could reach supersaturation and $CO_2$ could spontaneously begin to bubble up (Kerr, 1987; Kling et al., 1987; Evans et al., 1994; Kusakabe et al., 2000).

Regardless of the triggering mechanism, once $CO_2$ begins its ascent, it quickly becomes a self-sustaining fountain as $CO_2$-rich water is entrained with and pulled up beneath the ascending, expanding two-phase mixture. At Nyos, described below, one liter of bottom water exsolves ten liters of gas as the pressure drops to one atmosphere. This process is similar to the rapid degassing that occurs whenever someone opens a carbonated beverage. Evidence from lab experiments, chemical reactors, LNG transport, and limnology also suggests that the process is self-perpetuating once a packet of saturated water moves vertically enough for the pressure drop to allow degassing to begin (Oskarsson, 1990; Chau et al., 1996; Zhang, 1996, 2000; McCord and Schladow, 1998; Cotel, 1999; Woods and Phillips, 1999; Kusakabe et al., 2000; Rice, 2000).

Lake Nyos. The tragic occurrence at Lake Nyos in 1986 brought this new type of natural disaster to the awareness of the scientific community and the public. Two years earlier, a similar event took place at Lake Monoun, 60 miles to the southeast, where 37 people were killed. The reconstruction of events for Nyos suggests that the degassing process lasted approximately four hours during the evening of August 21, 1986, and that most of the wave damage resulted from one or several large events. During this time, the main violent explosion(s) generated directional 20–80-meter waves and scoured all vegetation and soil from one section of the crater wall. The survivors nearby did not report hearing anything, but people farther away in Subum described hearing an explosion just before being overcome. This suggests that the degassing had been going on for hours before the large explosions that caused the physical damage and large waves. Either the cloud of $CO_2$ filled the crater despite the spillway exit or one explosive release was large and vigorous enough that some $CO_2$ spilled out over the top and killed a few people there. The only avenue of escape for the gas was the drainage system of the lake, composed of long narrow valleys that prevented dispersion. The gravity-driven mass quickly accelerated down the valley below the spillway and caused some visible damage to vegetation. Because of the physiological effects of abnormally high amounts of $CO_2$ and low amounts of $O_2$, anything enveloped in the cloud dropped unconscious, comatose, or dead almost instantly. That included insects, birds, animals, and people. The minimal effects on vegetation and the absence of acid burns and severe eye irritation proved the lack of any significant component in the gas cloud aside from $CO_2$ and some water. Many of the exposed people whether living or dead exhibited large blisters and skin loss that remain unexplained. People were killed or rendered unconscious in their sleep or as they were walking around in the late evening. There was no significant sound, smell, or visible warning, nor was there evidence of any struggle or awareness of danger. The final toll was 1,746 people, over 3000 cattle, and innumerable other animals killed up to 27 km away and 24 hours after the initial release. The cloud dispersed once it entered the broad open valley beyond the towns of Subum and To. The last people killed walked into low-lying or confined areas where $CO_2$ had collected and not yet dissipated (Baxter and Kapila, 1989; Le Guern and Sigvaldason, 1989, 1990; Stupfel and Le Guern, 1989; Faivre-Pierret et al., 1992; Freeth, 1992; Le Guern et al., 1992; Evans et al., 1994; Holloway, 2000).

Fortunately, there is good news regarding the future of such disasters. Now that we are aware of the situation, an international team of scientists is in the process of mitigating the danger by degassing the lake in a controlled manner. They are using pipes that extend down near the lake bottom to channel deep, $CO_2$-rich waters to the surface. During pilot tests in January, 2001, there was a self-sustaining soda fountain 47 m high. According to calculations, Lake Monoun and Lake Nyos could have reached critical saturation levels again in as little as 10 and 30 years respectively, though more recent estimates suggest 100 years. Under the aegis of the current degassing project, Lake Monoun should be rendered safe in 2-3 years and Lake Nyos in approximately 5 years (Evans et al., 1993, 1994; Nojiri et al., 1993; Freeth, 1994; Kling et al., 1994; Halbwachs, 2001; Kling, 2001; Pickrell, 2001).

Other Crater Lakes. Since the Cameroonian disasters took place, many studies of crater lakes have been undertaken. Crater Lake in Oregon, Mt. Ruapehu crater lake in New Zealand, several lakes in Italy and the Azores, Lake Kivu in Rwanda, Lakes Wum, Bambuluwe and Njupi in Cameroon, and others have been studied (Sigurdsson, 1977; Tietze et al., 1980; MacDonald, 1983; Haberyan and Hecky, 1987; Sigurdsson et al., 1987; Schoell et al., 1988; Kusakabe et al., 1989; Freeth, 1990; Maley et al., 1990; Pourchet et al., 1990; Christenson, 1994; Kusakabe, 1994; Martini et al., 1994, USGS, 2000b, 2001d). With the exception of Lake Kivu, none has significant amounts of dissolved $CO_2$ or chemical profiles like Nyos and Monoun; therefore they do not pose a similar hazard. Lake Kivu is an enormous lake 485 m deep that lies along the East African Rift Zone. It has significant amounts of $CO_2$ and $CH_4$ in its bottom waters and is very stably stratified at present. Methane has been produced from its deep waters since the 1950s, but complete degassing is not possible due to its size (Tietze et al., 1980; MacDonald, 1983;

Haberyan and Hecky, 1987; Schoell et al., 1988). These lakes and the data from active volcanic crater lakes such as Soufriere reveal that Nyos and Monoun are uniquely situated. Although some questions remain, disasters like Nyos and Monoun can now be detected and prevented, and they are fortunately uncommon. Other volcanic $CO_2$ hazards are more frequent.

### *3.3.2. Vents and Fissures*

Dieng and Rabaul. With the exception of limnic eruptions, all other eruptive manifestations of $CO_2$ involve significant releases of energy, which lessens the hazard from gases. Lower energy releases from vents and fissures happen more often and pose greater direct danger. Two recent examples with the greatest number of casualties took place at the Dieng Volcanic Complex in Java, Indonesia in 1979 and in Rabaul, Papua New Guinea, in 1990. At Dieng, a series of earthquakes, phreatic or pneumatic eruptions, and lahars (debris flows) early in the morning of February 20 sent 142 inhabitants of Kaputjukan village fleeing toward the nearby town of Batur. They were found sprawled out single file along a path where they had been overcome by volcanic gases released from fissures above them. As with other cases of rapid asphyxiation, there was no sign of any struggle or awareness of danger. The lack of any warning suggests that the gas was not visible and therefore composed mostly of $CO_2$. Later samples consisted of mostly $CO_2$ with small amounts of $H_2S$. A few people apparently saw the others drop, went back to an elementary school in town for cover, and were overcome there. Later, several rescue workers were also killed by volcanic gas, bringing the final toll to 149 people. Many livestock and fish in local ponds were killed as well, but the fish kill was not attributed to any specific cause, e.g. heat, $CO_2$, $H_2S$, or acid gases (Le Guern et al., 1982; Allard et al., 1989; SI, 2001).

In another tragic event, six people were killed at Rabaul in Tavurvur crater on June 24, 1990. The crater was a nesting ground for birds, so three people had entered the crater to collect bird eggs. They were overcome by $CO_2$ that had built up inside the 25 m deep pit, then three more died trying to rescue them. The $CO_2$ was passively emitted from a small vent in the wall of the crater. The height of the $CO_2$ pool ranged from 2 m to 5 m deep over the following few days, and on windy days the concentration of $CO_2$ was less than lethal (Simkin and Siebert, 1994; SI, 2001).

The events at both Dieng and Rabaul were associated with active volcanism and should not be considered direct analogues for geologic carbon sequestration. They represent a dangerous type of $CO_2$ surface degassing due to the rate of release and surface topography. Examples such as these can provide some guidance for disaster management planning and for determining safe versus unsafe release rates and surface conditions.

Focussed Degassing and Diffuse Soil Emanations: Etna, Vulcano, and Mammoth Mountain. Focussed degassing is another natural guide for release rates. Mt. Etna in Italy accounts for a significant fraction of worldwide volcanic $CO_2$ emissions, and almost half is due to degassing along the flanks of the volcano. Vulcano Island, near Mt. Etna, is also known for significant gas emissions. Children and animals occasionally die near the volcano, probably from $CO_2$ asphyxiation. These Italian volcanoes represent active volcanic systems and surface release analogues. They provide an opportunity to assess how people adapt to volcanic and specifically volcanic gas hazards and also to assess the relationship among release rates, surface topography, meteoric conditions, and hazard potential (Baubron et al., 1990; Allard et al., 1991; Gerlach, 1991a; Simkin and Siebert, 1994; Allard, 1997; D'Allessandro et al., 1997; Graziani et al., 1997; SI, 2001).

The recent gas release at Mammoth Mountain in Long Valley caldera, California was associated with deep magmatic activity without any other coincident surface volcanism. Not long after a swarm of earthquakes in 1989, large areas of dead trees were noticed, and during the winter, a park ranger was overcome by $CO_2$ that had accumulated beneath the snow. A series of investigations, primarily soil gas surveys, revealed that an enormous flux of $CO_2$ was passing up through the soil in the tree-kill areas and was well correlated with known fractures and faults. Between 1990 and 1995, the total flux on the mountain was estimated to be greater than 1,200 tonnes $CO_2$/day. Soil air concentrations at 10 cm depth in the tree-kill area were between 20 and 95% $CO_2$, versus less than 1% in soils outside of the high-flux zones. Since then, the average flux has diminished to several hundred tonnes/day or less in 1999 (Sorey et al., 1999; USGS, 1999a). As much as 170 acres of forest was rendered barren, and one skier apparently died from $CO_2$ asphyxiation in a snow well near Horseshoe Lake (Farrar et al., 1995; Sorey et al., 1999; Hill, 2000). This elucidates the potential environmental impacts of high $CO_2$ release rates. The total amount of $CO_2$ released during the past 12 years was approximately 1 $MMTCO_2$.

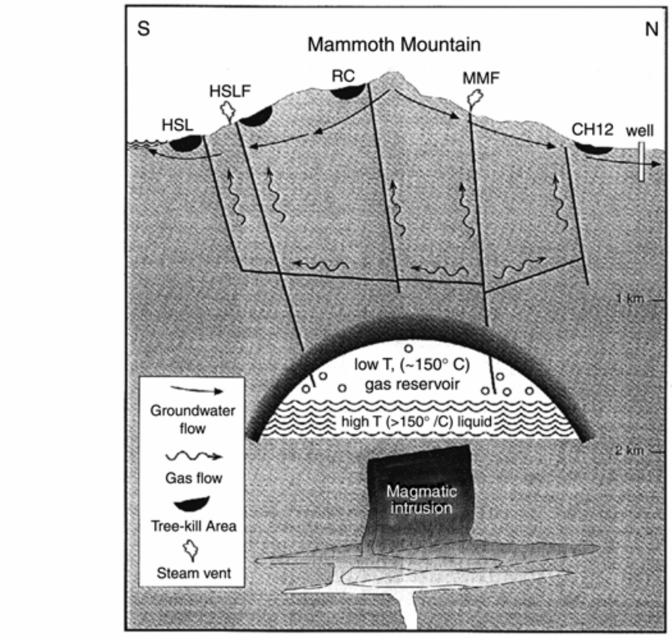


**Figure 3.7. Theoretical model of Mammoth Mountain structure, posited gas reservoir, and geothermal system to explain the variety of $CO_2$ manifestations observed. HSL = Horseshoe Lake, HSLF = HSL fumarole, RC = Reds Creek , MMF = Mammoth Mountain fumarole, and CH12 = chair 12 of the Mammoth Mountain ski resort (Sorey et al., 1999).**

The estimated volume of magma intruded and believed responsible for the intense seismic activity in 1989 cannot account for the $CO_2$ released in subsequent years. Although the convection of magma connected to deeper reservoirs might explain the disparity, the current working theory is that a high $CO_2$ gas phase accumulated over geologic time from both degassing magma and metamorphosed carbonates. This semi-sealed reservoir did not significantly exceed lithostatic pressure, so the $CO_2$ remained trapped. The new intrusion provided the force needed to open up faults and fractures that allowed $CO_2$ to migrate rapidly to the surface. This model of volcanism, degassing, and geothermal activity is depicted in Figure 3.7 (Sorey et al., 1993, 1996, 1998, 1999; Farrar et al., 1995; USGS, 1999a).

### *3.3.4. Diffuse Hydrothermal Degassing*

Geothermal, soda springs, and travertine. Geothermal and soda springs are concentrated in areas with active or quiescent volcanism and tectonic activity, but bicarbonate or $CO_2$-enriched springs occur in many groundwater systems. Carbon dioxide in nonvolcanic springs can come from the root zone, calcite dissolution, decomposing organic matter buried deep in sedimentary basins, or metamorphic decarbonation, but high levels only occur when the $CO_2$/water equilibration took place under pressure. Aside from volcanic vents and fissures, geothermal and cold soda springs are the most common manifestations of $CO_2$, and with rare exceptions, they pose little danger to humans or the environment. Only when they outcrop in caves or near confined spaces do $CO_2$ levels build up to hazardous levels. Vegetation around soda springs shows no adverse effects, though some physiological adaptation to higher levels of $CO_2$ is likely. When $CO_2$ comes from magmatic sources, altered carbon isotopic composition in local vegetation is possible, most notably depleted $^{14}C$ (Stupfel and Le Guern, 1989; Brown, 1995, 2000; Hietter, 1995; Barbier, 1997; Reid et al., 1998; Pasquier-Cardin et al., 1999; NOAA, 2001b; Soak.net, 2001).

Travertine deposits are another surface release analogue and common surface feature at high $CO_2$ discharge springs. High $CO_2$ groundwater in general and geothermal waters in particular dissolve carbonate and mobilize many cations in the subsurface and transport them to the surface (Duchi et al., 1987; Chafetz, 1991; Sheppard et al., 1992; Webster, 1995; Webster and Temperley, 1995; Klusman et al., 2000). When the high $pCO_2$ water reaches the atmosphere, $CO_2$ off-gases, and the resulting high pH carbonate saturated fluid precipitates calcium carbonate (Pentecost, 1990, 1995; Chafetz, 1991). Travertine is a common consequence of $CO_2$ off-gassing, and it is associated with natural accumulations that act as direct analogues for geologic containment (Ellis and Mahon, 1977; Allis et al., 2001).

### 3.4. Natural Accumulations of $CO_2$: Subsurface $CO_2$ Reservoirs—A Continuum of Processes

A pattern in the occurrence of $CO_2$ is discernable from the preceding discussion and was previously described by Giggenbach et al. (1991). Carbon and especially $CO_2$ degassing takes place continually all over the world, dispersing into the atmosphere harmlessly regardless of its source. As shown in Figure 3.8, a useful way to conceptualize the process is to start with the deepest sources and follow the migration of $CO_2$ to the surface. Carbon dioxide from the mantle ascends dissolved in magma until hydrostatic pressure decreases to the point that a separate $CO_2$-rich fluid phase forms. The magma can reach the surface and extrude lava during volcanic activity. In this case, the gas either takes part in the eruptions, vents through fissures in the volcanic pile, or off-gases diffusely from geothermal springs or dissolved in groundwater. If the magma remains trapped in the subsurface, then the possibilities for the gas are to accumulate in the subsurface or to migrate to the surface. As the $CO_2$ migrates through the subsurface, if pressure in the reservoir exceeds lithostatic, then phreatic or pneumatic eruptions like Dieng or focussed degassing as at Mammoth Mountain are possible. Near-surface accumulations and small explosions that nevertheless release dangerous concentrations of gas comparable to Nyos and Monoun are thought possible, even though examples are restricted to maar fields in volcanic areas. The normal process of dissolving in groundwater and eventually off-gasing benignly takes place when there is no trap and no fast path to the surface. The lack of surface releases suggests the presence of structural traps such as those known to contain hydrocarbons and/or natural $CO_2$ reservoirs.

The most relevant natural analogues for geologic containment over the long-term are $CO_2$ and $CO_2$-rich natural gas fields. Known and well documented examples are found at Mt. Gambier, Australia, in the Four Corners and Colorado Plateau area of the western U.S. (Big Piney-La Barge, Bravo Dome, Escalante, Estancia, Farnham Dome, Lisbon, McCallum, McElmo Dome, Rangely, Sheep Mountain, and Springerville/St. Johns Dome), in eastern China, and with $CO_2$ in hydrocarbon reservoirs all over the world (for example, Chivas et al., 1987; Broadhead, 1989, 1993; Giggenbach et al., 1991; Cappa and Rice, 1995; Dai et al., 1995; Xu et al., 1995; Hao et al., 1996; Pearce et al., 1996; Holloway, 1997; Imbus et al., 1998; Wycherley et al., 1999; Ballentine et al., 2000; Battani et al., 2000; Allis et al., 2001; Baines and Worden, 2001; Stephens et al., 2001; Zheng et al., 2001). For the Four Corners area, Cappa and Rice (1995) alone list 26 oil and gas fields and 14 wildcat wells with $CO_2$ content above 10% and ranging up to 98.6% for one well in McElmo Dome.

Essentially pure $CO_2$ reservoirs occur in many parts of the world and have acted as $CO_2$ traps over geologic time, from a proposed 50,000 to many millions of years. Trapping mechanisms for hydrocarbons have been studied extensively by the oil industry, and $CO_2$ traps appear to be the same as for natural gas, mostly structural or stratigraphic traps. In natural gas fields, the $CO_2$ carbon isotopic composition and C/He proportion usually varies with increasing $CO_2$. When $CO_2$ is less than 10% by volume, the $CO_2$ is usually organic or metamorphic in origin, but when $CO_2$ exceeds 10%, a metamorphic or mantle component is measurable. In reservoirs with 30% or more $CO_2$ the mantle-derived component usually predominates. The maps in Figures 3.9 and 3.10 show the location of some $CO_2$ reservoirs in the western U.S., and Table 3.3 lists a number of high $CO_2$ reservoirs, their locations worldwide, and some characteristics. The emissions data in Figure 3.9 shows the geographic distribution of emissions sources (i.e., power plants) relative to reservoir locations.

In the Four Corners area of the United States, vertically stacked reservoirs are common; suggesting that leakage from reservoirs over geologic time scales is normal. Trying to distinguish between obvious structural flaws in deeper reservoirs versus slow migration through tight, very low permeability caprocks would greatly improve our understanding of seal integrity. Stacking and leakage also suggest that soil gas surveys and surface flux measurements above known reservoirs should be performed to determine what level of subsurface leakage is detectable at the surface. Understanding surface-release characteristics above $CO_2$ reservoirs is directly relevant to risk assessment.

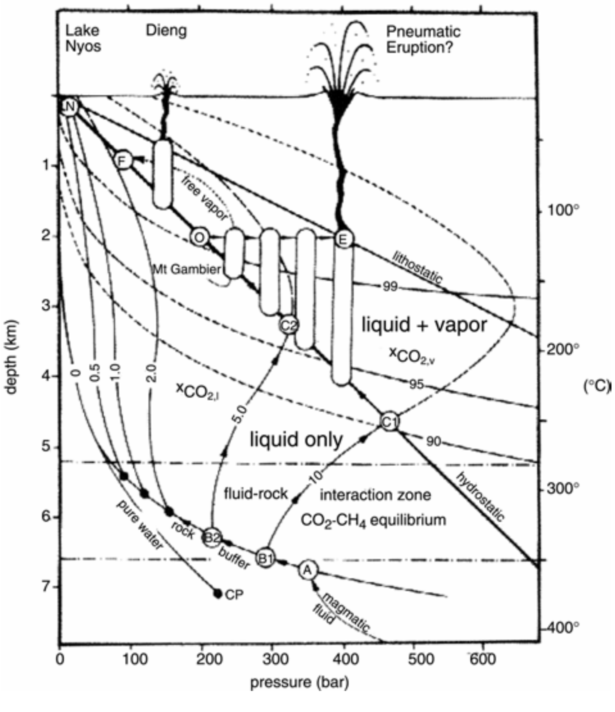


**Figure 3.8. Schematic of continuum of $CO_2$ vertical migration relative to temperature, pressure, and depth. Hydrostatic and lithostatic pressures are the most important determinants of release type (Giggenbach et al., 1991).**

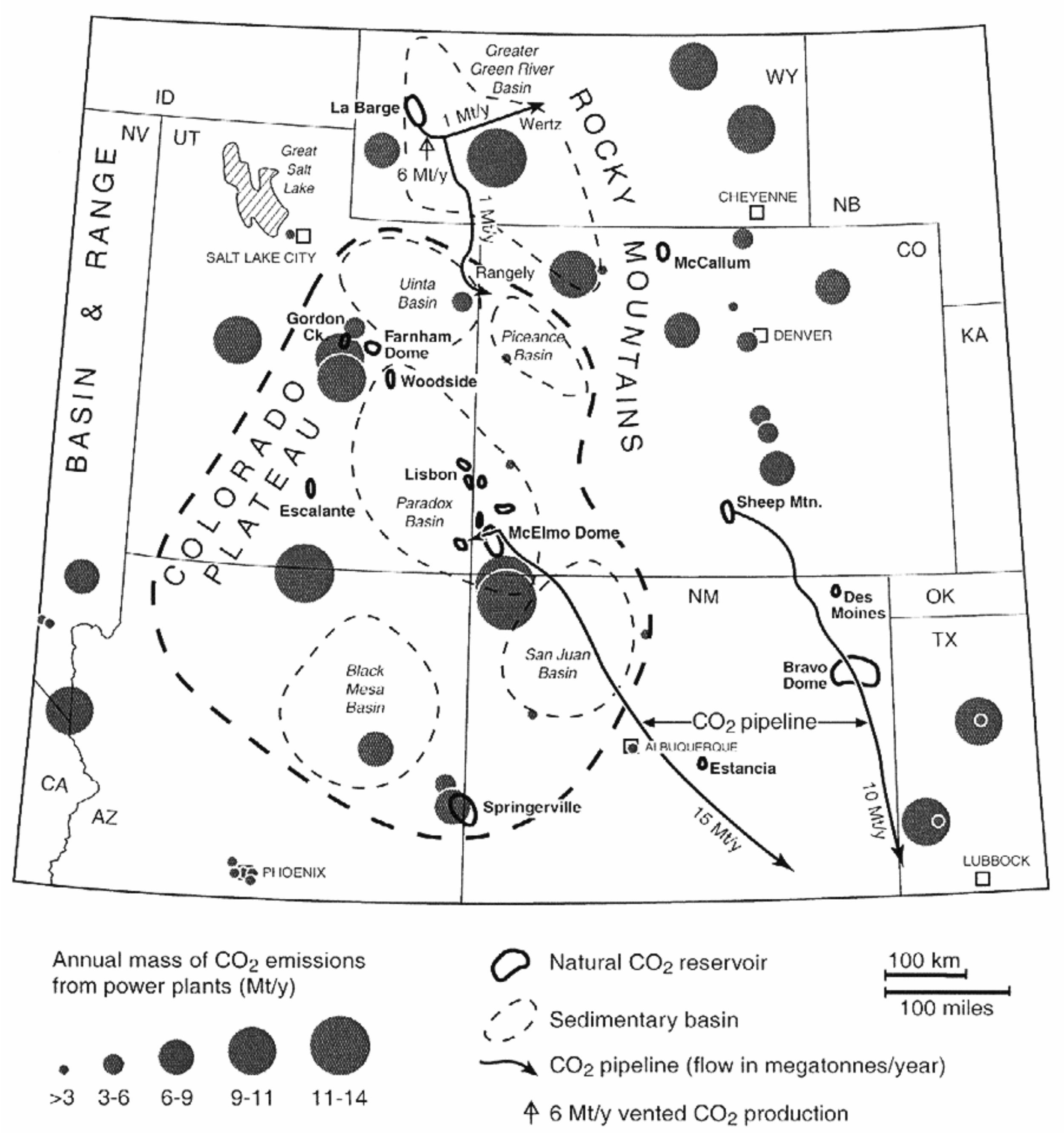


**Figure 3.9. Natural $CO_2$ reservoirs in the Four Corners area, Colorado Plateau, and Wyoming. Emissions data from Hovorka (1999) (Allis et al., 2001).**

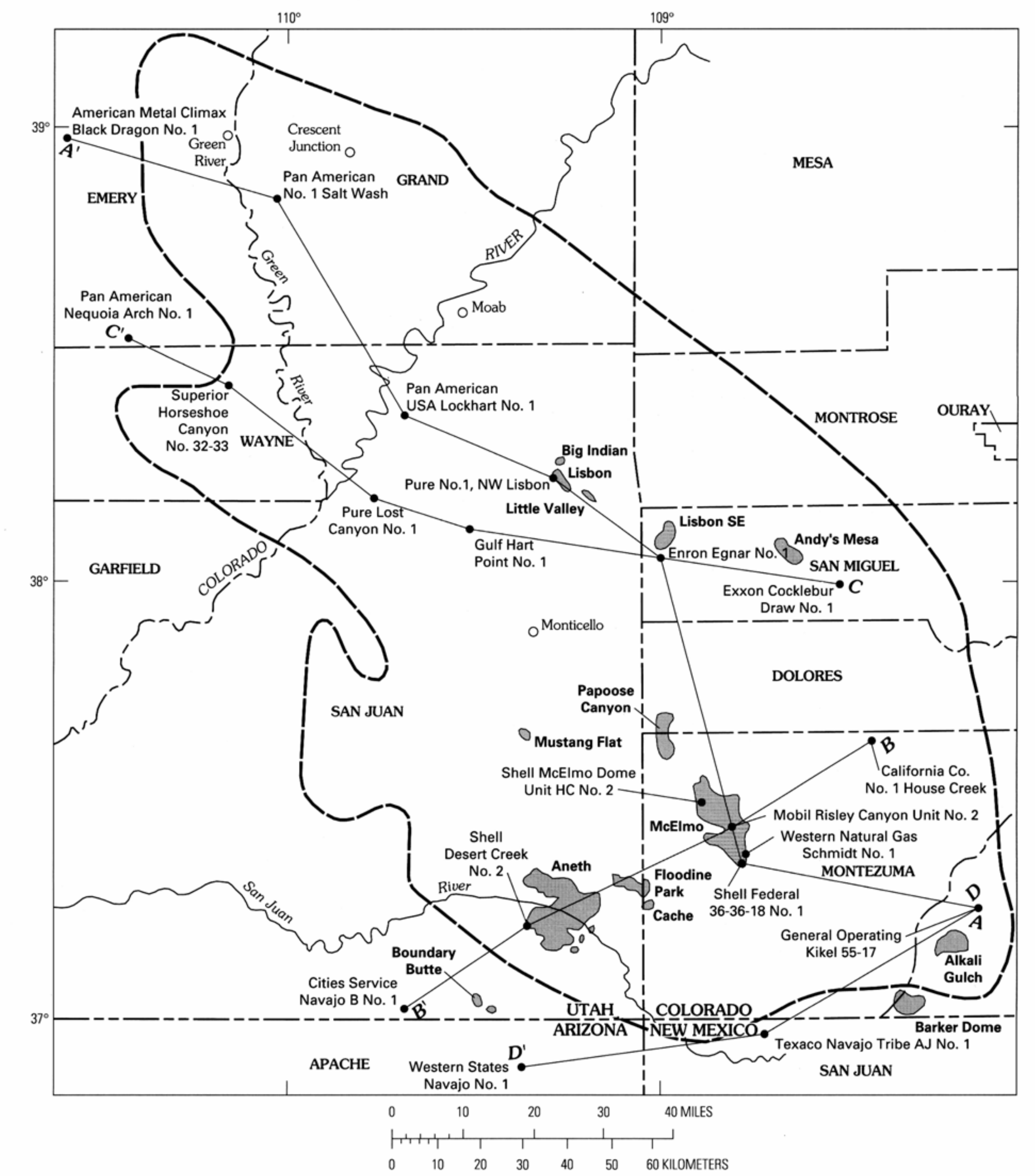


Figure 3.10. Natural $CO_2$ reservoirs in Paradox Basin in the Four Corners area of the western United States. Shaded areas are $CO_2$ reservoirs, e.g. Lisbon or McElmo. Letters (e.g., A, A') connected by solid lines are cross sections discussed in detail in the text of Cappa and Rice (1995). Dashed lines indicate the approximate limits of the evaporite (halite) facies in the Pennsylvanian Paradox Formation (Cappa and Rice, 1995).

**Table 3.3. Natural $CO_2$ reservoirs and high $CO_2$ natural gas reservoirs ($CO_2$ > 10% by volume). Not a comprehensive listing, e.g., commercial low BTU natural gas reservoirs were not included here.**

| Name | Location | Area | Avg. Depth | Composition | Amount | Reference |
|---|---|---|---|---|---|---|
| *Big Piney/ La Barge* | *Green River Basin, WY* | 3500 km$^2$ | 4500m | 66-90% $CO_2$<br>7% N2<br>1-22% $CH_4$<br>4.5% $H_2S$<br>0.5% He | 134 TCF reserves<br>6.4 Mm$^3$/d vented* | Allis et al. (2001) and references there-in |
| *Bravo Dome* | *NM* | 2000 km$^2$ | 700m | 99% $CO_2$<br>trace $N_2$<br>0% $CH_4$ | 16 TCF | Allis et al. (2001) and references there-in, Broadhead (1989, 1993) |
| *Des Moines* | *NM* | | | | | Allis et al. (2001) and references there-in |
| *Escalante* | *UT* | 150 km$^2$ | 730m | 93.1-96.1% $CO_2$<br>2-5.5% $N_2$<br>0.4-0.7% $CH_4$<br>0.1-0.3% He<br>0-0.4% $H_2$ | 1.5-4 TCF | Allis et al. (2001) and references there-in |
| *Estancia* | *NM* | | | | | Allis et al. (2001) and references there-in |
| *Farnham Dome* | *UT* | 10 km$^2$ | 900m | 98.9% $CO_2$<br>0.9% $N_2$<br>0% $CH_4$ | 4.8 BCF produced 1931-1972 | Allis et al. (2001) and references there-in |
| *Gordon Creek* | *UT* | 34 km$^2$ | 3600m | 98.8-99.5% $CO_2$<br>0-1.0% $N_2$<br>0.1-0.14% $CH_4$ | 140 BCF reserves | Allis et al. (2001) and references there-in |
| *Jackson Dome* | *MS* | | | | | Ridgeway (1998) |
| *Lisbon* | *Paradox Basin, UT/CO* | | 2500m | 17.7-35.6% $CO_2$<br>0-20.9% $N_2$<br>9.1-43.6% $CH_4$ | | Cappa and Rice (1995) |
| *McCallum* | *CO* | | | | | Allis et al. (2001) and references there-in |
| *McElmo Dome* | *Paradox Basin, UT/CO* | 800 km$^2$ | 2100m | 98.2% $CO_2$<br>1.6% $N_2$<br>0.2% $CH_4$ | 17 TCF | Allis et al. (2001) and references there-in, Cappa and Rice (1995) |
| *San Arroyo* | *Utah* | | | 19.6-26.1% $CO_2$<br>17.0-27.1% $N_2$<br>45.1-51.4% $CH_4$ | | Cappa and Rice (1995) |
| *Sheep Mountain* | *CO* | 20 km$^2$ | 1500m | 97% $CO_2$<br>0.6% $N_2$<br>1.7% $CH_4$ | 2.5 TCF | Allis et al. (2001) and references therein |
| *Springerville/St. Johns* | *AZ/NM* | 25 km$^2$ | 600m | 90% $CO_2$<br>5-10% $N_2$<br>0% $CH_4$<br>0.5-0.8% He | unknown | Allis et al. (2001), Stevens et al. (2001) |
| *Woodside* | *Paradox Basin, UT* | | | | | Allis et al. (2001) and references there-in |
| *JM-BB* | *Val-Verde Basin, Permian Basin* | | | 20-55% $CO_2$<br>45-80% $CH_4$ | | Ballentine et al. (2000) |
| | *Cooper-Eromanga Basin, Australia* | | | 2-98% $CO_2$ | | Wycherley et al. (1999) from Rigby and Smith (1981) |
| *Caroline #1* | *Otway Basin /Gambier Embayment, South Australia* | | 2670m | 98.6% $CO_2$<br>0.46% $N_2$<br>0.93% $CH_4$ | | Wopfner and Thornton (1971) |
| *Hof* | *Vienna Basin, Austria* | | | 15.8% $CO_2$<br>73.1% $CH_4$ | | Sherwood-Lollar et al. (1997) |
| *ST* | *Vienna Basin, Austria* | | | 0.29-12.7% $CO_2$<br>83.3-96.5% $CH_4$ | | Sherwood-Lollar et al. (1997) |
| | *Bohai Bay Basin, China* | | | 74.9-98.6% $CO_2$<br>0.2-5.4% $N_2$<br>0.1-19.0%$CH_4$ | | Dai et al. (1995) |

**Table 3.3 Cont.**

| | | | | | | |
|---|---|---|---|---|---|---|
| *Jiang Sag* | *Bohai Bay Basin, China* | | 1470m | 68.9-97.0% $CO_2$<br>0.25-5.4% $N_2$<br>0.14-26.4% $CH_4$ | | Zheng et al. (2001) |
| *Huabei Field* | *North China Basin, China* | | 4180m | 0-50.4% $CO_2$<br>37-88% $CH_4$ | | Xu et al. (1997) |
| *Dagang Field* | *North China Basin, China* | | | 0-11.4% $CO_2$<br>80.4-96.8% $CH_4$ | | Xu et al. (1997) |
| *Shengli Field* | *North China Basin, China* | | 1500m | 0-78.7% $CO_2$<br>18.1-98.6% $CH_4$ | | Xu et al. (1997) |
| | *Sanshui Basin, China* | | | 99.5% $CO_2$<br>0.25% $N_2$<br>0.19% $CH_4$ | | Dai et al. (1995) |
| | *Sanshui Basin, China* | | 1200m | 0-98.6% $CO_2$<br>0.55-83.8% $CH_4$ | | Xu et al. (1997) |
| *Nanhai Field* | *South China Sea* | | 1430m | 0-16.8% $CO_2$<br>64.9-80.1% $CH_4$ | | Xu et al. (1997) |
| | *Songliao Basin, China* | | | 80.7-99.0% $CO_2$<br>0-16.2% $N_2$<br>0.61-9.7% $CH_4$ | | Dai et al. (1995) |
| *Jilin Field - Wan* | *Songliao Basin, China* | | 860m | 91.5-99.1% $CO_2$<br>0.06-1.78% $CH_4$ | | Xu et al. (1995, 1997), |
| *Jilin Field – Qian* | *Songliao Basin, China* | | 1814m | 14.7% CO2<br>26.5% N2<br>53.7% CH4 | | Dai et. al. (1995)<br>Xu et al. (1995, 1997) |
| | *Subei Basin, China* | | 2300m | 0-99.1% $CO_2$<br>0.29-96.6% $CH_4$ | | Xu et al. (1997) |
| | *Subei Basin, China* | | | 92.1-97.4% $CO_2$<br>0-5.3% $N_2$<br>0.81-2.7% $CH_4$ | | Dai et al. (1995) |
| | *Yinggehai Basin, South China Sea* | | | 62.9% $CO_2$<br>6.6% $N_2$<br>28.7% $CH_4$ | | Dai et al. (1995) |
| | *Yinggehai Basin, South China Sea* | | 1500m | 0.94-93.0% $CO_2$<br>0.95-58.3% $N_2$<br>5.57-81.4% $CH_4$ | | Hao et al. (1996) |
| | *Zhujiang-Kou Basin, China* | | | 93.6-99.5% $CO_2$<br>0.1-5.3% $N_2$<br>0.2-0.6% $CH_4$ | | Dai et al. (1995) |
| *Kismarja* | *Pannonian Basin, Hungary* | | | 28.3-95.4% $CO_2$<br>3.6-61.9% $CH_4$ | | Sherwood-Lollar et al. (1997); Clayton et al. (1990) |
| *LHP* | *Pannonian Basin, Hungary* | | | 100% $CO_2$ | | Sherwood-Lollar et al. (1997) |
| *Sleipner Vest* | *North Sea, Norway* | | | 4-9.5% $CO_2$ predominantly $CH_4$ + HC condensate | $173x10^9m^3$ gas<br>$98x10^6$ $m^3$ condensate | Kongsjorden et al. (1997)<br>Korbol and Kaddour (1995) |
| | *Middle Indus Basin, Pakistan* | | 2160m | 5.4-68.9% $CO_2$<br>0.61-23.0% $N_2$<br>13.5-87.7% $CH_4$ | | Battani et al. (2000) on-line background data set |

## 3.5 Summary Conclusions and Remarks

Natural analogues for the geologic storage of $CO_2$ provide information useful for demonstrating that long-term containment is possible and for characterizing the nature of potential risks from surface leakage, should it occur. Many studies are now underway to investigate natural $CO_2$ reservoirs and what they may tell us about the effectiveness of geologic sequestration. Less attention has been paid to $CO_2$ releases in this context. For this reason, most of this analysis was focused on reviewing the literature about natural releases of $CO_2$.

Carbon dioxide is contained $CO_2$, natural gas, and oil reservoirs throughout the world. In locations where $CO_2$ concentrations exceed 10%, the origin is attributed, in part or primarily, to magmatic sources. Lower concentrations are traced to the decomposition of hydrocarbons and organic matter and the thermal decomposition of carbonate rocks. Effective containment of $CO_2$ occurs in the same types of geologic settings that trap hydrocarbons, mostly in sedimentary rocks overlain by low permeability strata. There is no evidence that $CO_2$ is stored underground any less effectively than other gases. Moreover, $CO_2$ accumulates underground as a gas, mixture of gases, supercritical fluid, and/or solute dissolved in oil or aqueous phase, thus providing confidence that storage will be possible for the range of conditions expected for intentional man-made geologic storage. Aside from the low-BTU (high $CO_2$) natural gas reservoirs, the best-known high $CO_2$ reservoirs are in the Four Corners and Colorado plateau regions of the western United States and in eastern China. No mention of natural catastrophic releases from conventional hydrocarbon or gas reservoirs were found during this literature review. Nevertheless, all hydrocarbon reservoirs, whether oil or gas, are thought to leak over geologic time. Vertically stacked $CO_2$ reservoirs are known and provide opportunities to study $CO_2$ migration, containment, and leakage over geologic timeframes of thousands to millions of years.

A comprehensive global review of $CO_2$ reservoirs and $CO_2$ in hydrocarbon reservoirs would be a valuable source of information to help determine whether or not geologic storage of $CO_2$ can be safe and effective. Assessing the seal integrity of known trapping systems like those in oil and gas reservoirs should be undertaken. A study of sealing mechanisms, caprock properties, leakage rates, and surface manifestations for hydrocarbon reservoirs would answer many of the questions currently being asked about long-term subsurface $CO_2$ storage and possible leakage. For large, brine-filled formations where the seal integrity has not been established, a more thorough site and regional characterization of containment structures and regional groundwater flow will be necessary. Also, the fate of brine displaced by the injected $CO_2$ remains a major uncertainty.

Examples of settings where $CO_2$ releases occur span the full range from the ubiquitous benign examples of diffuse off-gassing from soda springs to catastrophic examples from volcanic provenances. Diffuse $CO_2$ fluxes from the ground cover most of the surface of the Earth and take place from bulk earth de-gassing, biological respiration, and organic matter decomposition. Most detectable leaks that lead to elevated $CO_2$ concentrations and virtually all hazardous leaks occur in volcanic areas that are highly fractured and therefore unsuitable for sequestration. Large natural releases from these environments have led to catastrophic consequences and continue to pose significant hazards. The most recent and publicized of these is the limnic eruption that occurred at Lake Nyos in Cameroon and killed over 1700 people and thousands of animals.

Note that the amount of $CO_2$ involved at Lake Nyos and four other known natural $CO_2$-related disasters was small in comparison to the amounts to be injected annually for sequestration. On the other hand, the amount of $CO_2$ released in many volcanic eruptions is enormous but poses little or no direct hazard due to the force of release and subsequent dispersion high in the atmosphere. This apparent inconsistency leads to the conclusion that the level of hazard is defined more by the nature of the release and subsequent concentration versus dispersion of $CO_2$, rather than simplistically defined by the total volume released. These natural $CO_2$ leaks can be used to validate air dispersion models and/or coupled land surface-atmospheric models in assessing the potential hazards of various release scenarios.

A number of observations and research needs are apparent after reviewing natural analogues for geologic carbon sequestration. The analysis of known surface releases reveals that natural disasters involving $CO_2$ are unusual, yet when they occur, the associated risks are significant. There are persistent risks of $CO_2$ accumulation in low lying or confined spaces near natural releases, even though most disperses harmlessly. Therefore, sequestration efforts must define and prove either that containment is completely effective or that the leakages are small enough and that dispersion is sufficient to prevent hazardous concentrations from accumulating.

The monitoring program at Mammoth Mountain reveals that we can detect significant leaks, and degassing Lakes Nyos and Monoun demonstrates that we can mitigate the potential hazard of limnic eruptions. Of greater importance is that all of the significant $CO_2$ hazards are associated with volcanism and not with any known $CO_2$ reservoirs or geologic settings that would be considered for sequestration. Diffuse emissions, cold soda and geothermal springs, and travertine deposits are common and generally benign surface manifestations of $CO_2$, though some accidents in geothermal areas from pulses of $CO_2$ are known.

In conclusion, models for successful underground $CO_2$ storage exist but so do potential risks. To be deemed acceptably safe by the public, our understanding of containment must improve. Natural reservoirs provide the opportunity to study many aspects of geologic containment and surface releases by taking soil gas and flux measurements, testing remote sensing and monitoring techniques, assessing caprock seals, measuring gas composition to determine its origins, and analyzing cores of reservoir rock for diagenetic alteration and to gain a better understanding of the long-term physical and chemical interactions between the stored gas and the reservoir rocks. The risk-assessment process would be aided by finding, mapping, and quantifying any surface leaks and scouting for ecological effects above natural accumulations. The relationship of leakage rate and surface topography versus hazard potential must be assessed for natural manifestations of all types and tied to models of plume dispersion to understand adequately the human health and ecological risks of $CO_2$ releases from geologic carbon sequestration projects.

# CHAPTER 4. DISPOSAL OF LIQUID INDUSTRIAL WASTES IN DEEP GEOLOGIC FORMATIONS

## 4.1. Introduction

The technology of deep well injection disposal of hazardous industrial liquid wastes has many similarities to that envisioned for the sequestration of $CO_2$ in deep saline aquifers. In fact, many, if not all of the formations currently used for deep well disposal are also suitable candidates for $CO_2$ sequestration. The issues raised in the implementation of deep underground storage of $CO_2$—technical, legislative, regulatory and social—would be similar to those relating to disposal of hazardous liquid wastes in comparable subsurface environments. However, it should be recognized that stabilizing or halting the increasing inventory of $CO_2$ in the atmosphere by subsurface sequestration would require the disposal of volumes of $CO_2$ approximately two orders of magnitude larger than those of hazardous waste historically disposed of by deep well injection. Thus, concerns over the consequences of sequestering such large volumes of $CO_2$ in deep aquifers will likely generate public apprehension similar to those raised over deep well injection of hazardous waste.

A review of deep well injection technology and the regulatory framework governing the disposal of hazardous wastes by this method is particularly valuable in anticipating corresponding issues affecting the subsurface disposal of $CO_2$.

In the following sections, we consider the historical, technical, and regulatory basis for deep injection disposal of industrial and municipal wastes:

- History of the development of deep well injection technology in the United States.
- Risk assessment framework and methods, including key issues, performance specifications and performance assessment methods.
- Risk management approaches, including regulatory oversight and permitting, site characterization methods, monitoring and performance confirmation.
- Risk mitigation and remediation methods employed or planned in the event that performance specifications are not met or other unintended consequences arise.
- Post-operational monitoring, site and well closure, and performance verification requirements.
- Case studies documenting responses to historical accidents.

## 4.2. History of Underground Disposal of Liquid Wastes

Deep-well-injection disposal of industrial wastes came into prominence following World War II, although the technology had its roots much earlier during the first part of the twentieth century. With the development of oil and gas fields in the United States, substantial quantities of saline formation brines were co-produced. The initial practice was to separate and discharge these brines, and other waste products from drilling and production, into surface evaporation or infiltration pits. However, it was soon recognized that such a disposal method compromised the integrity of shallow groundwater aquifers, which were a valuable source of water for domestic and agricultural purposes, and states banned the practice. The oil and gas industry therefore turned to injection of liquid wastes. By 1987, of over 160,000 oil and gas injection wells, about 100,000 "enhanced recovery wells were in operation, and a further 20,000 wells were dedicated strictly for the purpose of brine disposal" (Clark, 1983; Chemical Manufacturers Association, 1984 (both cited in Gordon and Bloom, 1985); GAO, 1987). Currently, more than 300 billion gallons (1.1 billion $m^3$) of brine are injected yearly into approximately 175,000 wells (Ground Water Protection Council, 2000). But the disposal of oilfield brines is still not without attendant risks of groundwater pollution. In fact, according to Gordon and Bloom (1985) 17 of the 32 oil and gas producing states have reported groundwater contamination resulting from the disposal of these brines.

By the early 1970s, nearly 90% of the U.S. population had become dependent on groundwater supplies for drinking water, and large regions of the United States also drew on groundwater supplies for agricultural irrigation. At the same time, industry was increasingly looking for alternatives to surface effluent discharges, which had become an undesired focus of attention under the Clean Water Act. Liquid waste could be minimized through modification of the manufacturing process, treated and rendered harmless, converted into marketable products, or solidified for disposal in solid waste landfills. Another alternative could be to dispose of liquid waste into the subsurface environment by injection down wells. The disposal of any liquid waste by this means was technically feasible, but this choice was particularly attractive for those plants producing large-volume dilute waste streams that were difficult to dispose of by other means, because of their hazardous nature. Furthermore, although the capital cost of developing an injection facility was high, the operating costs were usually low. The lack of public awareness of this disposal method initially allowed industry to proceed without close scrutiny or adequate regulation.

The domestic organic chemical and petrochemical industry, in particular, was not only strategically located, but also conceptually oriented to take advantage of deep-well-injection disposal, and become the largest user of the technology. Other industries, municipalities, and government agencies also took advantage of this disposal method. However, most deep-injection facilities are privately owned, and of these over 90% are "onsite" wells, i.e., they are owned and operated by the waste generator (Brasier and Kobelski, 1996). The remaining wells are at commercially operated facilities, which were set up to dispose of wastes generated by other users "off-site."

The growing importance of the deep disposal of hazardous waste is reflected in the growth of facilities for that purpose. In 1950, there were only five such facilities. By 1963, there were 30, (Donaldson, 1964), but by the early 1970s, the number had jumped to 270. The drilling of injection wells peaked between 1973 and 1975, following passage of the Clean Water Act of 1972. By 1985, the total number of wells injecting hazardous waste had fallen to 252 at 95 facilities. However, only 152 wells were under continuous operation, 43 were operated intermittently, and 56 were inactive or abandoned (USEPA, 1985). Even more stringent regulations were implemented in 1988 (see below) in response to the passage of the Resource Conservation and Recovery Act (RCRA) in 1984. RCRA made it a national policy to eliminate, or at least reduce, hazardous waste generation, and consequently, its passage impacted the practice of deep-well disposal. By 1990, EPA estimated that the number of hazardous waste facilities had been reduced to 51, although some of the reduction could be attributed to waste minimization efforts. Currently, the number of facilities remains about the same, comprising 123 so-called Class I hazardous waste wells (i.e., wells injecting hazardous waste below the lowest aquifer containing a potential source of drinking water). Most of these wells are found in Texas (64) and Louisiana (17). Another 221 facilities comprising 350 Class I wells injecting nonhazardous waste are also in operation, most of which are found in Florida (122) and Texas (49). Of those operating in Florida, 104 are dedicated to the disposal of municipal waste, the only state operating this class of well, (USEPA, 2001c). Figure 4.1 illustrates the variation in the number of deep well injection facilities over time.

The siting of deep disposal wells is critically dependent on there being suitable geology for the placement and storage of the wastes for at least 10,000 years. To conform to Environmental Protection Agency (EPA) Underground Injection Control (UIC) regulations, waste can only be disposed of in "injection zones" that meet certain criteria for permeability and porosity. The receiving formation must possess chemical properties that are compatible, or at least do not cause adverse reactions with the injected waste. And finally, the injection zone generally cannot be a source of drinking water, nor can its utilization for the disposal of waste lead to contamination of subsurface drinking water supplies. If the injection well is used for the disposal of so-called "hazardous waste," the requirements for proper containment are very stringent. In general, the regulations constrain waste disposal to deep sedimentary formations underlying potable water aquifers, which usually necessitates injection at depths between 1,500 ft (360m) and 6,000 ft (1830m).

Sites favorable for deep well disposal commonly overlie deep sedimentary basins that have not been subject to metamorphism, where deep formation waters are highly saline, and where permeable aquifers are interspersed with relatively impermeable "confining beds." Fortunately, the 48 contiguous states are endowed with several such basins, some of which are fortuitously located with respect to centers of industrial development, especially those in the raw materials sector. Figure 4.2 illustrates the distribution of major sedimentary basins in the 48 contiguous states.

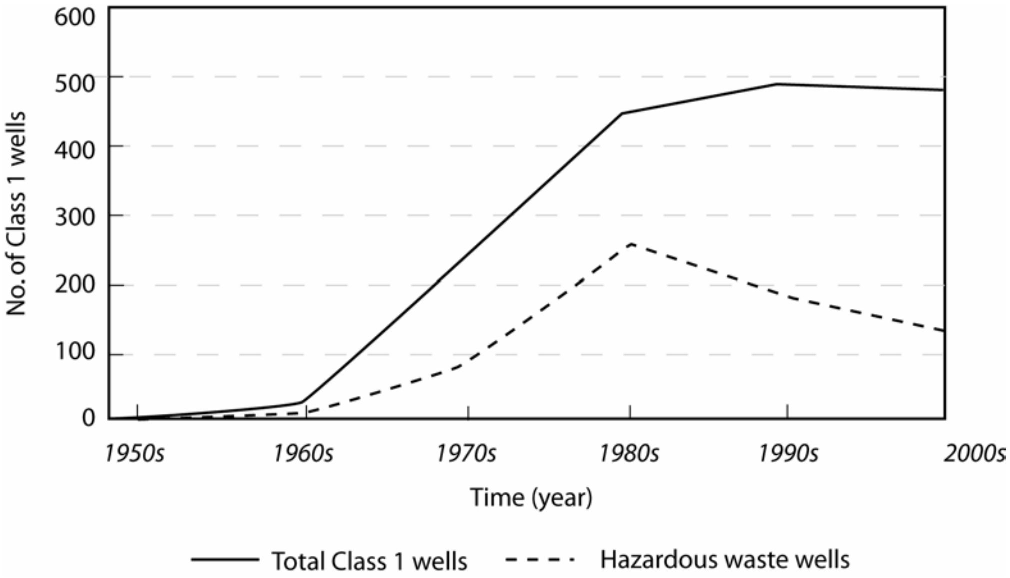


**Figure 4.1. Number of Class I wells operating in the United States on a yearly basis since 1950 (modified after Brasier and Kobelski, 1996).**

Most of the deep injection disposal wells are located on the coastal plain of the Gulf Coast, and in states surrounding the Great Lakes. In the Great Lakes region, deep injection well depths range from 1,700 to 6,000 ft (520-1830 m), whereas those along the Gulf Coast range from 2,200 to 9,000 ft (670-2740 m). (Kozlowski, 1997). About 60% of the wells are located within the EPA jurisdiction of Region VI, which includes Texas and Louisiana. According to Gordon and Bloom (1985), manufacturers of organic chemicals account for nearly 65% of the injected volume, while the petroleum refining and petrochemical industries account for a further 25%.

The quantities of liquid waste injected by deep well disposal facilities are enormous. By 1985, 11.5 billion gallons (43.5 million $m^3$) of industrial liquid wastes were injected annually (USEPA, 1985). At the time, this was ten times the amount going to landfills and twice that going to surface impoundments (Gordon and Bloom, 1985). By 1990, the quantity injected had fallen to 9 billion gallons (34 million $m^3$) (USEPA, 1991) and currently remains at about the same level (Ground Water Protection Council, 2001). The injected waste constitutes approximately 60 percent of all liquid hazardous waste generated in the United States. During the 1990s, the quantity of hazardous waste injected has tended to decline in the face of stringent regulation and positions taken by industry to minimize waste production. However, industrial expansion may be offsetting these trends.

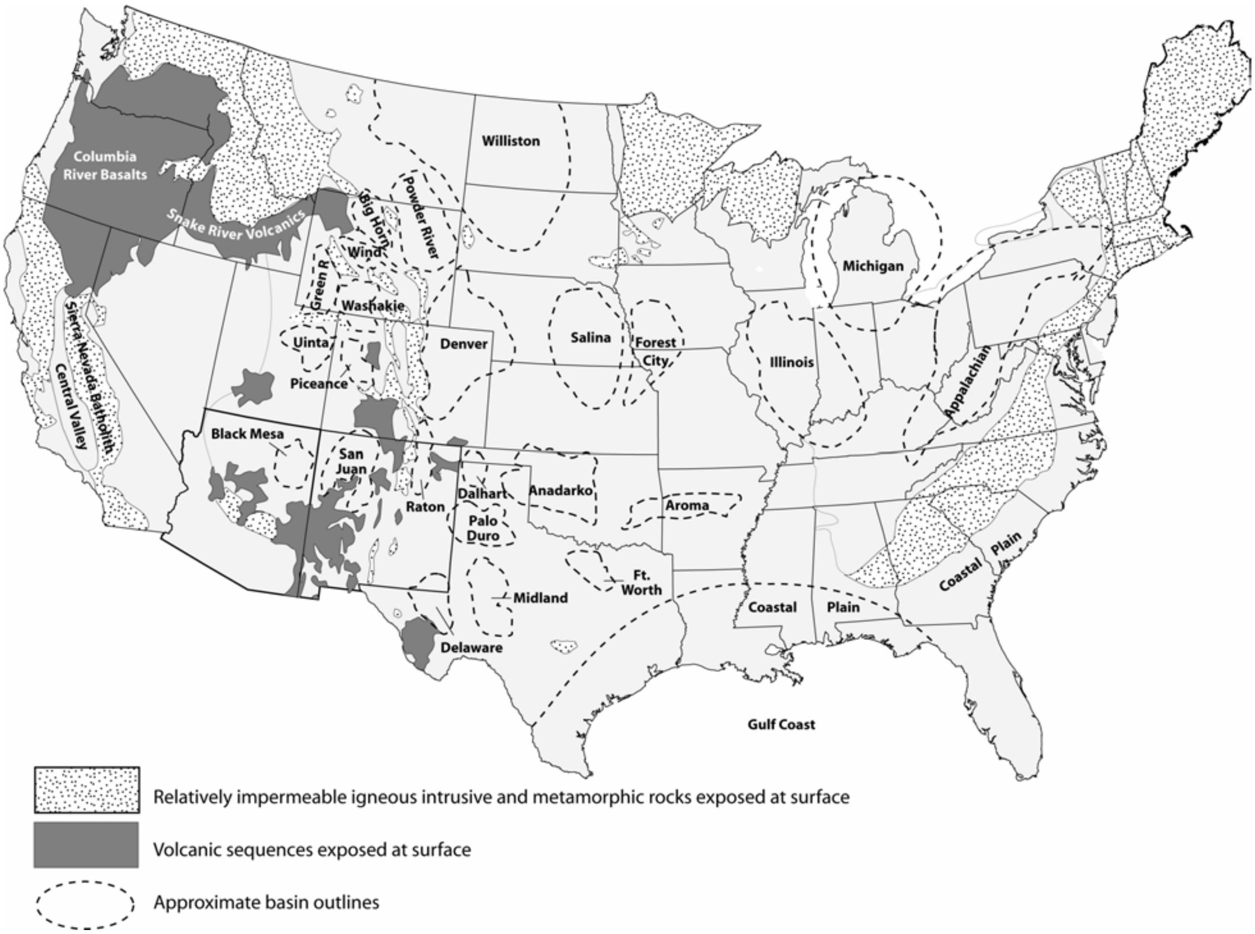


**Figure 4.2. Map of the contiguous 48 states, showing major sedimentary basins (adapted from Warner, 1968).**

*4.2.1. Legislative History Governing Deep Well Injection Disposal*

The unregulated nature of deep well disposal practices commonly resulted in poorly engineered or constructed facilities, which were carelessly operated, and resulted in an increasing number of reported occurrences of potable aquifer contamination. Individual states early saw the need for regulation, including Kansas, whose State Board of Health adopted rules and regulations in 1952 requiring permits for industrial waste disposal in wells other than those relating to oil recovery (Walker and Cox, 1976). Later, Texas enacted the first legislation relating to the injection of wastes other than oil field brines with adoption of The Injection Well Act in 1961. This was followed by legislation by Ohio in 1967, Michigan, New York and West Virginia in 1969 and Colorado in 1970. In 1971, Missouri enacted legislation prohibiting disposal wells, followed in 1973 by North Carolina (Walker and Cox, 1976). Having watched the states seize the initiative, the federal government belatedly decided to get involved. While Congress debated the organization of the EPA, the Federal Water Quality Administration (FWQA) published policy guidelines governing the deep well injection of hazardous wastes (USFWQA, 1970). The USFWQA policy "opposed the disposal or storage of wastes by subsurface injection without strict controls and a clear demonstration that such [injected] wastes will not interfere with present or potential use of subsurface water supplies, contaminate interconnected surface waters or otherwise damage the environment" [cited by Herbert (1996)]. Furthermore, according to Herbert (loc. cit.), "The policy broadly provided for the critical evaluation by the FWQA of all proposals for subsurface injection of wastes in order to determine that:

- Alternative measures have been explored.
- Appropriate preinjection tests have been made to allow prediction of the fate of wastes to be injected.
- [It has been] ... demonstrate[d] that such injection will not interfere with present or potential use of water resources nor result in other environmental hazards.
- [The] best practical measures for pretreatment of wastes have been applied.
- The subsurface injection system has been designed and constructed using the best available techniques….
- Provisions for adequate and continuous monitoring ... have been made.
- Appropriate provision[s] will be made for plugging such [injection] wells...when their use for disposal is discontinued."

The FWQA also "…declared that subsurface injection of wastes should be recognized as merely a temporary means of ultimate disposal to be discontinued when alternatives providing for greater environmental protection become available."

The responsibility for regulating the deep well injection of hazardous wastes ultimately fell upon the EPA with the incorporation of the FWQA in 1970.

In 1972, the EPA issued a Technical Studies Report concerning technical issues relating to deep well injection (USEPA, 1972). This report noted problems arising through the use of this technology could be avoided if the fate of the injected wastes could be monitored. However, the report also indicated that other major problems had to be resolved, including identification and classification of areas where waste could be safely injected as well as the amounts and chemical nature of the waste to minimize problems relating to incompatibility with host rocks and groundwaters of the injection zone. The report concluded that deep well injection should be regulated through a system of laws and that a permitting process should be implemented, based on both injection site and the nature of waste injected (as cited in Herbert, 1996).

In April 1974, EPA finally set forth its own policies regarding deep well injection (USEPA, 1974a), superceding those policies earlier detailed by the FWQA (USFWQA, 1970). EPA reiterated the position that deep well injection was a temporary means of disposal that would be approved only for a permitted duration at a given facility. EPA was opposed to the storage or disposal of contaminants by subsurface injection "…without strict control and clear demonstration that such wastes will not interfere with present or potential use of subsurface water supplies, contaminate interconnected surface waters or otherwise damage the environment" (Brasier and Kobelski, 1996). But EPA also recognized that for some industries, such practice was currently the only feasible means of disposal. The latter concession recognized *de facto* practices of waste disposal in the oil and gas and geothermal industries where reinjection of large volumes of liquid wastes had been standard practice for several decades. However, a formal differentiation of these practices was to be recognized only later. Accompanying the updated EPA policies were "Recommended Data Requirements" for deep well injection disposal (USEPA, 1974b). These requirements covered a range of specifications to be obtained from the operator of a deep injection disposal facility, to allow EPA to determine whether a permit should be issued to allow operation.

Shortly after the EPA had published its policy on deep well injection, Congress passed the Safe Drinking Water Act (SDWA) of 1974. Congress had found that legislative authority was necessary to ensure that water supplies in the United States met certain minimum national standards for the protection of human health. Part C of the SDWA is the Underground Injection Control (UIC) program, which implemented EPA's policy concerning deep well injection and mandated controls on injection practices. According to Herbert (1996), the SDWA was the first federal statute to address in detail deep well injection practices. Furthermore, it provided for a joint system involving both state implementation and federal oversight, in which EPA would implement the policy guidelines set forth by the federal government by setting minimum requirements for state programs.

One of the purposes of the SDWA was to ensure that presently used underground drinking water supplies were protected from contamination by injected substances that might adversely affect public health or contribute to making the water unfit for human consumption, whether or not these substances were deemed to be contaminants subject to national primary drinking water regulations. EPA was to be allowed discretion in requiring states to use a permit system, rule making, or both to control underground injection. The reason for this discretion was to allow compatibility with permit provisions already in place under the Federal Water Pollution Control Act (FWPCA). EPA responded with the publication of technical UIC regulations in June 1980. These regulations were based on information relating to then-current practices associated with deep well disposal, most of which were compiled in Warner and Lehr, (1977). Minimum requirements were also established to ensure the safe siting, construction, operation, monitoring and abandonment of injection wells.

It was also in these regulations that an underground source of drinking water (USDW), as set forth in 40 CFR §144.3, was first defined as containing fewer than 10,000 mg/L and containing a sufficient quantity of groundwater to supply a public water system. The regulations also categorized injection wells into five classes, as set forth in 40 CFR §144.6 Classification of Wells. The class of most relevance to deep injection disposal is Class I, that class of wells injecting waste below the deepest USDW.

Although the SDWA was promulgated to ensure the protection of the nation's water supplies, it did not specifically address the public's concern over the improper handling of hazardous waste. This omission was addressed through passage of RCRA in 1976. With this act, Congress made it a national policy to eliminate, or at least reduce, hazardous waste generation as expeditiously as possible. The act also designated responsibility to EPA for promulgating regulations governing standards applicable to owners and operators of facilities for the treatment, storage, and disposal of hazardous waste. According to RCRA, hazardous waste disposal facilities included injection wells if used for the disposal of hazardous waste and are therefore subject to regulation under the act.

Because of the technical complexity of the issues involved, and an overlap between SDWA and RCRA, EPA decided to coordinate their implementation by regulation of aboveground facilities under RCRA and injection well under SDWA. For a number of reasons relating in part to delegation of the well permitting process to states under SDWA, full protection of drinking water supplies under SDWA was not achieved (Herbert, 1996). During Congressional hearings considering RCRA reauthorization early in 1982, the ineffectiveness of EPA's coordination of SDWA and RCRA with respect to well disposal of hazardous wastes, and consequent failure adequately to protect underground sources of drinking water was highlighted. This concern was heightened by the discovery of groundwater contaminated with hazardous chemicals due to malfunctioning and poorly regulated hazardous-waste injection wells (Bloom, 1982). Congress therefore gave EPA specific directives regarding the implementation of its UIC program to ensure that vulnerable subsurface drinking water supplies were adequately protected in the Hazardous and Solid Waste Amendments (HSWA) to RCRA in 1984. Specifically, EPA was required to ban the deep well injection of hazardous waste, unless regulations were promulgated in a timely manner. Congress further mandated that land disposal of hazardous waste could only occur if an applicant for a permit exempting restriction on land disposal could demonstrate that no migration of the waste would occur. (Herbert, 1996).

EPA responded to the 1984 RCRA amendments with amended UIC regulations governing hazardous-waste injection in 1988. Henceforth, the subsurface injection of hazardous wastes would be prohibited unless EPA was to issue a permit exempting the operator of a deep well injection facility from the prohibition. To obtain a permit, the operator had to petition EPA and provide supporting documentation demonstrating that the injected waste would not migrate outside of a designated injection zone within 10,000 years, or that the waste would become nonhazardous.

EPA was also required to promulgate prohibitions and standards for wastes identified as hazardous in the HSWA listing within six months of passage of the amendments, but failed to do so. Consequently, the Environmental Defense Fund (EDF) filed a lawsuit, resulting in a consent decree in which a schedule for the adoption of prohibitions and treatment schedules were defined (USEPA, 2001e). EPA implemented the restrictions with respect to the so-called "California List" wastes and "characteristic" wastes in three stages, the third stage addressing the characteristic wastes being completed in 1990. As a result of a legal challenge by CMA in 1992, the D.C. Circuit Court ruled that the Land Disposal Restriction (LDR) must apply to characteristic wastes, even though they no longer exhibit the hazardous characteristic. Further, the court also ruled that dilution to eliminate the hazardous characteristic was also not acceptable. The court's rulings had far-reaching implications, because many Class I nonhazardous waste wells were receiving waste that had been rendered nonhazardous through treatment or mixing of wastewaters from different sources (USEPA, 2001e).

To rectify the problem, Congress passed the Land Disposal Program Flexibility Act in 1996 to amend the land disposal provisions of RCRA. This act provided for relief from the requirement that hazardous waste remain classified as hazardous even after it had been treated to render it nonhazardous (i.e., even after it had been "decharacterized"). The decharacterized waste was thereby exempted from the restrictions governing the deep well injection disposal of hazardous waste (EPA, 2001; Van Voorhees, 2001). In other words, waste that no longer displayed the characteristics that made it hazardous in the first place was legally no longer considered hazardous.

Suspicious that the permitting process for Class I wells was merely a loophole for continuing deep well injection disposal of hazardous wastes, the Oversight and Investigations Subcommittee of the House Commerce Committee decided to investigate EPA's implementation of land disposal restrictions in 1992. EPA was asked to submit documentation relating to the UIC program governing the permitting of Class I wells. In addition, the General Accounting Office (GAO) was also asked to conduct an independent investigation of the program. EPA responded by commissioning a comprehensive study of purported well failures, which was submitted to the Subcommittee in 1993. The information turned over to the Subcommittee by EPA was reviewed by the GAO, which found no basis that the Class I UIC program was a loophole or any major problems in its implementation. (Van Voorhees, 2001).

### *4.2.2. Implementation of Regulations for Underground Disposal of Liquid Wastes*

As noted above, Congress allowed EPA to delegate responsibility to the states to administer their own UIC programs, should a state wish to assume primacy. States also have the option of administering all or part of the UIC program. To date, 34 states have been delegated full authority to regulate Class I wells within their territory, and six share responsibility with the federal government. The remainder are administered under the federal program (USEPA, 2001d). Four states have placed an outright ban on Class I wells. Although Class I wells are not specifically banned in several other sates, a *de facto* prohibition effectively exists, because the sub-surface geology is unsuitable for the emplacement of liquid waste. This applies specifically to states in New England, much of northern Minnesota and Wisconsin, and much of the states of the northwest where igneous or high-grade metamorphic rocks dominate the subsurface terrain. (Figure 4.1.) Likewise, the geology underlying the southeastern Atlantic seaboard states is also largely unsuitable, consisting of buried igneous intrusions and high grade metamorphic rocks and buried Triassic impermeable mudstones, all overlain by Tertiary fluvial and marine littoral sediments containing major sources of drinking water for those states. Local political considerations can also lead to a *de facto* prohibition. Figure 4.3 illustrates the distribution of states with primacy.

Although states follow federal regulations quite closely, specific variations do occur. For example, Utah requires that the injection zone of a Class I nonhazardous-waste well be located at least 2 miles (3.2 km) from an underground source of drinking water instead of the federal limit of 1/4 mile (0.4 km) (State of Utah, 2001). Several states require larger so-called Areas of Review (AoR) than required by federal regulations [e.g. Texas requires 2-1/2 miles (4 km), Louisiana requires 2 miles (3.2 km), and Florida and Kansas require a 1-mile minimum (1.6 km) (USEPA, 2001e)]. The upper limit in concentration of total dissolved solids in an underground source of drinking water also varies within those states with primacy. In comparison with federal regulations, which set the concentration limit at 10,000 mg/L, New York is very liberal, requiring only those underground waters with a TDS concentration of 1,000 mg/L or less to be protected, whereas Alabama sets a very restrictive level at 33,000 mg/L. Texas permits a range, from 3,000 to 10,000 mg/L (Clarke, 1999). Another area where federal and state regulations can differ concerns monitoring wells. Some states (e.g., Florida) require them, but others, in conformity with federal regulations, do not.

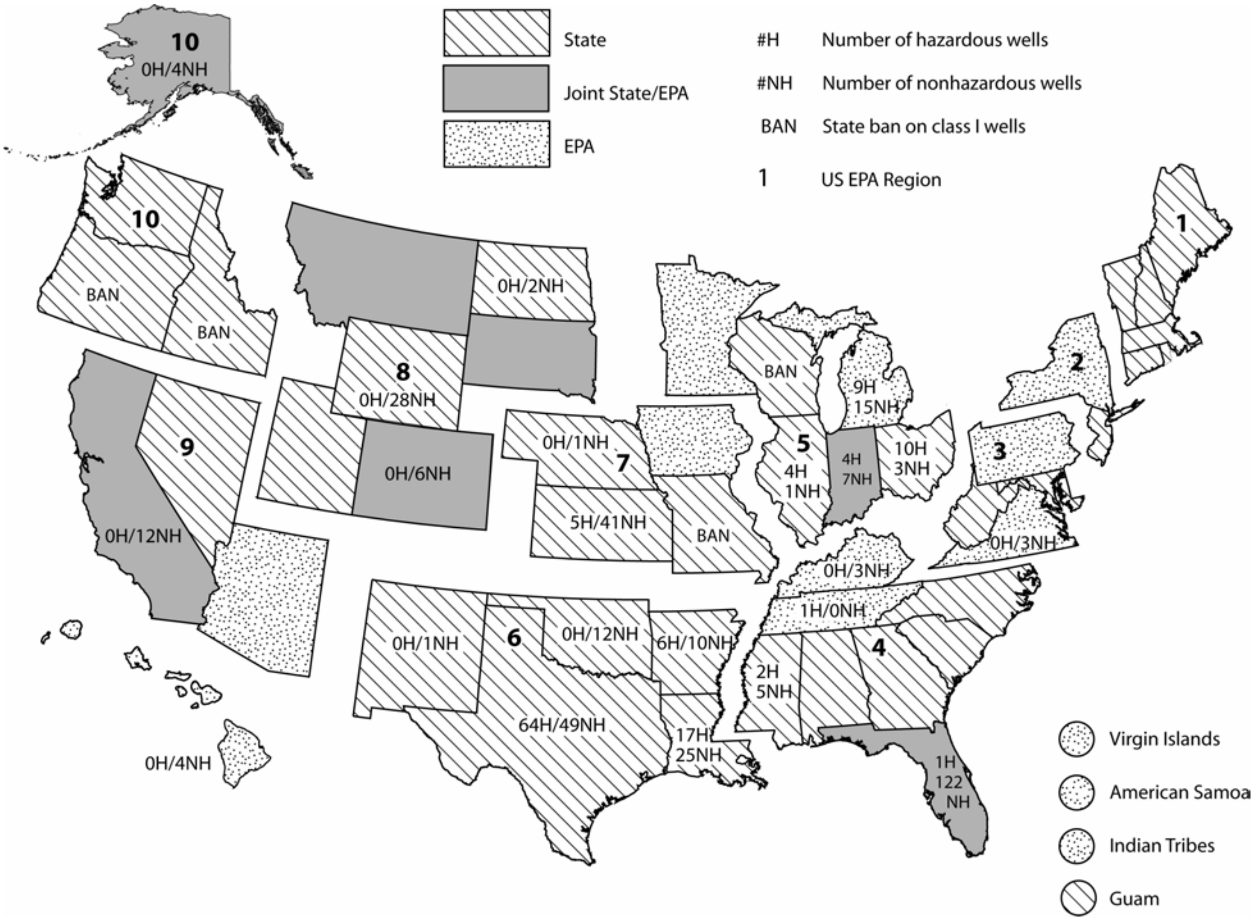


**Figure 4.3. Distribution of states with primacy over regulation of Class I wells (adapted from Brower et al., 1986 and USEPA, 2001c).**

### *4.2.3. Current Status of Underground Disposal of Liquid Wastes*

There has been no evidence of subsurface leakage into USDWs from Class I hazardous waste injection wells since 1988, and no evidence of contamination of USDWs due to the migration of hazardous waste from well injection zones. The sole exception applies to the injection of nonhazardous sewage waste in Class I wells in Florida (which is discussed further in Section 4.6 below). Deep well injection technology as it applies to industrial wastes appears to be working, not only for the cited examples, but also in general, as supported by relatively recent independent investigations [e.g., see USEPA (2001e)]. However, both the regulatory philosophy—in which subsurface disposal by deep well injection is treated as an interim expedient, the operator or owner liability for containment of hazardous wastes—and opposition from environmental groups has caused industry to reassess the merits of continued subsurface disposal. Companies are actively investigating other options and have in some cases developed alternatives to injection disposal of their hazardous waste. Data reported by the Chemical Manufacturers Association (CMA, 1996) shows that underground injection has declined progressively from 675 million pounds (306,000 tonnes) in 1987 to 365 million pounds (166,000 tonnes) in 1993.

However, it is not clear what the trends have been since that date. The decisions of individual companies vary. Dow Chemical, for example, closed their last hazardous waste Class I well as long ago as 1980. Vulcan Chemicals, acting on the advice of a local community-involvement group, and despite concern that the decision was not in the best interest of the environment, dramatically reduced deep well injection as a means of hazardous-waste disposal at their Wichita, Kansas Plant (Public Relations Society of America, 1996). DuPont, which operates nearly 30 Class I hazardous waste wells for their chemical manufacturing operations, has gone on record that it would decrease the amount of toxic resource inventory (TRI) waste injected to less than 10 million pounds (4540 tonnes) by the year 2000 from a high of 256 million pounds (116,000 tonnes) in 1989 (DuPont, 1998). However, it is not known whether this goal was met, as DuPont, even before its self- imposed deadline, had solicited EPA for an extension of all of its Class I well operating permits (Sutherland, 1999). Solutia Inc., formerly the chemical manufacturing business of the Monsanto Company, reported that its deep well injection disposal actually increased 31% in 1999 over that of the previous year, as a result of increased production (Solutia, 2000). This suggests that economically favorable alternatives to deep injection disposal may be less easily developed than previously anticipated.

Deep well injection disposal remains one of the cheapest, safest, and most convenient disposal options for many hazardous waste generators. In 1987, the cost of liquid-hazardous-waste disposal ranged from $49 to $207/ton (Sigman, 2001). This compares with $776-1426/ton for incineration, $85-394/ton for chemical treatment, and $131-329/ton for resource recovery (in the case of organics from the aqueous phase). Although present costs are probably higher, the economic costs of deep well injection are generally expected to remain lower than alternative waste mitigation methods in the absence of significant technological advances. Alternative disposal methods, involving treatment and surface disposal, all increase the potential risks of adverse consequences to the environment and public health. Furthermore, these methods add considerably to the cost. Brower et al. (1986) estimated that the treatment of injection waste to remove the hazardous components could increase the operating costs 3 to 40 times. Thus, although subsurface disposal may eventually be phased out through reductions in the volumes of waste generated, recycling, or elimination through the development of alternative technologies, it will remain a preferred method of hazardous liquid waste disposal for the foreseeable future.

### *4.2.4. Opposition to Deep-Well-Injection Disposal*

Although many wells were authorized under the Land Ban regulations, difficulties remain in providing a technically convincing demonstration of waste containment. These deficiencies have been exploited by environmental groups in their unswerving opposition to the underground disposal of hazardous liquid wastes. However, opposition to deep well injection is not limited to technical issues related to the ultimate fate of the injected waste. Opposition is particularly strong in the case of off-site injection facilities, because the hazardous waste must be trucked in from various sources and transferred and temporarily stored in surface tanks or impoundments. Furthermore, wastes from different sources may vary widely in chemical composition and react with undesired consequences when mixed. Off-site facilities are therefore prone to toxic releases to the atmosphere and to contamination of surface waters and shallow ground waters. They also tend to be more frequently in violation of federal and state regulations governing deep well injection disposal. Appendix 14 describes three examples to illustrate the nature of disputes and litigation arising from such facilities. It should be emphasized, however, that at none of these cited facilities has it been shown that the deep well injection system failed to contain wastes as required under the UIC program since implementation of the 1988 UIC regulations.

## 4.3. Risk Assessment Framework and Methods

In this section, we discuss the current regulations governing the deep well disposal of wastes, including hazardous wastes. The emphasis of this section is on regulations pertaining to Class I wells, because these wells usually penetrate to considerable depths and discharge their waste below aquifers containing potable water. Operating conditions are therefore somewhat similar to those expected of wells injecting supercritical $CO_2$, in which the optimum depth range would fall between 3,000 and 6,000 feet (915-1830 m**)**. The injection depth would also be dependent on the lowermost USDW, the availability of a suitable aquifer, and cost/benefit considerations regarding volume reduction versus energy consumption for compression.

### *4.3.1. Current Regulations Governing Well Injection*

Regulations governing the injection of waste in the subsurface environment are found in the Code of Federal Regulations, Chapter 40, Parts 144 through 148.

Part 144—Underground Injection Control Program
Part 145—State UIC Program Requirements
Part 146—Underground Injection Control Program: Criteria and Standards
Part 147—State Underground Injection Control Programs
Part 148—Hazardous Waste Injection Restrictions

In addition, 40 CFR Part 124—Procedures for Decision-Making, includes public-participation requirements that must be met by UIC programs.

### *4.3.2. Underground Sources of Drinking Water*

The most important issue bearing on the injection of all wastes through wells into the subsurface environment is the potential for contamination of drinking water supplies. With the regulation of well disposal of waste, it became necessary to define what drinking water actually is in relation to those waters that are unsuitable for that purpose. The term "Underground Sources of Drinking Water" (USDW) was coined for that purpose, and is defined in 40 CFR § 144.3:

*"Underground source of drinking water (USDW)* means an aquifer or its portion which supplies any public water system, or which contains a sufficient quantity of ground water to supply a public water system, and currently supplies drinking water for human consumption, or contains fewer than 10,000 mg/L total dissolved solids, and which is not an exempted aquifer."

The "sufficient quantity of ground water to supply a public water system" has been variously interpreted. However, EPA guidelines indicate that the minimum yield criteria need be only 1.5 gallons per minute (gpm) (5.7 Liters per minute, Lpm). This is based on the assumption that a public water system supplies 20 people at 100 gpd (379 Lpd). An *exempted aquifer* is an "aquifer" that meets the criteria in the definition of a USDW, but which has been exempted according to procedures in §144.7 using criteria set forth in §146.4. Such aquifers would have no real potential to be used for drinking water, and are therefore not USDWs. An aquifer could not, for example, be used for drinking water, because it is currently being used in the production of oil, natural gas, or geothermal energy, or that it is so deep or saline (i.e., >3,000 mg/L) that its recovery and treatment would be impractical.

### *4.3.3. Classification of Wastes*

Injected liquid wastes can, depending on their chemical composition and origin, be classified as hazardous. Whether or not a waste is so defined depends upon a close reading of 40 CFR Part 261—Identification and Listing of Hazardous Waste. In general, hazardous wastes are either "listed" or identified by their "characteristics." The characteristics are subdivided into six groups and given respective Hazard Codes, as shown in Table 4.1, below:

**Table 4.1. Hazardous waste characteristics.**

| Waste Characteristic | Hazard Code |
|---|---|
| Ignitable | (I) |
| Corrosive | (C) |
| Reactive | (R) |
| Toxicity Characteristic | (E) |
| Acute Hazardous | (H) |
| Toxic | (T) |

The characteristic must cause or significantly contribute to an increase in mortality or serious irreversible or incapacitating reversible illness, or possess a substantial present or potential threat to human health and the environment if improperly handled. The criteria for listing a hazardous waste are extensive and are provided in Subpart C of Part 162. If a waste is listed, it is assigned an EPA Hazardous Waste number. This number must be used in complying with applicable regulations. The hazardous waste number can apply to a waste type, chemical compound or contaminant. Extensive tabulations of hazardous wastes are given in Part 261 and its appendices.

Waste that is not classified as hazardous is, by default, nonhazardous. However, such waste cannot be allowed to contaminate a USDW unless it meets the criteria set forth in 40 CFR Part 141—National Primary Drinking Water Regulations. As an example, consider a waste stream containing benzene. The waste would be considered hazardous if it were to exceed the regulatory level of 0.5 mg/L of benzene. However, the enforceable drinking water standard for benzene is a maximum concentration limit of 0.005 ppm (or 5 ppb) with a maximum contaminant-level goal of zero for drinking water. Therefore nonhazardous waste must contain less than 5 mg/L benzene, but could not be injected into a USDW. To be injected, it would have to contain less than or equal to 5 ppb, or approximately a 1,000-fold lower concentration than the level that would classify it as hazardous (provided, of course, that no other contaminants are present at levels exceeding national primary drinking water standards). Now, some naturally occurring groundwaters, which would be classified as USDWs, contain benzene in excess of drinking water standards, but that will not be covered here.

### *4.3.4. Classes of Wells*

As noted in Section 4.1 above, injection wells are used for a wide range of wastes, each with distinctive attributes and requirements. Therefore the promulgation of UIC regulations, of necessity, required the classification of wells by use. This classification is set forth in 40 CFR § 144.6, in which injection wells are divided into five classes:

- *Class I.* (1) Wells used by generators of hazardous waste or owners or operators of hazardous waste management facilities to inject hazardous waste beneath the lowermost formation containing, within one- quarter mile (0.4 km) of the wellbore, an underground source of drinking water. (2) Other industrial and municipal disposal wells which inject fluids beneath the lowermost formation containing, within one quarter mile (0.4 km) of the wellbore, a USDW.
- *Class II.* Wells which inject fluids related to the production of oil or natural gas.
- *Class III.* Wells which inject for extraction of minerals such as sulfur, salt, potash, or metals such as uranium by solution mining.
- *Class IV.* Wells used to dispose of hazardous or radioactive waste, into or above a formation which, within one-quarter (1/4) mile of the well, contains a USDW or an exempted aquifer. These wells are now effectively prohibited.
- *Class V.* Injection wells not included in Classes I, II, III, or IV.

### *4.3.5. Regulations Governing the Operation of Class I Wells*

Of the five classes of wells recognized by EPA, the regulations governing Class I wells are likely to be relevant to regulations governing the eventual storage of $CO_2$ in brine-filled formations. Regulations regarding Class II wells are likely to be relevant to geologic storage of $CO_2$ in oil, gas and coal-bed methane reservoirs. The criteria and standards applicable to Class I wells are very stringent, and even more so for those Class I wells injecting hazardous waste. Those applicable to wells injecting nonhazardous waste are given in Subpart B of Part 146, and those for wells injecting hazardous waste are given in Subpart G of Part 146. Each subpart is loosely subdivided into seven categories covering the following requirements:

- Information Required for Authorization (Permitting) by the Director of EPA.
- Siting.
- Construction.
- Operation.
- Monitoring
- Ambient Monitoring.
- Reporting.
- Closure and Post Closure requirements.

Permit requirements, and the requirements for siting, construction, and operation, are abstracted in the following paragraphs of this section (Section 4.3). Monitoring and reporting requirements are abstracted in Section 4.4 and post-closure requirements are abstracted in Section 4.5. Some regulations for Class I wells that inject hazardous waste are much more stringent than those for wells that inject nonhazardous waste. Where differences are significant, they are noted. The following discussion refers only to federal regulations; where states have primacy, the regulations are sometimes even more stringent.

#### *Application for a Permit to Operate a Class I Well*

The permitting process for authorization to operate a Class I well is elaborate, time consuming, and sometimes expensive. To obtain a permit, the owner or operator must submit a petition to EPA describing all aspects of the proposed operation, including well siting, design, and operation, and conduct hydrologic modeling and geochemical modeling (if feasible) to demonstrate that migration will not occur beyond the injection zone.

The need for adequate site characterization, especially for Class I hazardous waste wells, is particularly critical to ensure that no failure occurs for whatever reason, and that hazardous waste will be contained for at least 10,000 years or become nonhazardous during that period. The petition has therefore come to be known as a “No-Migration Petition.” Because of the 10,000-year period required for post-closure regulatory compliance, experimental verification is not feasible, and therefore much of the justification necessary to demonstrate waste containment must depend on predictive modeling. This modeling usually takes the form of numerical simulations, supported by limiting-case analytical models used to verify the numerical model, and conceptual models based on an understanding of the hydrologic and chemical processes occurring in the subsurface environment. The no-migration petition could take one or both of two forms: “A Fluid Flow Petition,” or a “Waste Transformation Petition” (USEPA, 2001e). Because quantitative information describing the chemical processes that render waste nonhazardous are usually understood only qualitatively, geochemical arguments supporting the fate or attenuation of hazardous wastes are not normally invoked, and therefore, waste transformation petitions are rarely submitted. Instead, most modeling invokes hydrologic arguments to demonstrate confinement over the 10,000-year period. Furthermore, because many parameters used in the models are not precisely known, it is also common practice to select limiting conservative values, leading to modeling results that represent worst-case scenarios. If these results show satisfactory containment, then it can be argued that a more realistic assessment would predict an even smaller likelihood of failure.

A flowchart illustrating the permitting process is given in Figure 4.4. The EPA regional offices are responsible for reviewing all no-migration petitions for Class I hazardous waste wells. As pointed out by USEPA (2001e), the review process allows EPA to gain valuable experience that may affect future land-disposal restrictions (LDRs). The review process is lengthy and time consuming, owing to the vast quantity of information required, and the interdisciplinary nature of the petition. This requires that a close working relationship be established between the petitioner, EPA regional staff, and any consultants brought in by EPA to aid them in a detailed analysis of the petition contents. The petition documents can fill as many as a dozen full-size binders, and it is inevitable with so much technical material that deficiencies are identified, and these must be rectified through the issuance of so-called “Notices of Deficiency” (NoDs). Thus, the petition review process is not only labor intensive, it is also time consuming, and can take the best part of a year to accomplish. Brasier and Kobelski (1996), citing an earlier report by the EPA (USEPA, 1991), state that the EPA dedicated over 2,000 employee hours to the review of each demonstration, and that industry, for its part, spent an average of $343,000 for each demonstration. According to USEPA (2001e), factoring in the costs for geologic testing and modeling, a no-migration petition can cost in excess of $2,000,000.

Each petition is subject to public notice and comment, and EPA publishes a preliminary notice concerning its disposition. EPA also offers public hearings, prepares a “fact sheet” or statement of basis, and responds to all submitted comments. Notice of the final decision regarding the petition is published in the Federal Register (USEPA, 2001e).

The application for a permit for construction and operation of an injection well must be submitted to the EPA Director in accordance with the UIC program. A permit will not be issued unless the application contains all of the information required by UIC regulations, which is very comprehensive.

The duration of the permit for a Class 1 well does not exceed 10 years. For a period extending beyond ten years, the permit may be reissued, in which case, the entire permit application is reopened and subject to revision, and the permit is issued for a new term.

One of the conditions of the permit is that the permittee shall at all times properly operate the facility to achieve compliance, including proper operation and maintenance, adequate funding, staffing, and training, adequate laboratory and process controls, and appropriate quality assurance procedures.

### *4.3.6. Information Required in a Permit Application*

To obtain a permit for the operation of a Class I well, the owner or operator must submit a petition to the EPA Director containing a substantial amount of information. Apart from normal administrative requirements relating to the adherence to all applicable federal and state laws (including environmental laws), location and ownership of the facility, and record keeping, many technical information needs must be met. These can be subdivided into information needs prior to well construction and those after well construction.

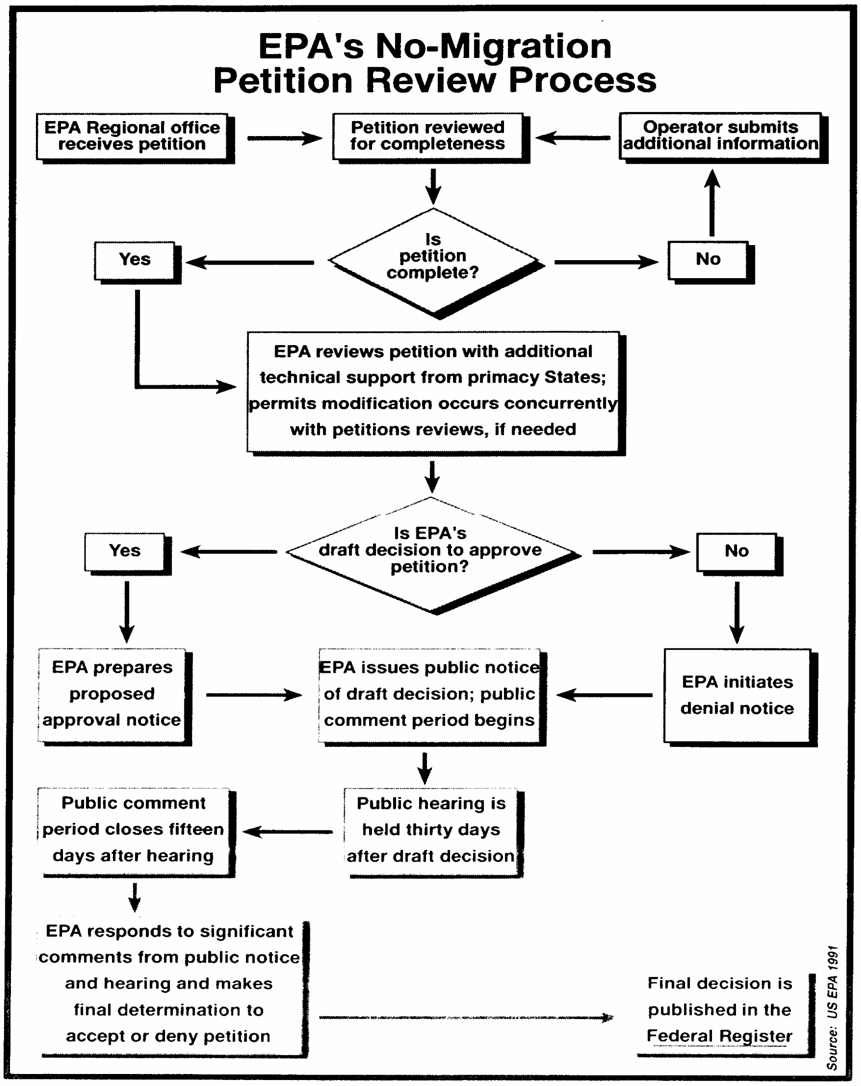


**Figure 4.4. A flow chart illustrating EPA's no-migration review process for Class I deep-well-injection disposal facilities (from Clark, 1999).**

In the following discussion regarding information needs, frequent reference is made to the so-called "area of review" (AoR). The AoR refers to the area surrounding an injection well, which is determined by criteria set forth in §146.06, or in the case of a project, the project area plus a circumscribing area, the width of which is either 1/4 of a mile (0.4 km) or a number calculated according to §146.06, using a modified Theis equation. The options for establishing the AoR under §146.06 include one based on the lateral distance from a well or designated area in which the pressures in the injection zone could cause the migration of fluid from the injection zone into a USDW, or alternatively, it could be based on calculations using a modified Theis equation.

*Information Needs Prior to Construction of the Well*

- A topographic map extending one mile (1.6 km) beyond the property boundaries of the source depicting the facility and its component parts and the injection well(s) for which a permit is sought and the applicable AoR. Within the AoR, the map must show all producing wells, dry holes, surface bodies of water, springs, mines (surface and subsurface), quarries, water wells and other pertinent surface features including residences and roads.[1] The map should also show geologic faults. For wells injecting nonhazardous waste, only information of public record needs be included on this map.
- A tabulation of data on all wells within the AoR which penetrate into the proposed injection zone.
- For wells injecting hazardous waste, the protocol followed to identify, locate, and ascertain the condition of abandoned wells within the AoR which penetrate the injection or the confining zones.
- Maps and cross sections depicting all USDWs within the AoR.
- Maps and cross sections detailing the geologic structure of the local area and the regional geologic setting.
- Proposed operating data including the daily rate of the fluid-injected, the injection pressure, and an analysis of the chemical, physical, radiological and biological characteristics of injection fluids.
- Proposed formation testing program to analyze the chemical, physical and other characteristics of the receiving formation and, in the case of well injecting hazardous waste, also the confining zone.
- Proposed stimulation program.
- Proposed injection procedure.
- Drawings of the construction details of the well.
- Contingency plans to cope with shut-ins or well failures so as to prevent migration of fluids into any USDW.
- Plans for meeting monitoring requirements.
- Corrective action for improperly completed or plugged wells within the AoR, which penetrate the injection zone.
- Construction procedures.
- A performance bond is necessary to close, plug or abandon the well and, in the case of hazardous waste wells, also for post-closure care.

*Information Needs Consequent to Construction of the Well*

- Logging and testing program data on the well.
- A demonstration of mechanical integrity.

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[1] EPA estimates that there may be as many as 300,000 abandoned wells and 100,000 producing wells potentially in AoRs of Class I injection wells (USEPA, 2001).

- Maximum operating pressure and flow rate.
- The results of the formation testing program. For wells injecting hazardous waste, the injection zone and confining zone must be tested specifically.
- The actual injection procedure.
- The compatibility of injected waste with formation fluids and host rocks in both the injection zone and the confining zone.
- For wells injecting hazardous waste, the calculated AoR based on data obtained during logging and testing of the well and the formation.
- Corrective action on defective wells in the AoR.

Finally, the owner or operator has to certify that the generator of the hazardous waste has a program to reduce the volume, or quantity and toxicity of the waste, and that the injection of the waste is currently the most practical method that, if hazardous, minimizes "present and future threat to human health and the environment."

### *4.3.7. Siting Requirements*

All Class I wells must be sited in such fashion that they inject into a formation, which is beneath the lowermost formation containing, within 1/4 of a mile (0.4 km) of the wellbore, a USDW. However, wells injecting hazardous waste also have the following additional minimum siting requirements:

Class I hazardous waste injection wells must be restricted to geologically suitable areas. An analysis must be conducted of the structural and stratigraphic geology, the hydrogeology, and the seismicity of the region, and of the local geology and hydrogeology of the well site. The geology of the area must be described with sufficient confidence that the limits of waste fate and transport can be accurately predicted through the use of models.

The injection zone must have sufficient permeability, porosity, thickness, and areal extent to prevent migration of fluids into USDWs. The confining zone must be laterally continuous and free of crosscutting, transmissive faults, or fractures over an area sufficient to prevent the movement of fluids into a USDW, and it must contain at least one formation of sufficient thickness and characteristics to prevent vertical propagation of fractures. Furthermore, the confining zone must be separated from the base of the lowermost USDW by at least one sequence of permeable and less permeable strata, which will provide an added layer of protection for the USDW in the event of fluid movement in an undetected transmissive pathway. Finally, within the AoR, the piezometric surface of the fluid in the injection zone must be less than the piezometric surface of the lowermost USDW, or a USDW must be absent.

### *4.3.8. Construction Requirements*

The requirements for construction of a Class I well vary somewhat, depending on the nature of the waste, i.e., whether hazardous or nonhazardous, and if nonhazardous, whether or not the waste is treated sewage. The most stringent requirements pertain to wells injecting hazardous waste, and a design incorporating all of the desired features for such wells is illustrated in Figure 4.5.

In the following paragraphs, the pertinent regulations regarding the construction of Class I wells are summarized.

All Class I wells must be cased and cemented to prevent the movement of fluids into or between USDWs. Materials used in the construction of each newly drilled well must be designed for the life expectancy of the well and to prevent potential leaks.

Hazardous waste wells must also be constructed and completed to prevent the movement of fluids into any unauthorized zones, allow the use of appropriate testing devices and workover tools, and permit continuous monitoring of injection tubing and long-string casing.

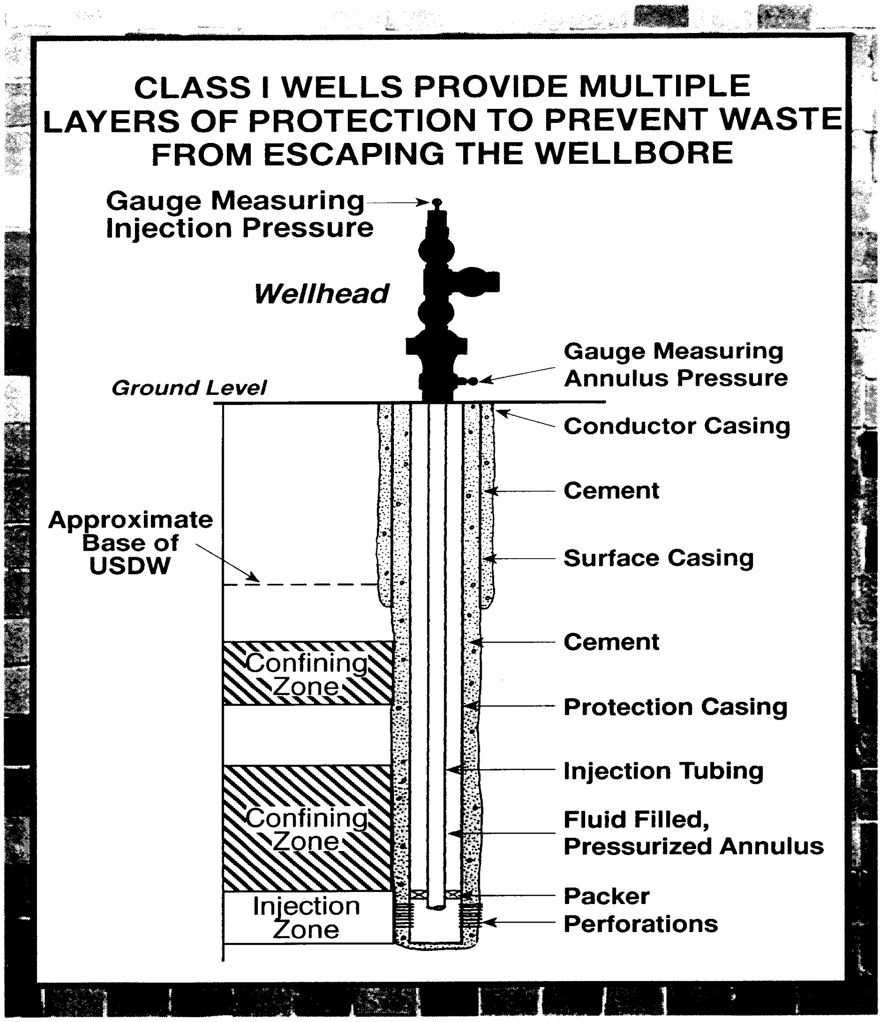

**Figure 4.5. A typical configuration of a Class I hazardous waste injection well (from Clark, 1999).**

In determining and specifying casing and cementing requirements, the following factors must be considered:

- Depth to the injection zone.
- Injection pressure, external pressure, internal pressure, and axial loading.
- Hole size.
- Size and grade of all casing strings.

- Corrosiveness of injected fluid, formation fluids, and temperatures.
- Lithology of injection and confining intervals.
- Type or grade of cement.

Furthermore, for hazardous waste wells, specifically, all well materials must be compatible with fluids with which the materials may be expected to come into contact and must be designed for the life expectancy of the well, including the post-closure care period. (See section 4.6.4.) For this reason, the quantity and chemical composition of the injected fluid must be considered.

All Class I injection wells, except those municipal wells injecting noncorrosive wastes, shall inject fluids through tubing with a packer set immediately above the injection zone, or tubing with an approved fluid seal as an alternative. The tubing, packer, and fluid seal shall be designed for the expected service.

For wells injecting hazardous waste, the requirements for emplacing the casing are more stringent. One surface casing string must extend into the confining bed below the lowest formation that contains a USDW and be cemented by circulating cement from the base of the casing to the surface. In addition, at least one long-string casing, using centralizers, must extend to the injection zone and be properly cemented by circulating suitable cement to the surface in one or more stages.

In determining and specifying requirements for tubing, packer, or alternatives, the following factors shall be considered:

- Depth of setting.
- Characteristics of injection fluid (chemical content, corrosiveness, and density).
- Injection pressure.
- Annular pressure.
- Rate, temperature and volume of injected fluid.
- Size of casing.

In addition, for wells injecting hazardous waste, the tubing tensile, burst, and collapse strengths must be considered. The EPA Director specifies the position of the packer.

Appropriate logs and other tests must be conducted during the drilling and construction of new Class I wells. Information concerning fluid pressure, temperature, fracture pressure, and other physical and chemical characteristics of the injection zone formation matrix, and physical and chemical characteristics of the formation fluids, must be determined or calculated for new Class I wells. For wells injecting hazardous waste, these requirements apply to both the injection and confining zones. Whole cores or sidewall cores of the confining and injection zones and formation fluid samples from the injection zone must be taken. The fluid temperature, pH, conductivity, pressure, and the static fluid level of the injection zone must also be recorded.

The logging requirements for wells injecting hazardous waste are more stringent, as follows. During the drilling and construction, logs and tests must be run to determine or verify the depth, thickness, porosity, permeability, rock type, and salinity of any entrained fluids in all penetrated geologic units to assure conformance with performance standards. Such logs and tests are also needed to establish accurate baseline data against which future measurements may be compared. For surface casing intended to protect USDWs, resistivity, spontaneous potential, and caliper logs must be run before the casing is installed, and a cement bond and variable density log, and a temperature log run after the casing is set and cemented. Upon installing the long-string casing, resistivity, spontaneous potential, porosity, caliper, gamma ray, and fracture finder logs must be run before the casing is installed. A cement bond, variable density log, and a temperature log must be run after the casing is set and cemented. In addition, a mechanical integrity test must be run consisting of pressure test, a radioactive tracer survey, and a temperature or noise log.

Upon completion of a Class I well injecting hazardous waste, but prior to operation, the owner or operator must conduct pump or injectivity tests to verify the hydrogeologic characteristics of the injection zone.

### *4.3.9. Operating Requirements*

During operation of a Class I well, the injection pressure at the wellhead must not be so high that new fractures are initiated or existing fractures are propagated in the injection zone. Furthermore, injection pressures must never initiate fractures in the confining zone or cause the movement of injected or formation fluids into a USDW.

Unless an alternative to a packer has been approved, the annulus between the tubing and the long string of casings must be filled with an approved fluid and maintained at an approved pressure.

For hazardous waste wells, the pressure in the annulus between the long-string casing and the injection tubing must, in general, always exceed the injection pressure. The fluid in the annulus must be noncorrosive and contain a corrosion inhibitor. The chemical integrity of the injection well must be maintained at all times. If the injected waste could react with the injection formation and generate gases, conditions limiting the temperature, pH, or acidity of the injected waste will be imposed, and procedures must be in place to assure that pressure imbalances that might cause a backflow or blowout do not occur.

In addition, the injection pressure, flow rate, volume, and temperature of injected fluids, as well as the pressure on the annulus between the tubing and the long-string casing, must be monitored and recorded continuously. Automatic alarm and shut-off systems, designed to sound and shut-in the well where pressures, flow rates, or other parameters exceed specified values, must be incorporated in the monitoring system, or trained operators should be on hand to take action if automatic shut-off facilities are not installed. If an automatic alarm or shutdown is triggered, the cause must be identified expeditiously. If the well appears to lack mechanical integrity, the injection of waste fluids must cease, and steps must be taken to determine whether a leak or loss of mechanical integrity has occurred. EPA must also be notified within 24 hours. If, in addition, there is evidence that the injected wastes leaked into an unauthorized zone, steps must be taken to identify and characterize the extent of the release and an EPA-approved remediation action implemented. If the release is into a USDW currently serving as a water supply, a notice must be posted in a general circulation newspaper.

Finally, EPA must approve of any workover of a hazardous waste well.

## 4.4. Risk Management Approaches: Monitoring and Reporting Requirements

To ensure that a Class I well is operated in a safe manner, certain monitoring activities are required of the operator or owner. Monitoring falls into four broad categories:

- Monitoring of the integrity of the components of the injection well.
- Monitoring of the composition, volume and physical characteristics of the waste stream to ensure compatibility with the well construction materials.
- Monitoring of injection pressure.
- Ambient monitoring.

The last category refers to conditions in the injection zone, confining zone, and adjacent USDW aquifers, and includes any monitoring wells that, if installed, must be monitored. Monitoring requirements for hazardous waste wells are more stringent than those injecting nonhazardous waste, and are noted in the following description.

### *4.4.1. Testing and Monitoring Requirements*

Testing and monitoring requirements must include:

- The analysis of the injected fluids with sufficient frequency to yield representative data of their characteristics.
- Installation and use of continuous recording devices to monitor injection pressure, flow rate and volume, and the pressure on the annulus between the tubing and the long string of casing.
- A demonstration of mechanical integrity at least once every five years.
- Identifying wells within the AoR to monitor any migration of fluids into and pressure in USDWs.

Materials must be monitored quarterly for corrosion to ensure that the well components meet the minimum standards for material strength and performance.

For hazardous-waste injection, an approved waste analysis plan must be followed that describes the procedures to obtain a chemical and physical analysis of the waste. The plan must specify the parameters to be analyzed and the test and sampling method used. The injected wastes must be analyzed at frequencies specified in the waste analysis plan and when process or operating changes occur that may significantly alter the characteristics of the waste stream. Continuous or periodic monitoring of selected parameters may also be required.

It must be shown that the hazardous waste stream and its anticipated reaction products will not alter the permeability, thickness, or other relevant characteristics of the confining or injection zones. The hazardous waste stream must be compatible with the well materials with which the waste will come into contact. Continuous corrosion monitoring of the construction materials used in the well for wells injecting corrosive waste is required by placing coupons fabricated of well construction materials in contact with the waste stream. Such materials must be continuously exposed to the operating pressures and temperatures and flow rates of the injection operation.

Wells injecting hazardous waste must also be subjected to mechanical integrity testing, including:

- Annual pressure testing of the long-string casing, injection tube, and annular seal, or whenever there has been a well workover.
- Annual testing of the bottom-hole using a radioactive tracer survey.
- Temperature, noise, or other logs every five years to test for movement of fluid along and behind the borehole.
- Casing inspection logs whenever a workover is conducted in which the injection string is pulled.

### *4.4.2. Ambient Monitoring*

A monitoring program will be required, the extent depending upon the potential for fluid movement from the well or injection zone, and on the potential value of monitoring wells to detect such movement. At a minimum, annual monitoring of the pressure buildup in the injection zone will be required. EPA may also require continuous monitoring for pressure changes in the first aquifer overlying the confining zone and, if a well is installed, the aquifer must be sampled and analyzed periodically for selected constituents and for water quality. If a well is installed in the lowermost USDW, it must also be analyzed periodically for water quality. Any additional monitoring necessary to determine whether fluids are moving into or between USDWs may be required. For wells injecting hazardous waste, EPA may require seismicity monitoring if injection has the capacity to cause seismic disturbances.

### *4.4.3. Reporting Requirements*

The EPA and state agencies responsible for environmental protection require certain minimum reporting requirements as related to monitoring of a deep well injection facility. The following requirements are specified in 10 CFR Part 146, Subparts B and G. Additional reporting requirements may be specified by EPA depending on site-specific conditions.

Reports must be submitted to EPA on a quarterly basis. They must include:

- The physical, chemical and other relevant characteristics of injection fluids.
- Monthly average, maximum and minimum values for injection pressure, flow rate and volume, and annular pressure.
- Monitoring results.

Results of periodic mechanical-integrity tests or any well workover must be submitted to EPA with the first quarterly report after completion, or within 30 days for hazardous waste wells.

Additionally, for wells injecting hazardous waste, the quarterly reports must also include:

- The maximum injection pressure.
- A description of any event that exceeds operating parameters for annulus pressure or injection pressure.
- A description of any event which triggers an alarm or shutdown device and the response taken.
- The total volume of fluid injected.
- Any change in the annular fluid volume.

### *4.4.4. Discussion of Monitoring and Reporting Requirements*

Extensive monitoring is required to ensure the continuing integrity of the well components through physical and mechanical integrity testing, and through continuous monitoring of the waste stream, to ensure that the waste stream will not corrode the well components. However, required "ambient" monitoring (i.e., monitoring of what is going on in the injection zone, confining horizons, and adjacent USDW aquifers) is restricted only to periodic pressure testing using the injection well. If additional wells have been installed or are available for monitoring contaminant migration or detecting communication with the injection zone through pressure testing, EPA can mandate that monitoring be conducted using these wells. Otherwise, no requirement exists to perform ambient monitoring for contamination of aquifers overlying the confining layers, including USDWs. According to the EPA (1985), in the originally proposed UIC regulations, the installation of monitoring wells was required, but was relaxed in the final regulations because there was no technology available that would define the siting of these wells. Furthermore, the drilling of multiple monitoring wells into a very deep interval would be prohibitively costly. Thus, the application of monitoring wells has been limited, mainly for hydrologic testing (Warner, 1996).

Concern that *in situ* monitoring was not required was brought up by Gordon and Bloom (1985), who considered that UIC regulations at the time failed "…to require monitoring of (a) underground sources of drinking water through which or near where the wellbore passes; (b) the injection zone; and (c) the confining layers to determine whether contaminants have migrated." They concluded that the technical controls of injection well operations should be strengthened so as to better detect and prevent migration of wastes to groundwater by "requiring the owner or operator of the injection well to continuously monitor the injection zone, the confining strata and underground sources of drinking water to indicate any adverse effect of the waste on the injection zone or confining strata or the migration of waste into fresh water supplies. Monitoring wells should be required in numbers sufficient to document waste movement, composition, and pressure within the injection zone and to document pressure changes and waste migration into resource-bearing strata."

Another feature of the monitoring program is the nonspecific nature of the requirements for monitoring the composition of the injected waste stream. The actual time interval required for conducting chemical analyses is left to the discretion of EPA, or the responsible state authority if the state has assumed responsibility. Given the wide range of chemical compositions within the waste streams, and range of potential toxicities, such flexibility in setting analysis schedules appears reasonable.

## 4.5. Risk Mitigation and Remediation Methods

Injected wastewaters can contaminate an overlying potable aquifer or USDW (USEPA, 1980; Gordon and Bloom, 1985) by:

- Leakage through inadequate confining beds.
- Leakage through confining beds caused by unplanned hydraulic fracturing.
- Leakage caused by preferential dissolution and creation of channels through the confining layers (otherwise known as rat-holing).
- Displacement of saline groundwater into a potable aquifer.
- Migration of injected liquid into a potable water zone within the same aquifer.
- Injection into an aquifer that is eventually reclassified as a potable water source.
- Upward migration of waste liquid from the confining zone along the outside of the well casing.
- Escape into potable aquifer due to wellbore failure.
- Vertical migration and leakage through abandoned or closed wells in the vicinity.

Not all of these mechanisms are equally plausible, and some are rendered highly unlikely by changes in UIC regulations governing the design of Class I wells in 1988 to minimize the likelihood of USDW contamination resulting from well failure.

Recently, the CMA undertook a probabilistic risk assessment of component failure of a hazardous waste well system (Clark, 1999; Rish and Long, 2001)) and showed that failure of any of the system components under current regulations was very unlikely, in most cases, much less than $10^{-6}$. See Table 4.2.

**Table 4.2. Probabilistic assessment of component failure of a Class I hazardous-waste-injection well (from Clark, 1999).**

| Failure Mode | Probability |
|---|---|
| Packer leak | $2.0\ 10^{-17}$ |
| Major packer failure | $1.5\ 10^{-15}$ |
| Injection tubing leak | $2.7\ 10^{-17}$ |
| Major injection tubing failure | $2.1\ 10^{-8}$ |
| Cement micro-annulus leak | $2.1\ 10^{-6}$ |
| Confining zone(s) breach | $8.8\ 10^{-10}$ |
| Inadvertent injection zone extraction | $6.6\ 10^{-7}$ |

The risks associated with well failure have been drastically reduced through enhanced engineering design of the well components, the imposition of multiple barriers in well design, the requirement of multiple confining beds, and rigorous monitoring and reporting requirements. However, the ambient environment remains difficult to characterize, despite the application of hydrogeologic testing, well logging of the geology from drill cores and cuttings, and seismic imaging. Therefore, quantification of failure-event probability distributions relating to waste containment in the injection zone is challenging, and commonly requires estimates based on professional judgment rather than the statistical evaluation of parameters from field data. Furthermore, unlike failure probabilities associated with well design, emplacement, and operation (which are insensitive to well location), the ambient geology can vary markedly with geographic location. Thus, a very large uncertainty about the containment integrity of an injection zone will remain at many sites.

Were an aquifer containing a USDW to be contaminated, it would be very difficult, if not impossible, to restore it to a pristine condition. Many factors are involved: the nature of the contaminant, the distribution of the contaminant within the aquifer, the chemical properties of the contaminant, i.e., whether it strongly adsorbs to organic and inorganic substrates, whether it undergoes rapid hydrolysis, decomposition or biologic degradation or, by its nature, never decomposes or transforms to innocuous products. The treatment options are also numerous, ranging from pump-and-treat to containment or natural attenuation *in situ*. The unit cost of recovering and treating contaminated water will vary greatly, depending on the factors listed above, the depth of the aquifer, the nature of the separation procedure, and local sociological pressures.

With deep wells, the problem is compounded by the cost associated with field measurements necessary to define the magnitude and extent of any contamination. Although indirect methods of measuring the distribution of waste in an aquifer exist, particularly if a large density contrast exists between the groundwater and the contaminant (as is the case with $CO_2$), in most other cases plume migration can only be defined through the drilling of a multiplicity of wells. For shallow aquifers, this approach is acceptable, because the cost of drilling and casing wells is relatively small and using strategic design methods can minimize the number of holes drilled. However, the costs escalate dramatically with depth and, as a result, plume delineation becomes economically infeasible. It would be less costly to monitor an overlying shallow USDW, particularly one that is currently being exploited for potable or agricultural use. However, if contamination were to be detected, the damage would already have been done, and depending on the nature of the contamination and water usage, remediation could also be prohibitive.

Faced with the regulatory dilemma that cleanup of a deep aquifer containing USDW would be practically impossible to enforce, if detected, EPA has adopted the approach of stringent regulation of deep-well-injection operation, with the goal of ensuring that contamination does not occur in the first place. Most of the regulatory control targets the siting, construction, and operation of the well itself and peripheral injection facilities. As for contamination of USDW aquifers distant from the wellbore, some efforts to detect transmissive faults between the injection zone and overlying USDW aquifers are mandated, and if monitor wells are already in place in overlying protective aquifers, EPA also requires that these must be monitored for contamination.

As for detection of contamination distant from the wellbore, both industry and EPA have adopted a policy that does not require monitoring wells. An owner or operator of a new Class I facility who goes to the expense of installing monitoring wells in aquifers overlying the injection zone and confining beds, only to be exposed to litigation, fines, and possible bankruptcy should contamination of a USDW occur, may not be motivated to do so unless required to. This liability extends, in the situation where hazardous waste is injected, in perpetuity. There are, however, sound technical arguments that such contamination is unlikely to occur when the waste stream is denser than the ambient groundwater in the injection zone, and when injection pressures are maintained in accordance with permit requirements. Furthermore, after injection has ceased, and the pressure transient caused by fluid injection has decayed, there would be no pressure gradient through the confining beds to force the waste into an overlying USDW. Hence, the actual amount of contaminant migration by transmission through faults or joints in the confining beds would be small in magnitude even if it were to occur. For hazardous waste injection wells, an additional level of protection is afforded through the requirement that more than one confining layer be present overlying the injection zone. Multiple confining layers would increase the level of confidence that containment would be effective, because the probability of all layers failing would be much less than the failure of a single layer. In fact, expert judgment assigns a failure probability of only one part in $10^{10}$ (Rish and Long, 2001).

Should the waste fluid be less dense, upward migration through conductive paths in the confining beds would occur whether or not injection were taking place. Under these conditions, a multiplicity of confining beds separated by permeable aquifers could lead to progressive dispersion and dilution of the waste, increasing the host rock reactive-surface area, and allowing for immobilization by sorption before the waste stream encounters a USDW. However, such favorable conditions may not always be present. It is also possible that a conductive fault could penetrate or offset the confining beds, allowing a direct conduit for the buoyant waste to ascend to an overlying USDW.

The consequence of stringent regulations governing Class I hazardous waste wells has been that there have been no observed and reported occurrences of contamination of USDWs by facilities operating these wells under current regulations since amended UIC regulations were promulgated in 1988. Most violations before 1985 (and probably since that time) were minor and were related to paperwork procedures, failure to install barriers or improper recording devices (USEPA, 1985). Since that time, two additional studies have been conducted to assess the nature and frequency of operational problems ($CH_2M$ Hill, 1986; USGAO, 1987). According to USEPA (2001e), the $CH_2M$ Hill study identified 26 malfunctions involving 43 wells, suggesting an overall malfunction rate of 9%. Only six wells (or 2% of all Class I wells) experienced malfunctions that resulted in contamination of a USDW. The GAO study reported only two cases of USDW contamination and eight cases of contamination of nonpotable aquifers. In all cases, contamination occurred prior to 1980.

More recently, EPA has analyzed mechanical integrity (MI) failures in all Class I wells in selected states between 1988 and 1991 (USEPA, 2001e). One hundred thirty cases of internal MI failures were reported, i.e., those attributed to leakage from the injection tubing or failure of the long-string casing. Only one external MI failure occurred, involving flow along the outside of the casing. There were four cases of nonhazardous waste migration, three of which were detected by monitoring wells and a fourth during the drilling of a new injection well. EPA sponsored a second analysis of MI failures for the time period 1993–1998 (ICF Inc., 1998). Although the overall rate of failures declined to half the rate in all states, they increased in Texas to 65%. This rate was challenged by the Texas Resource Conservation Commission (TNRCC), which estimated a failure rate of 37%. These latest results require further review. The relatively high failure rate of well components reinforces the need for multiple safeguards in containing the waste (i.e., a system of barriers and continuous monitoring to detect failure).

According to USEPA (1985), cases of noncompliance or violations are handled at a level commensurate with the nature of the violation. Where states have jurisdiction, operating violations were generally resolved through informal agreements, which are regarded as effective in attaining compliance. For more serious violations, enforcement tools used by state agencies include formal notices of violation, consent agreements, and judicial action. These are used in cases of failure to report data, well construction problems, loss of well mechanical integrity, and exceeding pressure limitations. However, the extent to which UIC regulations are enforced is not adequately known. For example, the Cadmus Group (1993) found that most radioactive tracer surveys in Texas were not conducted according to TNRCC guidelines, and 29 percent of the wells had no cement bond logs on file. Most wells that did have logs showed insufficient cement casing. There is also evidence of lax enforcement of monitoring requirements for Florida Class I municipal waste wells (as discussed below). Strict adherence to UIC regulations and ongoing federal or state enforcement (as appropriate) should ensure that deep-well-injection disposal operators and owners avoid serious infractions, and maintain a safe, efficient, and reliable operation of the injection facilities.

Since the promulgation of current regulations in 1988, contamination of potable aquifers in Florida by Class I wells injecting nonhazardous treated sewage has been reported. EPA's response to these violations by proposing amended regulations rather than a politically unacceptable cessation of injection and costly remediation is discussed in section 4.7.1 of this report. In addition, since 1988, EPA has pursued, through the U.S. Justice Department, two cases of purported contamination of USDWs through deep well injection. In both cases, the alleged violators were charged with injecting hazardous waste into an aquifer that was claimed to be a USDW. Continuing operation would, under RCRA, subject each company to substantial fines. In the case of one company, total potential fines were on the order of several hundred million dollars and would have been, if successfully levied, the largest environmental fine in history.

In the latter case, litigation was abandoned, because the evidence was insufficient to make a case that the aquifer was a USDW. Critical records giving the composition of the formation fluids were no longer available or were of insufficient quality to make an incontrovertible demonstration that the fluid salinity was less than 10,000 mg/L. In the other case, the company settled with a $3,500,000 fine, which was imposed for numerous smaller violations including surface as well as subsurface contamination (USDOJ, 1998). The subsurface contamination also involved the alleged injection of hazardous liquid waste into a USDW. The hazardous nature of the waste was decided by a site inspection by EPA, Environmental Services Division, Region 4, early in 1994, where it was determined that the waste stream contained MCL violating contaminants. The classification of the injection zone as a USDW was based on a series of drill-stem tests taken during construction of the injection wells. The recovered water samples had tested out with a TDS of less than 10,000 mg/L. However, there was no proof that the samples were formation fluids rather than drilling-fluid contamination of permeable formations during drilling, since no tracers had been used at the time of drilling. Because the chemical analyses of the recovered waters were incomplete, no incontrovertible interpretations could be made to show that the recovered waters were not formation fluids. The company tried to defend injection into the "USDWs" on the basis that no the recovery of potable water from an aquifer with marginal salinity from a depth of 5,000 ft., was economically or technically impractical. However, an analysis of the drill-stem test data showed that pumping of a "sufficient quantity of ground water to supply a public water system" was achievable. Therefore, regardless of the practicality of recovering water from such deep aquifers, the injected aquifers met the requirements under the definition of a USDW.

Despite the depth of the injection wells, and the fact that aquifers underlying the injection zone were highly saline, the company could only defend its position through the drilling of another injection well and conducting comprehensive tests. Yet this action also raised numerous other technical issues relating to the validity of the proposed hydraulic testing program, and the company finally decided that settlement was the preferred option.

In summary, the goal of the present regulatory climate regarding USDW contamination by waste, whether hazardous or not, is first and foremost to operate a Class I facility in such a manner that the risk of failure is extremely small. Secondly, regulations focus only on those failures that can be easily and effectively demonstrated. Finally, the laws as they are written, are erratically enforced, ranging from strict through lax enforcement, and even non-enforcement where the remedy was politically unacceptable. In the latter case, the regulations were modified to accommodate the situation at hand. The preferred enforcement approach, however, is through consent decrees and fines, rather than by remediation.

## 4.6. Closure and Post-Operational Monitoring

### *4.6.1. Well Closure*

The EPA is particularly concerned that deep injection wells, especially those that have injected hazardous waste, are properly plugged and abandoned. Furthermore, the owner or operator of a well that injected hazardous waste must not only be responsible for proper closure, but also assume responsibility in perpetuity for any contamination to a USDW. The regulatory details concerning the closure and post-operational monitoring of wells used for the injection of hazardous waste are summarized in the following paragraphs.

### *4.6.2. Petitioning for Abandonment or Closure*

The owner or operator of a Class I hazardous waste injection well must submit and comply with a closure plan as part of the permit application. This obligation remains after cessation of injection activities and is enforceable regardless of whether the requirement is a condition of the permit.

Prior to granting approval for the plugging and abandonment of a Class I well, the EPA will consider the plugs to be used and the placement of each plug, the material to be used, and the method for placement of the plugs. Additionally, information will be required on the casing and any other materials to be left in the well. Also, the procedure to be used to meet the requirements, the estimated cost of closure, and any proposed tests or measurements must be submitted.

### *4.6.3. Procedure for Closure*

At least 60 days before closure, the owner or operator must notify EPA of his intention to close the well. Within 60 days after closure, he must also submit a closure report to EPA. Before closing the well, the pressure decay must be recorded and mechanical integrity testing conducted to ensure the integrity of any long-string casing and cement that will be left in the ground after closure. Such testing may include pressure tests, radioactive tracer surveys, and noise, temperature, pipe evaluation, or cement bond logs. The well must also be flushed with a buffer fluid.

Upon closure, a Class I hazardous waste well must be plugged with cement in a manner that will not allow the movement of fluids into or between USDWs. Each plug must be tagged and tested for seal and stability before closure is completed. The well must be in a state of static equilibrium.

### *4.6.4. Post-Closure Care*

The owner or operator of a Class I hazardous waste well must prepare and comply with a plan for post-closure care. This obligation to implement the post-closure plan remains after cessation of injection activities, and is enforceable regardless of whether the requirement is a condition of the permit. The plan must assure financial responsibility. It must include information on the pressure in the injection zone before injection began, the anticipated pressure in the injection zone upon closure, and the time predicted until the pressure decays to the point that the well's cone of influence no longer intersects the base of the lowermost USDW. The plan must also include the predicted position of the waste front at closure, the status of any cleanups required, and the estimated cost of proposed post-closure care.

The owner or operator must continue to conduct any required groundwater monitoring until pressure in the injection zone decays to the point that the well's cone of influence no longer intersects the base of the lowermost USDW. The owner or operator must also meet a number of administrative requirements. These include submission of a survey plan to the local zoning authority with a copy to EPA, and notification of state and local authorities having cognizance over drilling activities, to enable them to impose appropriate conditions on subsequent drilling activities that may penetrate the well's confining or injection zones. The owner or operator must retain, for three years following well closure, records reflecting the nature, composition, and volume of all injected fluids, after which the records must be submitted to EPA.

A notation must be placed on the deed to the facility that will in perpetuity provide any potential purchaser of the property with information that the land was used to manage hazardous waste. Information must also be provided on the type and volume of waste injected, the injection interval(s) into which it was injected, and the period over which injection occurred.

*4.6.5. Financial Responsibility for Post-Closure Care.*

The owner or operator must demonstrate and maintain financial responsibility for post-closure care. This obligation survives the termination of a permit or the cessation of injection and is enforceable regardless of whether the requirement is a condition of the permit.

## 4.7. Case Histories

In the past, a number of incidents occurred when deep injection wells operated out of compliance, or caused contamination to formations other than those designated for injection. A summary of these incidents is provided in Table 4.3. Most of the cases have been abstracted from Gordon and Bloom (1985) with supplemental material from Hickey and Wilson (1982), Lester and Sullivan (1985) and USEPA (1993). The latter sources of information were critiques of then-current deep well injection practice, and the examples served to illustrate deficiencies not addressed by regulation at the time.

Since 1988, when more stringent regulations were introduced, substantive incidents involving contamination of formations or USDWs not designated as injection zones have been rare. Of those few known violations since that time, all but one can be traced to actual contamination when less stringent regulations were in force. The exception concerns USDW contamination by Class I injection facilities in Florida injecting treated sewage waste. Although it has been pointed out by a lobbyist for the CMA (Van Voorhees, 2001) that these Class I wells are “significantly different from Class I industrial wells,” in reality, it is only those wells injecting hazardous waste that are subject to significantly more stringent requirements. The nature of the problems arising from the operation of some of the Florida Class I municipal waste wells illustrate the need for extending stricter regulations governing hazardous waste injection to nonhazardous wastes. Because of its importance, reasons for the failure of some of the Florida waste wells and the environmental consequences are discussed further below.

Perusal of Table 4.3 indicates that many failures were caused by the use of well construction materials that were incompatible with the injected waste, leading to excessive corrosion of the well casing. Inadequate monitoring of annulus pressure to detect leaks, lack of early detection of fluid migration behind the well casing, or injecting waste at excessive pressures were also common failings. All such practices are prohibited under current regulations. In two cases, formation damage resulted from failure to remove particulate from the waste stream, resulting in the clogging of transmissive pores in the injection zone. Such practice, while not prohibited, jeopardizes the functioning of the well for waste disposal and would be costly to the owner. Somewhat more troubling are the reported occurrences of aquifer contamination, which cannot unequivocally be attributed to well failure, although detailed investigation might assign the cause in some cases to the latter. In at least two instances, detection of waste migration outside of the injection zone was made possible only through use of monitoring wells, which are not required under current federal regulations. In these cases, migration is presumed to have taken place along undetected fractures or transmissive faults in the confining horizons, or along lateral channel ways in the injection zone.

Given the frequency with which monitoring wells alone have detected contamination, it is somewhat disturbing to contemplate the potential frequency of undetected contamination caused by the absence of monitoring wells at many current Class I injection facilities. In this respect and others, the case involving Florida Class I injection wells injecting municipal waste is particularly relevant to issues that may arise during the deep-well-injection disposal of $CO_2$. The injected municipal waste is less dense than the formation fluids into which it is injected, and therefore has a tendency to migrate buoyantly upwards, finding and transiting structural breaks in the overlying confining beds. The mandated presence of monitoring wells in Florida makes it more likely that such leaks will be detected. However, current monitoring capabilities are insufficient to define the extent of contamination. Finally, the extraordinarily large volumes of sewage injected approach in scale the volumes of supercritical $CO_2$ that will require disposal. Therefore, it is important to understand the reasons underlying the multiple failures associated with deep well injection of sewage in Florida.

### *4.7.1. The Case of USDW Contamination by Class I Municipal Disposal Wells*

With passage of the SDWA of 1972, municipal authorities in Florida were faced with a dilemma regarding the disposal of treated sewage effluent. Prior disposal into waterways was now proscribed without expensive tertiary treatment. Alternatives were deep well injection or disposal at sea. The latter option was rejected because the sewage nutrient load would have stimulated uncontrolled algal growth and destruction of coral habitats, and compromised the pristine nature of Florida's tourist beaches. With federal subsidies, and encouragement from the EPA, municipalities therefore chose to dispose of treated sewage by subsurface injection. This low-cost disposal option, coupled with favorable state taxation, a favorable climate, and other factors, stimulated rapid urban development within south Florida, leading to sewage disposal rates far larger than originally anticipated. Quantities now approaching 450 million gallons (1.7 million $m^3$) are injected daily (USEPA, 2000c).

The geology underlying the state of Florida consists primarily of a sequence of Tertiary limestone formations overlain by shallow unconsolidated sands. Most of the limestones are relatively permeable, and some of the surficial formations have been subjected to karstic weathering. However, several relatively impermeable units within the limestone sequence have been identified. The Upper Floridan aquifer is the dominant permeable hydrologic unit within the limestone stratigraphic sequence, cropping out in the north of Florida, but dipping below unnamed surficial and intermediate aquifers, and thickening progressively towards the south. The Upper and Middle Confining Units bound it on the upper and lower sides, respectively. In the region of Miami-Dade County, the Upper Floridan is approximately 900 ft (275 m) thick and lies about 1,000 ft (305 m) below the surface. In the north, the water of the Floridan is potable and is recovered for domestic and industrial use. However, down dip it becomes increasingly saline, attaining 7,000 mg/L TDS (Sutherland, 1998). In Dade County, the base of the USDW is within the lower part of the Upper Floridan aquifer at a depth of approximately 1,600 ft (490 m). Overlying the Floridan is the Biscayne aquifer, which is the primary source of potable water for the 5 million inhabitants of southern Florida (Ground Water Protection Council, 2000).

Increasing demand for water has necessitated ground water pumping by counties and municipalities, and emplacement of so-called Aquifer Storage and Recovery (ASR) wells in the Upper Floridan aquifer. ASR facilities are used to store seasonal excess fresh water underground for future recovery when surface water is less freely available. They are becoming an essential component of water management in southern Florida and will be critical in restoring and protecting the Everglades from further environmental degradation (SFWMD, 2001). Increasing demand for water has necessitated ground water pumping by counties and municipalities, and emplacement of so-called Aquifer Storage and Recovery (ASR) wells in the Upper Floridan aquifer. ASR facilities are used to store seasonal excess fresh water underground for future recovery when surface water is less freely available. They are becoming an essential component of water management in southern Florida and will be critical in restoring and protecting the Everglades from further environmental degradation (SFWMD, 2001).

## Table 4.3. Problems associated with the operation of deep well injection facilities

| Company | Location | Period of Operation | No. of Wells | Depth of Injection (ft/m)) | Host formation | Amount of waste (gallons/$m^3$)) | Waste composition | Date of failure | Nature of Failure | Cause | Remedy | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hammermill Paper Co. | Erie, PA | 1964-1972 | 3 | 1500ft/460m | Bass Island Formation | 1100 Mgal /4.2 million $m^3$ | Spent pulping liquor | 1979 | Seepage of waste from an abandoned oil well 4.2 miles (6.8 km) away. Contamination of USDW | Inadequate plugging of abandoned oil well. Company denies responsibility for contamination | Listed in Superfund Priority List, 1982 | Migration of waste was more extensive than anticipated |
| Browning Ferris industries (BFI) commercial waste disposal facility | Lake Charles, LA | 1980 | 1 | 4000ft/ 1220m | Shale | | Multiple waste streams, not specified, | | Chemical contamination of uppermost aquifer below facility, identified from chemical analyses of 27 on and off-site monitoring wells. Recurrent leaks and corrosion of well casing. 40-60% l of well wall thickness observed | Company maintained that contamination was due to surface impoundments of waste, as a lower overlying aquifer was not contaminated | Revocation of permit to inject waste recommended | |
| Ohio Liquid Disposal, a subsidiary of Chemical Waste Management (CWM) | Vickery, OH | 1983 | 6 | | | 450 Mgal/ 1.7 million $m^3$ | Process waste waters containing PCBs | | 20 M gal. (76,000 $m^3$ lost into a shallower formation, separated from the lowermost USDW by 1500 ft (457 m), 1000 ft (305 m) of which is confining shale. Leaks in carbon steel casings of all wells, possibly due to exposure to corrosive fluids due to tubing damage during well cleaning. | Inability of well head monitoring to detect annulus leaks, migration of waste outside the wellbore, and failure of the operator to investigate signs of tubing and casing leaks. Pressure excursions due to leaks were too small to detect. | Ohio EPA levy a \$10M fine for groundwater contamination, and \$2.5M for violations of RCRA and TSCA. An additional \$10M for upgrading injection wells and implementing a comprehensive monitoring program | |
| Kaiser Aluminum And Chemical Corporation | Mulberry, FL | | | Below 4000ft/ 1220m | dolomite | | High chloride acidic wastes | | Leakage through confining beds detected through hydraulic tests using a satellite monitor well | | Apparently no action. It was assumed that the overlying beds were relatively impermeable and significantly retarded movement of neutralized waste | Acidic wastes produced a cavity in carbonate rock, 100 ft (30.5 m) high by a maximum of 23 ft (7 m) in diameter. |
| Hercules Chemical Corporation | Wilmington, DE | 1968 | | | | | Industrial organic waste, pH = 4.0, from production of diethyl terephthalate | | Vertical leakage through confining layers into overlying aquifer detected within 3 years | | | |
| Rocky Mountain Arsenal | Denver, CO | 1962-1966 | | 12000ft/ 3660m | Fractured gneiss | | | | Injected waste apparently induced rock failure, causing earthquakes ranging between 0.5 and 5.3 up to 5 km (3 mi) from the well at a depth of 5 km (3 mi). | | | |

## Table 4.3. (cont)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N/A | Pensacola, FL | 1963-1974 | 2 (1/4 mi. or 2/5 km apart) | 1400-1700ft/ 425-520m | Saline portion of limestone aquifer,<br>220 ft (67 m) clay confining bed. | | Industrial liquid from nylon plant, including acids, salts and organics. | | Pressure effects due to injection extended more than 40 miles (64 km) by 1974, extending beyond current area of review. Waste migrated at least 1.5 miles (2.4 km) from the wells. | | | 7 monitoring wells, of which 6 were used to observe hydrologic and geochemical effects of the injected waste; other well was shallow and used to monitor e limestone. |
| Browning Ferris industries (BFI) | Odessa, TX | 1979 | | | | | Incompatible waste streams | | Formation plugging. Injection pressures exceeded permissible limits over a six-month period. | No pretreatment is required to prevent plugging | | |
| E.I. DuPont de Nemours Co. | Orange Co., TX | 1973-1985 | >2 | | | | Incompletely filtered wastes | | Repeated plugging of the injection zone. | | In one well the original injected formation was abandoned, and injection started in an overlying stratum | |
| Chemical Resources Inc. (CRI) | Tulsa, OK | | | | | | | | Leakage of waste into formations overlying the injection zone. | Injection was conducted without monitoring, chemical analyses, and at excessive injection pressures | Operator under state orders to repair wells and subject to ongoing enforcement action | Leaks discovered as a result of mechanical integrity tests. |
| Sonic International inc. | Ranger, TX | | | | | | Corrosive chemical wastes | | Deteriorated tubing, packer and well casing, resulting in leaks. Waste entered formations other than those intended although no groundwater contamination occurred. A series of blowouts occurred. A neighboring oil well was contaminated, causing it to be shut down. | Blowouts presumably caused by $CO_2$ back pressures due to the reaction of the waste with carbonate rocks | Sonic International was cited for utilizing inadequate well monitoring and recording devices. Site was cleaned up, and wells plugged and abandoned. | |
| | Belle Glade, FL. | | | | | | Hot acidic and highly toxic organic waste from a sugar mill | | Upward migration of wastes through confining layers, reaching both deep and shallow groundwater monitoring wells, contaminating freshwater aquifers. | Severe dissolution of receiving strata. | | |

**Table 4.3. (cont)**

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Velsicol Chemical Corporation | Beaumont, TX | 1976 | | | | | Highly acid herbicide wastes, including dioxins, pH < 4. | | Contamination of formation water with a TDS of 4000 mg/L. by as much as 5 M gal (19,000 $m^3$) of waste. | pH of the injected waste was lower than authorized. No tubing installed. Corrosion of inner and outer casings, and cement grout. | Velsicol used an injection well to clean up contamination. Additional wells were drilled and 1.5 M gal. (5700 $m^3$) Pumped out. | |
| Tenneco | Chalmette, LA | | 1 | | | | Sour water refining waste | | Waste corroded through casing and tubing | | Well plugged and abandoned. Contamination was cleaned up through recovery wells and reinjection through several new injection wells. | |
| Hercofina | N.C. | | 4 | | | | | | Water leaked from the Injection zone into the Black Creek formation, containing TDS <150 ->10,000 mg/L | | Two injection wells were plugged and abandoned and two were used for monitoring. | |
| Aristech Chemical Corporation | Ironton, OH | | 1 | | | | Organic wastes | | Contamination of overlying Rose Run Formation. Migration attributed to small scale fracturing | | | Company denied responsibility |
| Zeneca Holding Inc. | Mount Pleasant, TN | 1973-1998 | 3 | | | | Waste waters from pesticide manufacture | | Rupture of casing between 2,000-3,000 ft (610-915 m). Contamination of Lower Knox aquifer. Injected aquifer was identified as a USDW. Injected wastewater contained contaminants in excess of drinking water standards. | Drill stem tests indicated that formation water contained less than 10000 ppm TDS | Company fined $3,500,000 for injecting 40 M gal (150,000 $m^3$) contaminated waste water annually, and for other infractions unrelated to deep well injection. Additional $15 M to be spent on new wastewater treatment facilities. All deep well injection disposal terminated | |
| Miami-Dade Water and Sewer South District | Miami-Dade Co., FL | | 17 | 2400ft/730m | Oldsmar Fm. | 20 M gpd/ 75,000 $m^3$ per day | Sewage after secondary treatment | 1994 | Migration of effluent into overlying UDSW, detected by monitoring wells. Evidencethat 10 wells were improperly completed. | Failure to discharge waste below impermeable bed. Failure to properly assess hydrologic properties of the confining layers. | EPA proposes changes to regulations to accommodate current violators. | Sites in two other counties are also in violation. |

At the base of the Middle Confining Unit is a thin impermeable dolomite horizon, approximately 15 ft (4.6 m) thick, beneath which is a so-called "boulder zone" of the Lower Floridan aquifer, an extremely permeable horizon, noted for its cavernous porosity. This boulder zone also contains highly saline pore water, which, together with the entire Middle Confining Unit and the lower part of the Upper Floridan aquifer, are excluded from qualification as a USDW. Municipal authorities chose to inject partially treated sewage into the boulder zone, anticipating that the Middle Confining Unit would isolate the injected waste from the Upper Floridan aquifer. Furthermore, the potentiometric surface within the Boulder Zone implied that groundwater migrated eastwards toward the Atlantic Ocean and would eventually discharge beneath the sea after several thousand years had elapsed and the waste had decomposed. Because the sewage was nonhazardous, and was to be discharged below the lowermost USDW, the injection wells fell under the classification of Class I for nonhazardous waste.

In contrast to federal regulations, the State of Florida requires the positioning of monitoring wells adjacent to Class I injection wells to monitor for contamination, and operators are required to monitor USDWs. However, the Florida Department of Environmental Protection (DEP) does not have funding to collect the data, and EPA Region 4 relies solely on voluntary compliance. Furthermore, despite the signing in January 1998 of a court settlement in the Eleventh Circuit Court of Appeals between the State of Florida and the Legal Environmental Assistance Foundation (LEAF), ordering the Florida DEP UIC program to abide by the SDWA, the DEP has failed to comply (Sutherland, 1998). Thus, efficient reporting of effluent contamination of USDWs in Florida is subject to the operators' cooperation (Sutherlan*d loc. cit*, FICUS 2001). Despite this defect, four counties in southern Florida (Miami-Dade, Broward, Palm Beach, and Pinellas) have detected sewage effluent in the Upper Floridan aquifer overlying the injection zone (Sutherland *loc. cit.*). More extensive contamination might be revealed with systematic data collection by the DEP. Under federal regulations, evidence of contamination would require EPA to order immediate cessation of injection. However, economic and political pressures against such action are overwhelming. After abortive attempts to force municipal authorities to upgrade their treatment of sewage so that the effluent met federal drinking water standards by "Advanced Wastewater treatment with Non-Endangerment Demonstration" (Bernstein, 2000), the EPA is now proposing a second option as an alternative means of complying with UIC regulations. This option, "In-depth Hydrologic Demonstration and Advanced Treatment," places on operators the onus of demonstrating "that the injected fluid would not cause USDWs to exceed national primary drinking water regulations." Operators contaminating USDWs would be allowed to continue to do so long as the effluent entering the USDW did not exceed any drinking water or health-based standards (USEPA, 2001c). However, those facilities already polluting USDWs could also request exemption on the basis that the contaminated aquifers are not currently and are not expected to be a future source of drinking water.

The economic implications regarding local contamination of the Upper Floridan aquifer are not immediately clear. The potential of the Upper Confining Unit to retard effluent migration into the overlying Biscayne aquifer has not been determined. However, the increasing utilization of the Upper Floridan aquifer as a source of drinking water and for ASR storage, coupled with uncertainties regarding the extent or magnitude of the pollution, raises concerns over the potential costs of remediation. But far more troubling is why, despite regulatory safeguards, such incidents of contamination should have occurred in the first place (Bernstein, 2000).

McNeill's investigation of the problems associated with deep-well-injection disposal of sewage effluent at the Miami-Dade Water and Sewer South District Plant (McNeill, 2000) suggests a multiplicity of causes for the current problem:

- Failure to conduct a sufficiently detailed evaluation of the stratigraphy and hydrology of the region targeted for deep well injection.
- Failure to take continuous cores of the confining beds.

- Inadequate testing and evaluation of the permeability and hydraulic conductivity of the Middle Confining Unit.
- Inability to deal adequately with cement grout losses in thief zones encountered in the vicinity of the injection zone, thereby compromising proper sealing around the wellbore.
- *Ad hoc* changes to the well completion interval in order to overcome grout losses in the Boulder Zone, resulting in well completion *above* the highly impermeable dolomite bed.

McNeill shows that critical mistakes and omissions were made in making a proper evaluation of the Middle Confining Unit above the dolomite horizon, leading site evaluators to conclude, or at least assert, that this unit would protect the upper Floridan Aquifer from upward migration of waste. In fact, the vertical permeability originally estimated by site evaluators for the Middle Confining Unit was thirty times less than McNeill subsequently determined from core material from another site 20 miles (32 km) away. This estimate, in turn, is corroborated by the observed effluent breakthrough in monitoring wells of 11 years instead of the originally predicted 343 years. Had the original site evaluators determined the permeability correctly in the first place, they would have realized that the Middle Confining Unit is moderately to highly permeable, and would not reasonably be considered adequate for protection of the overlying Upper Floridan USDW. Confinement of the waste therefore rested critically on the thin (<15 ft (4.6 m) thick) dolomite horizon at the base of the Middle Confining Unit. Because this bed is so thin, it would be justifiable to question whether this bed, while demonstrating superior matrix permeability, possesses no breaks, local discontinuities, or other defects that would compromise its ability to confine the effluent.

Additionally, because large losses of cement occurred in the underlying cavernous boulder zone when attempting to cement-in the casing, and because drill cores were not taken at the site, the well constructors instead completed ten of the seventeen wells above the impermeable dolomite bed. Thus, essentially no confining bed protection of the overlying USDW was provided by these wells. Furthermore, in some cases, the underlying dolomite horizon had also been punctured, allowing leakage of effluent through open holes from those remaining wells that had been satisfactorily completed below the thin dolomite bed.

Now that it is apparent that leakage has occurred (through the presence of ammonia in waters recovered from the monitor wells), the limitations of the existing monitoring wells are apparent. The small number of installed wells is quite inadequate to determine the spatial distribution and magnitude of contamination, including the rate of lateral and vertical movement. There is tenuous evidence that the less dense effluent is migrating up-dip to the west rather than down-dip to the east, as the initial hydrologic appraisal had anticipated. This is hardly surprising given the density contrast (≈0.999 vs. ≈1.010) between the effluent and the saline formation waters, and it would be expected that the effluent migration would be buoyancy-driven. To find out precisely the extent and distribution of the effluent would, as McNeill pointed out, require "a new series of monitor wells and core holes (with geophysical logs), located outside the injection well field." Such additional characterization work would be necessary to demonstrate that the effluent waste has not migrated into an aquifer that is not currently and is not expected to be a future source of drinking water.

Finally, it should be noted that the problems arising from the operation of Class I municipal waste wells in Florida could have been avoided had these wells been subject to the more stringent requirements laid down for Class I hazardous waste injection wells. EPA (USEPA, 2001e) recognizes the additional protection to public health and the environment afforded by the application of regulations pertaining to hazardous waste injection disposal, when applied to the disposal of nonhazardous decharacterized wastes. Given the problems arising from the operation of Florida Class I municipal waste wells, it is apparent that regulations governing the disposal of nonhazardous wastes by deep well injection should be reviewed in light of experience gained since the last revision of UIC regulations governing their disposal in 1988.

## 4.8. Summary Conclusions and Remarks

The USEPA's Underground Injection Control Program recognizes five classes of injection wells, including:

- *Class I.* Wells used to inject hazardous, industrial or municipal waste beneath the lowermost formation containing an underground source of drinking water.
- *Class II.* Wells which inject fluids related to the production of oil or natural gas.
- *Class III.* Wells which inject for extraction of minerals such as sulfur, salt, potash, or metals such as uranium by solution mining.
- *Class IV.* Wells used to dispose of hazardous or radioactive waste, into or above a formation which contains a USDW or an exempted aquifer. These wells are now effectively prohibited.
- *Class V.* Injection wells not included in Classes I, II, III, or IV.

*Class I* and *Class II* wells are most relevant to geologic storage of $CO_2$, particularly with regard to the potential for contaminating drinking water aquifers. However, it is important to recognize that regulations regarding the health, safety and environmental effects of surface facilities and leakage of $CO_2$ back into the atmosphere are likely to be regulated through other programs. Confusion and inefficiencies from overlapping jurisdictions and requirements may create a regulatory morass. Early attention to this issue may prevent decades of frustration with an overly complicated and inefficient set of regulations.

Industrial liquid waste disposal by deep well injection was initiated in 1939. Since that time the practice has expanded so that now, nine billion gallons per year of hazardous, industrial and municipal wastes are injected into 485 Class I wells. In 1987, the cost of liquid-hazardous-waste disposal ranged from \$49 to \$207/ton (Sigman, 2001). Early performance was mixed, with many examples of well failures and contamination of drinking water aquifers. Failures were attributed to poor characterization of 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. Because of these problems and the inconsistent approach to oversight, progressively more stringent regulations were promulgated to make the practice of industrial waste disposal by liquid injection safer. By 1988, the current set of regulations was put in place and since that time there have been no incidents where drinking-water contamination has been reported.

Faced with the regulatory dilemma that cleanup of a deep drinking-water aquifer would be practically impossible to enforce, if detected, EPA has adopted the approach of stringent regulation of deep-well-injection operations, with the goal of ensuring that contamination does not occur in the first place. However, the regulations do not, in most cases, require extensive direct monitoring to detect waste leakage from the subsurface confining zone. Thus, the success of current regulations in preventing contamination may be due partly to the selective nature of the monitoring process.

To obtain a permit for hazardous waste disposal by deep-well injection, the operator must demonstrate that "No Migration" of the waste will occur outside of the formation into which it is injected. The formation must contain over 10,000 mg/L of dissolved solids, be overlain by a suitable caprock and be separated from a drinking water aquifer by at least one other impermeable formation.

The regulations mandate stringent controls for the siting, operation, reporting and abandoning of injection wells. Prior experience had shown that leaks from injection and abandoned wells were the most frequent short-term failure mechanisms. Consequently, much of the current regulatory approach focuses on minimizing the possibility of such failures. Current well completion and rehabilitation techniques appear to be adequate to prevent leakage, although finding abandoned wells remains a significant challenge. As for contamination of drinking water aquifers distant from the wellbore, some efforts to detect transmissive faults between the injection zone and overlying aquifers are mandated, and if monitoring wells are already in place in overlying protective aquifers, EPA also requires that these must be monitored for contamination. The permitting process for hazardous waste injection wells is extensive, time consuming and expensive. According to USEPA (2001e), the preparation of a no-migration petition typically costs $300,000. However, when factoring in the costs for geologic testing and modeling, a no-migration petition can cost in excess of $2,000,000.

When a facility is shut down, the EPA is particularly concerned that deep injection wells, especially those that have injected hazardous waste, are properly plugged and abandoned. Upon closure, a Class I hazardous waste well must be plugged with cement in a manner that will not allow the movement of fluids into or between drinking water aquifers. Class I hazardous waste well operators must also prepare and comply with a plan for post-closure care. The plan must include the predicted position of the waste front at closure, the status of any cleanups required, and the estimated cost of proposed post-closure care. In addition, the owner or operator must continue to conduct any required groundwater monitoring until pressure in the injection zone decays to the point that the well's cone of influence no longer intersects the base of the lowermost drinking water aquifer. The owner or operator must demonstrate and maintain financial responsibility for post-closure care. This obligation survives the termination of a permit or the cessation of injection and is enforceable regardless of whether the requirement is a condition of the permit.

For deep well injection of liquid wastes, the density of the injected fluid is usually within ±5% of the surrounding formation fluids. In this case, the injected wastes tend to migrate away from the injection well with little buoyant force driving it up or down. For $CO_2$ storage in oil or water-filled geological formations, this will never be the case. Buoyancy forces will tend to drive $CO_2$ upward. A case study of municipal waste disposal in Florida demonstrates that under these conditions, containment can be more difficult and there is evidence that the less dense effluent is migrating in the opposite direction than originally anticipated based on regional hydrologic gradients. This is an important lesson for geologic storage of $CO_2$ and highlights the unique requirements for characterizing sites where the injected fluid will migrate under the action of gravity and not necessarily follow the migration path or move at the same rate of regional groundwater.

Finally, experience has shown that opposition from communities near operating injection facilities can be strong, and in particular, facilities injecting wastes not generated on-site engender even more opposition. Issues cited include:

- Devaluation of property values.
- Accidents associated with mixing wastes.
- Leaking surface impoundments.
- Air pollution.
- Transportation hazards.

In general, facilities far from population centers are preferred, because they are less subject to local opposition.

# CHAPTER 5. UNDERGROUND NATURAL GAS STORAGE

## 5.1. Introduction

The practice of underground natural gas storage also provides useful insights related to risk assessment, management and mitigation for geologic storage of $CO_2$. In many ways, this type of operation is more directly relevant to geologic storage than industrial disposal of liquid wastes because, like $CO_2$, natural gas is less dense than water and consequently will tend to rise to the top of the storage structure.

Natural gas is stored underground in depleted gas and oil reservoirs, aquifers, and mined salt caverns to help meet cyclic seasonal and/or daily demands for gas. It is a practice that helps balance market swings and allows gas-production wells and transmission pipelines to work at their maximum capacities throughout the year. Recently, the importance of seasonal demand has diminished as natural gas is being increasingly used in the generation of electricity. Overview articles on underground storage of natural gas are given by Katz and Tek (1981) and Knepper (1997). A useful set of reprints on the subject has been published by the Society of Petroleum Engineers (1999).

In seasonal (or base-load) storage, natural gas is injected during the summer, when demand for heating is low, and is withdrawn during the winter season. Depleted gas reservoirs and aquifers are used for this type of storage. On the other hand, salt caverns are used for short-term storage, because they can quickly switch from injection to withdrawal and operate at large injection and extraction rates. Salt caverns are more expensive to construct, but have the flexibility to react to unexpected changes in gas demand and/or price.

The first successful underground natural gas storage project was in Ontario, Canada in 1915 (Beckman and Determeyer, 1997). The Zoar field, a depleted gas reservoir located south of Buffalo, New York, is the oldest U.S. storage project. It has been in use since 1916 and is still in commercial operation today.

Until about 1950, essentially all subsurface natural gas storage was in partially or fully depleted gas reservoirs. The first aquifer storage project (i.e., storing natural gas in water-bearing sands) was the Doe Run Field in Kentucky that started in 1946 (Knepper and Cuthbert, 1979). Storage in mined cavities came later. To this day, depleted reservoirs are the most commonly used underground storage sites because of their wide availability (Natural Resources Canada, 1994).

A remarkable increase in underground natural gas storage capacity began in 1950 (Katz and Tek, 1981). By 1975 there were 376 projects in use (Knepper, 1997). A slowdown occurred about the time of the 1983 recession, but a surge in new projects occurred after 1992 as demand for new gas storage increased (see Figure 5.1; Beckman and Determeyer, 1997). According to 1998 figures, there were 458 active projects in 35 states and provinces across the U.S. and Canada at that time; there were also eight inactive projects (American Gas Association, 1999). The gas was stored in 372 depleted reservoirs, 51 aquifers and 40 salt caverns. States with 30 or more such projects were Pennsylvania (62), Michigan (54), Texas (35), West Virginia (34), Illinois (30) and Indiana (30) (see Figure 5.2 and Table 5.1). Knepper (1997) mentions that approximately 18,500 gas-storage wells and 350 compressor stations were in operation.

In the year 2000, the largest monthly total amount of natural gas stored in subsurface formations in the U.S. was about 139 million metric tonnes (Mt) in November 2000; 50 Mt as working or active gas and 89 Mt as base gas. Base or cushion gas is the volume of gas that must be left underground to provide pressure and volume to cycle the normal working storage volume and to avoid water flooding it. Working or active gas is the maximum developed volume of gas in the storage reservoir above the designed level of base gas. It may or may not be completely injected or withdrawn during any particular season.

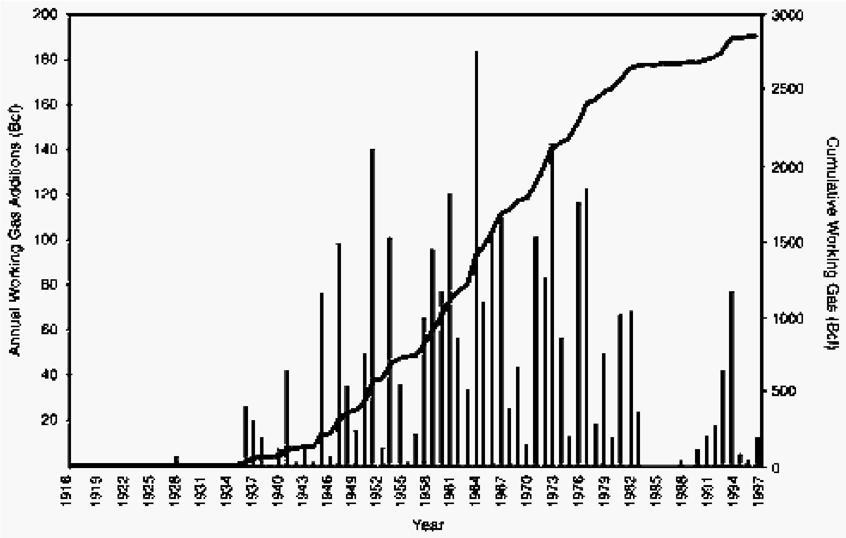

**Figure 5.1. U.S. underground natural gas storage working-gas capacity (from Beckman and Determeyer, 1997).**

In late March 2001, near the end of the 2000-2001 withdrawal season, the estimated quantities were: total, 103 Mt; working gas, 14 Mt; and base gas, 89 Mt. (The amount of base gas varies only slightly over the year.) During 2000, a total of 53 Mt was injected into underground storage projects, and 70 Mt were withdrawn. These numbers illustrate the large volume of natural gas handled by the underground storage projects. Because of differences in molecular weight, the volume of a ton of natural gas (assumed to be pure methane, molecular weight: 16.0 g/mol) corresponds to about 2.75 tons of $CO_2$ (molecular weight: 44.0 g/mol).

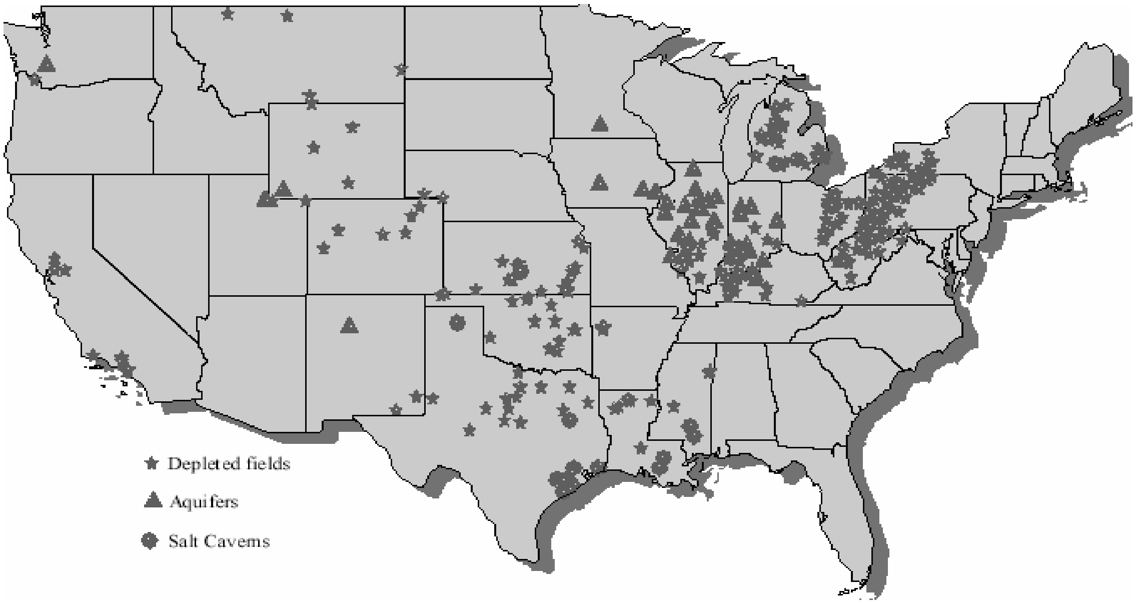

**Figure 5.2. Natural gas-storage facilities in the United States (from [www.naturalgas.org/STORMAP.HTM](www.naturalgas.org/STORMAP.HTM)).**

**Table 5.1. Underground storage of natural gas in the U.S. and Canada: 1998. (Based on data from the American Gas Association, 1999).**

| State/Prov | Number of Projects | Inactive Projects | Type of Storage Reservoir | | | | |
|---|---|---|---|---|---|---|---|
| | | | Depl. Res. | Aquifer | Salt | Coal | Unknown |
| AL | 1 | | | | 1 | | |
| AB | 4 | | 3 | | 1 | | |
| AK | 3 | | | | 3 | | |
| BC | 1 | | 1 | | | | |
| CA | 10 | 3 | 10 | | | | |
| CO | 9 | | 8 | | | 1 | |
| IL | 30 | | 11 | 19 | | | |
| IN | 30 | | 17 | 13 | | | |
| IA | 8 | | | 8 | | | |
| KS | 19 | | 18 | | 1 | | |
| KY | 23 | | 21 | 2 | | | |
| LA | 13 | 1 | 9 | | 4 | | |
| MD | 1 | | 1 | | | | |
| MI | 54 | 2 | 51 | | 3 | | |
| MN | 1 | | | 1 | | | |
| MS | 7 | | 4 | | 3 | | |
| MO | 1 | | | 1 | | | |
| MT | 5 | | 5 | | | | |
| NE | 1 | | 1 | | | | |
| NM | 3 | | 2 | 1 | | | |
| NY | 21 | | 20 | | 1 | | |
| OH | 22 | | 22 | | | | |
| OK | 14 | | 13 | | | | 1 |
| ON | 24 | | 24 | | | | |
| OR | 3 | | 3 | | | | |
| PA | 62 | | 62 | | | | |
| QC | 2 | | 2 | | | | |
| SK | 11 | | 4 | | 7 | | |
| TN | 1 | | | | | | 1 |
| TX | 35 | 2 | 19 | | 16 | | |
| UT | 3 | | 1 | 2 | | | |
| VA | 2 | | 1 | 1 | | | |
| WA | 2 | | | 2 | | | |
| WV | 34 | | 34 | | | | |
| WY | 6 | | 5 | 1 | | | |
| TOTALS | 466 | 8 | 372 | 51 | 40 | 1 | 2 |

**Notes**:
Depl.Res.: Depleted oil and/or gas reservoir; Salt: Salt dome or bedded salt; Coal: Abandoned coal mine;
Unknown: Data on type of storage reservoir is not available

Gas-storage projects extend over areas that vary between a few hundred and tens of thousands of acres. According to the 1999 Survey of the American Gas Association, the Baker (Cedar Creek) field in

Montana is the largest in surface area. This depleted gas reservoir covers an area of 90,338 acres (365.6 $km^2$); the total acreage of the project is 91,447 (370.1 $km^2$). Hall and Shikari (1999) give the average properties for gas storage reservoirs in the U.S. and Canada (Table 5.2).

**Table 5.2. Average reservoir properties for gas-storage reservoirs in the U.S. and Canada (from Hall and Shikari, 1999).**

| | |
|---|---|
| Permeability | 278 md |
| Porosity | 14% |
| Pressure | 1240 psi (8550 kPa) |
| Temperature | 125° F (52° C) |
| Thickness | 69 ft (21 m) |
| Gas Gravity | 0.6 |
| Well Spacing | 160 acres (0.65 $km^2$) |

Only the experience gained from storing natural gas in aquifers and depleted reservoirs is relevant to geologic $CO_2$ sequestration. Salt caverns are of relatively small volume, the cost of mining them is high, and with $CO_2$ sequestration projects no need exists for fast switching from injection to production (i.e., $CO_2$ is injected underground for long-term storage and no withdrawal is expected). Therefore, in this and following sections, the discussion will focus on storage of natural gas in aquifers and depleted hydrocarbon reservoirs.

To store gas in the subsurface, there needs to be a "container." According to Katz and Coats (1968), such a container should have the following elements:

A geologic structure under which the fluid can accumulate (e.g., an anticline with sufficient closure; Figure 5.3). Closure is the vertical distance from the top of the anticline to the highest adjoining syncline (Figure 5.4). Typical heights are as low as 100 to 300 ft (30-91 m). One or both sides of the anticline may slope not less than 1 to 2 degrees from the horizontal.

- The container itself (i.e., porous and permeable layers of rock).
- A cap rock (i.e., impermeable or low-permeable, water-wet rock layers that prevent the stored fluid from rising or moving laterally to rise elsewhere).
- Water to be present to confine the stored fluid in all directions.
- Adequate overburden to allow the storage of fluids under sufficiently high pressures.

Depth of the container is an important factor since economical considerations require that it should be deep enough to permit fluid pressures sufficient to store satisfactory quantities in a given volume and to move them readily into and out of storage (Katz and Coats, 1968). If the container is too shallow and the overburden pressure is too low, gas may leak through the caprock (see next Section). Because of this working pressure requirement the storage formation is generally much deeper than the lowermost underground sources of drinking water.

Based on the data of the 1998 survey (American Gas Association, 1999), the underground projects with the shallowest storage formations are the Fredonia (depleted gas reservoir) field in Kansas and the West Point (aquifer) field in Indiana, where the minimum depth to the top of the formation is 225 ft (69 m) and 333 ft (102 m), respectively. These are older projects, Fredonia was activated in 1949 and West Point in 1957.

In depleted oil and gas reservoirs, and in aquifers, the geologic structure is at least partially filled with water. When the stored natural gas is injected into the reservoir it floats, and displaces the native water. The water is forced away from the injection wells and the formation pressure increases. If the volume injected is too large, gas may leak out of the reservoir at the spill point (Figure 5.4).

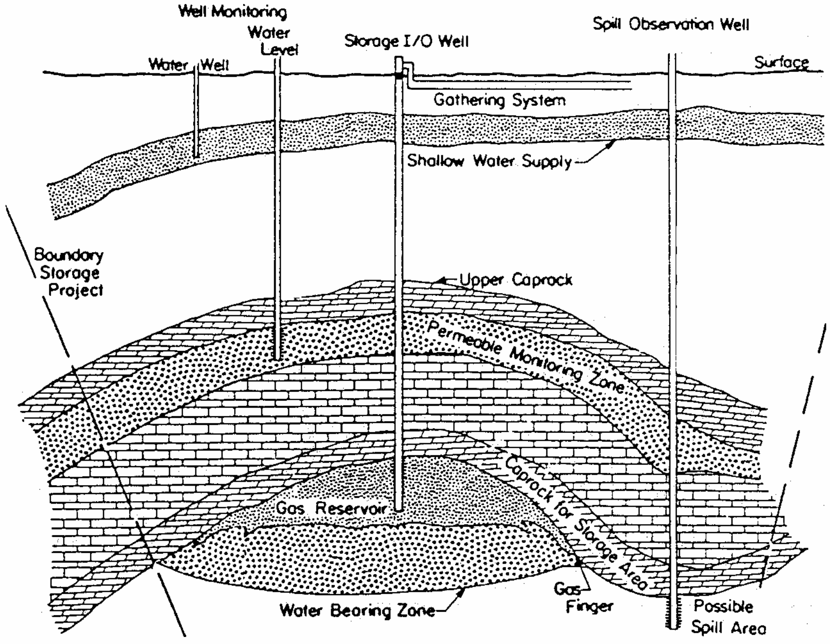

**Figure 5.3. Definition of a storage system (section of an anticlinal reservoir) (from Katz, 1978).**

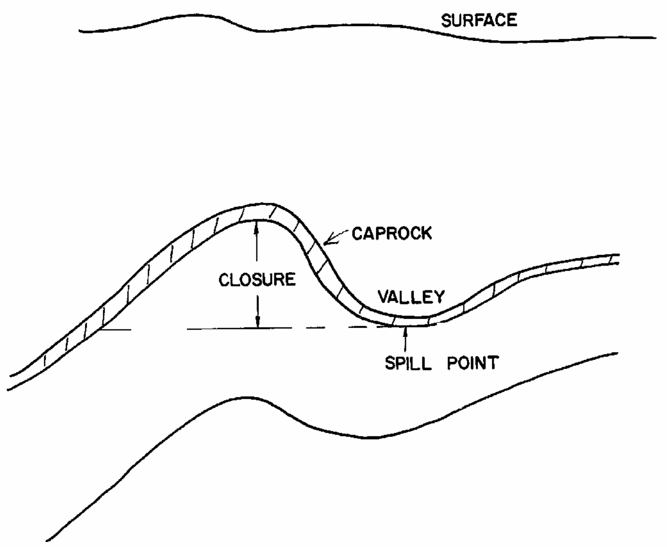

**Figure 5.4. Section of an underground structure (from Katz and Coats, 1968).**

Aquifer storage tends to be more expensive to develop than depleted reservoir storage because the geology, especially the structure of the aquifer, is usually unknown beforehand (Natural Resources

Canada, 1994). In the case of depleted reservoirs, the presence of hydrocarbons testifies to the existence of a "container" and of the quality of the cap rock to hold fluids below it. On the other hand, in aquifer storage projects the structure and quality of the storage formation and cap rock need to be determined during development (Katz and Coats, 1968).

The main effort in converting depleted reservoirs to natural gas storage projects is in the reconditioning of wells and pipelines, since wells will be used for injection as well as withdrawal, and because operating pressures tend to be higher than during original oil and gas production. Wells must also be able to withstand the changes in stresses and temperatures associated with the cycling operations. In addition, because the volumes of gas being withdrawn during peak winter periods are much larger than during normal oil and gas production operations, additional wells will have to be drilled. In depleted oil reservoirs, the gas withdrawn will contain traces of oil, requiring the installation of plants to strip the gas of propane and heavier hydrocarbon components (Katz and Coats, 1968; Knepper, 1997). Griffith and Rinehart (1971) describe the activities associated with the transition (or conversion) of a natural gas field into a storage project.

As indicated earlier, the development of aquifers to store natural gas requires a number of exploratory studies generally not needed for projects involving depleted reservoirs. An appropriate underground structure with sufficient closure has to be found. The quality of the cap rock needs to be determined by examining cores and testing them in the laboratory. To characterize the cap rock, especially its permeability, well tests have to be carried out (Witherspoon et al., 1967). These field measurements are particularly useful for determining 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.

If the results of these studies look favorable, the next step in the evaluation of the proposed aquifer-cap rock system is to carry out pilot injection to initiate the growth of the gas bubble and continue testing the tightness of the cap rock seal. For the gas to push the water away from the well(s), injection is performed at pressures that exceed initial aquifer values. The development of a commercial natural gas aquifer storage project requires between two and four years, and the size of the gas bubble is increased over periods of ten or more years (Katz and Coats, 1968).

Not all the gas injected into a depleted reservoir or aquifer can be withdrawn; some of the gas, the so-called "cushion or base gas," must be left underground. Once the gas zone is established, pressures can be changed somewhat during injection and withdrawal operations without destabilizing the gas zone (Natural Resources Canada, 1994).

## 5.2. Risk-Assessment Framework and Methods

The major risks associated with the operation of an underground natural gas storage project are related to leakage from the storage structure. Leakage leads to two very different risks. One is economic in that gas that has migrated from the structure may not be recoverable, and consequently, a valuable commodity is lost. Second, leakage from the structure may migrate into a drinking water aquifer and even to the land surface, in which case it could be a significant safety risk.

One of the main causes of leakage is that underground natural gas storage projects are in many cases operated at overpressures, or delta pressures (i.e., pressures exceeding the original, or discovery, values) to enlarge working gas content and obtain higher delivery rates, with only a moderate increase in risk of gas loss through defective wells. Natural gas reservoirs generally are found at discovery pressure gradients of 0.2 to 0.52 psi/ft (4.5-11.8 kPa/m). Overpressures up to 0.75 psi/ft (17 kPa/m) of depth have been used (Katz and Tek, 1981).

This way of operating the projects creates pressure gradients that the storage formations have not seen before. It could result in the displacement of the static water column, forcing water out of the cap rock and causing gas to leak from the storage formation (Katz, 1978). This is known as exceeding the threshold displacement pressure or threshold pressure (i.e., the gas pressure is high enough to displace water-gas menisci in the rock pores). Note that there is an inverse relationship between permeability and threshold displacement pressure (i.e., less permeable formations have higher threshold pressures).

Katz and Coats (1968, p.138) indicate that they have "not found any occasion in which gas pressures initiated fracturing (of the caprock) at pressures at or below 1 psi/ft (22.6 kPa/m) of depth." They believe that it could possibly happen at 1.5 psi/ft (33.9 kPa/m) of depth and that gas may open existing fractures at 1.0 to 1.1 psi/ft (22.6-24.9 kPa/m) of depth. These values are higher than the maximum overpressures used in underground gas storage projects.

In other words, to avoid leakage through the caprock the applied overpressures must be below threshold displacement pressures and thus, less than fracturing pressures. Some states stipulate a maximum wellhead injection pressure (Pmax). For example, Indiana's Oil and Gas Rules (under Permit Applications; Rule 312 IAC 16-3-2) specify that that pressure (in psi) is given by: $Pmax = \{0.8 \text{ psi/ft} – [0.433 \text{ psi/ft} (Sg)]\}d$, where Sg is the specific gravity of the injected fluid, and d is the depth to the top of injection zone given in feet.

Leakage may also be the result of well problems (i.e., breaks in the casings, joints, or defective cementing of casings) and by the presence of fractures, faults, and solution cavities that permit upward gas movement through the seal (Katz and Coats, 1968). Well mechanical flaws have been the most common cause of leaks in underground gas storage facilities. Generally, repairing or reconditioning the wells fixes the problems; in extreme cases the wells may have to be plugged and abandoned (e.g., Knepper and Cuthbert, 1979). Leaks that occur through the cap rock are more difficult to detect and control.

In many states, underground natural gas storage facilities are required to implement methods to detect gas leakage. Several methods to identify leaks have been used (Katz, 1978; Knepper and Cuthbert, 1979), such as:

- Monitoring water levels and water chemistry in observation wells completed above the cap rock.
- Observing pressures in the annulus between the production casing and the next larger casing.
- Studying changes in well shut-in pressures.
- Running down-hole logs in the injection/withdrawal wells (e.g., temperature logs to identify thermal anomalies, neutron logs to detect gas behind the casings above the storage formation, cement bond logs to determine the integrity of the cement behind the casings, caliper logs to find mechanical breaks in the casings, noise logs to "listen" to the flow of gas behind the casings, and a variety of casing inspection logs to determine the thickness and general condition of well casings and joints) (Gentges, 1985; Gunter et al., 1999).
- Carrying out gas inventory verifications (Mayfield, 1981).
- Identifying abnormally high injection rates.
- Installing gas detectors at the surface near wells and installations.
- Taking and analyzing samples of the stored gas to detect possible mixtures of gases of different origin, with or without the use of artificial tracers (Coleman, 1992).
- Surveying vegetation at the surface (Katz and Coats, 1968).

Gunter et al. (1999) give a general description of the monitoring techniques used in underground gas storage. They mention not only down-hole logs (to identify water movement, casing problems, leaks and gas movement behind pipe and cement, and cement integrity), but also microseismic studies to detect shear-induced deformation, and the use of (natural and man-made) tracers to keep track of the stored gas.

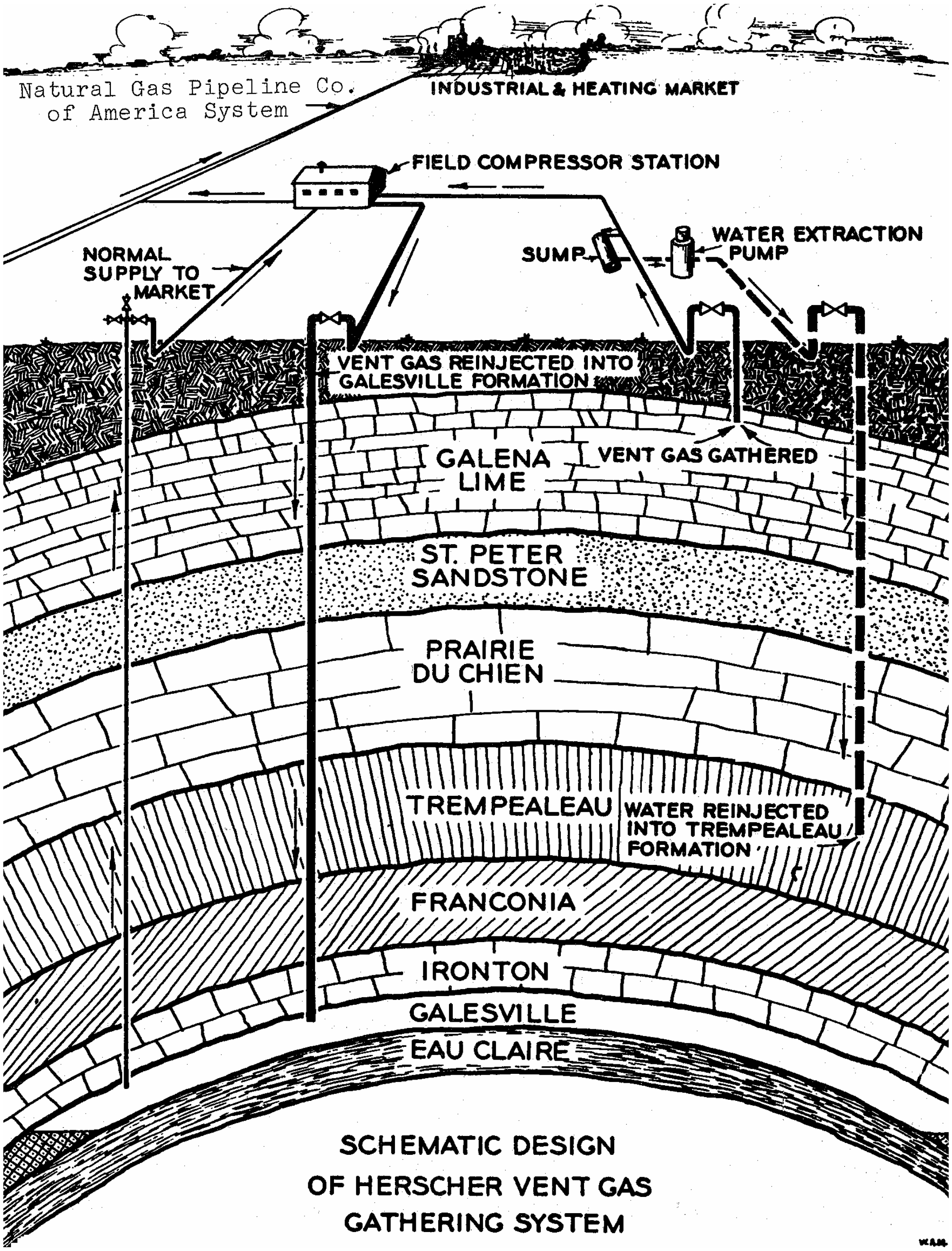

**Figure 5.5. Artist's conception of the vent gas cycling system at Herscher, Illinois (from Katz and Coats, 1968).**

The required monitoring activities vary from state to state (see Section 5.3); some mandate monthly measurements, others yearly. In a few states, like Indiana, no monitoring program is imposed on the operators of underground natural gas storage projects; however, they must report any problems to the Indiana Division of Oil and Gas. A number of storage projects do not have any observation wells. On the other hand, a few of them have more than one hundred of these wells (i.e., Hersher, Illinois, an aquifer storage project, has 163; and Fink-Kennedy-Lost Creek, West Virginia, a depleted oil and gas reservoir, has 124; American Gas Association, 1999). When an underground storage project is abandoned, the operator is required to plug the wells following regulations (i.e., according to detailed guidelines given by the appropriate state agency; see Section 5.3).

In a few instances, some leakage through the cap rock is allowed to occur as long as the gas accumulates in strata above the cap rock, without reaching shallower levels where it would affect the quality of the water in aquifers used for domestic, agricultural, or industrial purposes. The gas collected in the upper strata is either extracted and sent to a distribution pipeline or is injected back into the storage aquifer. Figure 5.5 illustrates one such operation at the Herscher, Illinois project, where natural gas leaks from the Galesville sandstone (the storage formation).

In summary, underground natural gas storage facilities are designed and operated to avoid leakage, and if they occur, leaks must be controlled or made manageable as soon as possible. In some instances, storage pressures have to be lowered to assure the safety of the project, which affects the economics of the operation. In extreme cases, the project must be abandoned (see examples in Section 5.5). That is, all (or most) of the remaining stored gas is withdrawn from the subsurface, and all injection/withdrawal wells are plugged, strictly following existing regulations (see next section).

## 5.3. Risk-Management Approaches for Natural Gas Storage

The mission of the U.S. Environmental Protection Agency (EPA) is to protect human health and to safeguard the natural environment—air, water, and land—upon which life depends. Its Underground Injection Control (UIC) program (40 CFR Parts 144-148) is geared to safeguard underground sources of drinking water (USDW) by regulating five classes of injection wells (see Section 4.3). Class II wells include those that are used to inject fluids brought to the surface in connection with natural gas storage operations or conventional oil and natural gas operations. However, according to 40 CFR Part 144.1 (g) (2) (iv), wells used for injection of hydrocarbons that are of pipeline quality and are gases at standard temperature and pressure for the purpose of storage are excluded.

EPA has delegated to most states the regulation and monitoring of underground natural gas storage projects. The key responsibility of the states is the protection of the environment, especially drinking water aquifers, from endangerment by the injection and subsurface storage of natural gas. States are in charge of issuing permits based on the assumption that the operators of the facilities will run them within the parameters of required federal, state, and local regulatory agencies' permits, and that operations in excess of permitted levels would require new discretionary permits and additional review.

Underground natural gas storage projects have to be designed and operated in accordance with recognized engineering procedures. Regulatory agencies rely on the expertise of their technical staffs and that of hired consultants to assure that this will actually happen. All geologic and engineering data and test results provided by companies applying for operating permits, following regulation requirements, have to be studied for completeness and accuracy before permits are issued. When the guidelines and regulations do not suggest criteria, professional judgment is used to develop reasonable thresholds and safeguards.

When soliciting the permit for an underground natural gas storage project, applicants have to provide information showing that the reservoir is suitable and that it can be operated safely in order to prevent waste of resources, uncontrolled escape of gases, pollution of drinking water aquifers, and endangering life or property. Regulations for underground natural gas storage operations and associated monitoring activities vary among states. Many are given on the Web; Table 5.3 lists the websites where the most relevant regulations for the 13 U.S. states that had 10 or more underground natural gas projects in 1998 (Table 5.1) can be found.

**Table 5.3. Web guide for the most relevant state regulations related to underground natural gas-storage projects, especially in depleted reservoirs and/or aquifers.**

| State | Webpage(s) |
|---|---|
| California | *California Code of Regulations*<br>Title 14, Division. 2, Chapter 4, Subchapter 1<br>http://www.consrv.ca.gov/dog/Publications/pubgen_b.htm Look for Publication No. PRC04 under Laws and Regulations<br>Title 14, Chapter 3. Guidelines for Implementing California Environmental Quality Act<br>http://ceres.ca.gov/topic/env_law/ceqa/guidelines/ |
| Illinois | http://dnr.state.il.us/mines/dog/rules.html (Especially Subpart R) |
| Indiana | http://www.state.in.us/dnroil/ogrules.htm#Definitions<br>http://www.ai.org/legislative/ic/code/title14/ar37/index.html |
| Kansas | Bill pending in the State Legislature (HB2200), it would require regulations to be in place by July 1, 2002.<br>www.accesskansas.org/legislative/statutes (Chapter 55, Article 12)<br>www.kcc.state.ks.us/conservation/rr/KCC_Regs.htm (especially K.A.R. 82-3-311, K.A.R. 82-3-13 and K.A.R. 82-3-120).<br>http://www.kdhe.state.ks.us/uic/index.html (Hydrocarbon Storage Wells) |
| Kentucky | http://www.lrc.state.ky.us/kar/805/001/080.htm<br>http://www.lrc.state.ky.us/kar/401/005/090.htm |
| Louisiana | http://www.legis.state.la.us/tsrs/RS/30/RS_30_22.htm<br>http://www.legis.state.la.us/tsrs/RS/30/RS_30_23.htm<br>http://www.dnr.state.la.us/cons/title43.ssi Part XVII, Chapter 3 - Hydrocarbon Storage Wells in Salt Dome Cavities<br>http://www.state.la.us/osr/lac/43v09/43v09.pdf |
| Michigan | http://www.michiganlegislature.org/law/GetObject.asp?objName=486-252&queryid=1317160&highlight=486%2E252<br>http://www.deq.state.mi.us/gsd/circ15.pdf |
| New York | http://assembly.state.ny.us/leg/?cl=37&a=97 |
| Ohio | http://onlinedocs.andersonpublishing.com/revisedcode/ (click on Title 15, then Chapter 1571. The other Oil/Gas statutes are 1509/1510. |
| Oklahoma | http://www.occ.state.ok.us/TEXT_FILES/Wordrule.htm Look for Rule #165:10-3-5 under Chapter 10 - Oil and Gas Conservation Rules |
| Pennsylvania | http://www.dep.state.pa.us/dep/deputate/minres/oilgas/act223ch3.htm#CHAPTER_3 |
| Texas | http://www.rrc.state.tx.us/tac/16ch3.html<br>Rule §3.96 Underground Storage of Gas in Productive or Depleted Reservoirs<br>Rule §3.97 Underground Storage of Gas in Salt Formations |
| West Virginia | http://www.legis.state.wv.us/ WV State Code Chapter 22, Article 9<br>http://www.dep.state.wv.us/og/ted/regs.htm#4 |

**Note:** Data given only on states that had more than 10 such projects in 1998 (see text).

In general, gas-storage facility operators are required to:

- Case and cement gas injection/withdrawal wells to ensure no gas can leak from them.
- Make periodic (e.g., monthly, quarterly or annual) inspections of all gas-storage wells and all wells used for observation.

- Periodically inspect the gas-storage reservoir and storage-protective area to make sure no gas is leaking or other hazardous condition exists.
- Implement gas-storage well monitoring and periodic integrity-testing programs.
- Not exceed pressures that may cause the gas to begin leaking.
- Notify the regulatory agency within a short period (e.g., 24 hours) of making emergency repairs to gas-storage wells and submit a written explanation of the emergency and what action was taken within a few (e.g., five) days.
- Keep records of well inspection results and pressure data, integrity testing data, and inspections of abandoned and plugged wells.
- Notify the regulatory agency before (e.g., 15 days) an injection/withdrawal well is plugged to prevent migration of gas or other fluids within or outside of the well.

In California, two state organizations are involved in the approval and monitoring of underground gas storage projects. The California Public Utility Commission (CPUC) is responsible for issuing operation permits, taking into consideration the environmental aspects of the projects. (Before making a decision, the CPUC checks if an array of permits required by a number of Federal, State and Local agencies has been issued; as an example, Table 5.4 lists the permit requirements for the Wild Goose Gas Storage Project.) The California Division of Oil, Gas and Geothermal Resources (DOGGR) regulates and monitors what should be done to assure the integrity of the reservoir and wells, and to prevent groundwater contamination.

The California Code of Regulations—Publication No. PRC04—under Title 14 (Natural Resources), Division 2 (Department of Conservation), Chapter 4 (Development, Regulation and Conservation of Oil and Gas Resources), Article 3 (Requirements), has two sections directly relevant to underground gas storage projects. They are Section 1724.6, "Approval of Underground Injection and Disposal Projects," and Section 1724.9, "Gas Storage Projects." Note that DOGGR is part of the California Department of Conservation. In these regulations, great weight is given to (1) geology of the site (e.g., structural and isopach maps, well logs), (2) properties of the cap rock (e.g., areal extent, average thickness and threshold pressure), (3) characteristics of the injection zones (e.g., porosity, permeability, thickness, extent, fracture gradient, original and present temperatures and pressures, and original and residual oil, gas, and water saturations), (4) injection installations, procedures, and plans, (5) well drilling and plugging and abandonment programs, and (6) safety programs.

In some states with abundant coal resources, like Pennsylvania (Oil and Gas, Chapter 3, Act 223), to avoid possible dangerous interference between underground natural gas storage and coal mine operations, the state requires the reporting of the location and condition of wells used in the operation of underground storage fields, and the location of underground mines. Operators of gas storage and coalmine projects are allowed to inspect each other's records and facilities. In Pennsylvania, to reduce the possibility of gas leakage into mines (and methane explosions) the injection of gas for storage in workable coal seams is prohibited. Similar regulations are in place in West Virginia, another state with a large number of underground coalmines and natural gas storage projects.

Because of the importance of properly plugging damaged injection/withdrawal wells or old abandoned wells, many of the states provide precise and detailed instructions on how to go about it (e.g., Illinois Division of Oil & Gas Laws & Rules, Subpart K).

Monitoring and reporting requirements and responsibilities differ from state to state. For example, Texas requires monthly inventory reports; well data on injection/withdrawal and pressures are gathered and monitored by the regulatory agency. In Louisiana the reports are quarterly and the regulators do the monitoring.

**Table 5.4. Permit requirements for the Wild Goose Storage Project, Butte County, California (from http://www.cpuc.ca.gov/Environment/info/goose.htm).**

| Permits | Agency | Jurisdiction/Purpose |
|---|---|---|
| **FEDERAL AGENCIES** | | |
| Section 404 Individual Permit | Army Corps of Engineers | Waters of the U.S. and EPA lead agency |
| Section 7 Consultation | U.S. Fish and Wildlife Service | Threatened and Endangered Species Biological Opinion (through Corps review process) |
| Section 106 Review | Advisory Council on Historic Preservation | Historic Properties Management Plan (through Corps review process) |
| **State Agencies** | | |
| Certificate of Public Convenience and Necessity (CPCN) | California Public Utilities Commission | Overall project approval and CEQA lead agency |
| Gas and Disposal Well Installation | Division of Oil, Gas & Geothermal Resources | Natural gas storage and produced water disposal well |
| NPDES General Permits and Section 401 Certification/Waiver | Regional Water Quality Control Board | Industrial and construction storm water, hydrotest water discharge, and water quality certification/waiver |
| Stream Crossing Agreements | Department of Fish & Game | Waterways and wildlife habitat areas |
| Endangered Species Consultation | Department of Fish & Game | Biological Opinion (through CEQA review process) |
| Consultation | State Historic Preservation Office | Cultural resources management (through CEQA review process) |
| **Local Agencies** | | |
| Road Encroachment Permit | Butte County Public Works | Pipeline installation in West Liberty Road and driveway access to the Remote Facility Site |
| Domestic Well and Septic System Permit | Butte County Environmental Health | Domestic water supply well, septic tank, and leach field at the Remote Facility Site |
| Hazardous Material Release Response Plan | Butte County Environmental Health | Storage, handling, and disposal of hazardous materials and wastes |
| Building Permits | Butte County Development Services | Building permits for structures and buildings |
| Authority to Construct/ Operate | Butte County Air Quality Management District | Air-emission reduction and monitoring |
| Encroachment Approval | Reclamation District #833 | Crossing District canals and ditches |

Prior to the abandonment of an underground storage project, the working and base gas should be withdrawn as much as economically feasible, and all wells must be plugged following existing regulations. None of the states requires long-term monitoring of the site or wells after the project is abandoned.

According to the Texas Administrative Code (Title 16, Part 1, Chapter 3, Rule 3.96: Underground Storage of Gas in Productive or Depleted Reservoirs), gas-leak detectors are required "at each gas storage well that is located 100 yards or less from a residence, commercial establishment, church, school, or small, well-defined outside area, and at each structurally enclosed compressor site.” These detectors have to be tested twice a year and repaired if found defective. They also have to be “integrated with warning systems that are audible and visible in the control room and at any remote control center. The circuitry shall be designed so that failure of a detector or pressure monitor will activate the warning.

Henry and Fix (1974) described the steps that had to be followed to develop an aquifer storage project in Iowa to assure minimum environmental impact. They review the various agencies to be dealt with during all phases of the project.

## 5.4. Risk Mitigation and Remediation Methods

Underground natural gas storage projects should be operated so as to avoid leakage of the stored gas, which might endanger life and property (including buildings and other man-made structures), water resources, and vegetation/crops. Regulations controlling the design, operation, and monitoring of the storage facilities (see Section 5.3) are meant to reduce this risk to a minimum. Even though natural gas (essentially methane) is a flammable gas that might produce fires and asphyxiation, once the leaks have been controlled, no long-term effects remain in the affected areas.

If a storage project presents an adequate geologic framework (i.e., appropriate structural closure and reservoir-cap rock system) and is operated within regulated guidelines (i.e., properly constructed wells and surface installations, reservoir pressure not exceeding prescribed values), and no unplugged abandoned wells are present in the area, no significant gas leaks should be expected.

If gas leaks to the surface, it might be necessary to evacuate nearby residents because of the danger of explosion, fire and/or asphyxiation. In any event, appropriate remediation measures should be taken to stop or reduce the leaks. Generally the repair or plugging of the leaking wells is sufficient to eliminate the problem. If the leaks are not related to well damage (i.e., caused by high storage pressures, inadequate geological framework), the pressure in the storage aquifer or reservoir might have to be reduced.

A project may be abandoned if leaks cannot be controlled or if the operations of the facilities have to be curtailed to such a low level that the undertaking is no longer practical. In that case, the gas remaining in the storage formation would be extracted – as much as economically feasible, and all injection/withdrawal and observation wells open in that formation would have to be plugged.

In several states, especially in those with abundant oil, gas, coal and/or mineral resources, when requesting and/or renewing a permit or license to operate an underground natural gas storage project, a map showing the location of the storage reservoir – as well as a reservoir protective area (also called protection or buffer zone) around it – has to be submitted. This is to avoid or reduce the risk of accidents caused by human intrusion. For example, the Oil and Gas Act of Pennsylvania (Chapter 3, Sec. 601.301) states: “Any person who is injecting into or storing gas in a storage reservoir which underlies or is within 3,000 linear feet of an operating coal mine which is operating in a coal seam that extends over the storage reservoir or the reservoir protective area shall, within 60 days thereafter, file with the department a copy of a map and certain data in the form and manner provided in this subsection or as otherwise prescribed by regulation of the department.”

It also says, “the map provided for herein shall be prepared by a competent engineer or competent geologist. It shall show the stratum or strata in which the existing or proposed storage reservoir is or is to be located, the geographic location of the outside boundaries of the said storage reservoir and reservoir protective area, the location of all known oil or gas wells within the reservoir or within 3,000 linear feet [ca. 1000 m] thereof, which have been drilled into or through the storage stratum indicating which of these wells have been or are to be cleaned out and plugged or reconditioned for storage and also indicating the proposed location of all additional wells which are to be drilled within the storage reservoir or within 3,000 linear feet [ca. 1000 m] thereof."

On the other hand, West Virginia's Code 22-9-1 defines the "reservoir protective area" as the area outside of and surrounding the storage reservoir boundary but within two thousand linear feet (610 m) thereof.

## 5.5. Case Studies for Natural Gas Storage

Little published information could be found on accidents or problems related to the operation of underground natural gas storage projects. Based on telephone and personal conversations with field operators and regulators, it was learned that initially there were a number of significant operational problems, but since stricter regulations and monitoring programs were put in place, very few incidents have occurred.

Wells are the most likely places for operating accidents to occur (Knepper, 1997). These accidents are related to improper well design, construction, operation and maintenance, resulting in damaged casings, leaking pipe joints, and inadequate cementing of casings that allowed the stored gas to move into permeable zones overlying the storage formation. In some past cases, the gas flowed to the surface, killing vegetation, damaging water supplies (e.g., gas was found in water wells), collecting in basements, and in a few instances, causing explosions and fires. Plugging or repairing the damaged well(s) and/or plugging old, abandoned wells that provided a flowpath to the surface solved the problems. The most difficult tasks in this effort are (1) to identify the leaking wells since the gas may flow laterally in the subsurface over large distances through permeable layers, and (2) to locate abandoned wells or geologic structures that allow the gas to reach the surface. (The leakage of stored natural gas from the Herscher-Galesville, Illinois aquifer project and how the escaped gas is being recycled was mentioned in Section 5.2.)

Uncontrolled migration (i.e., bubbling) of natural gas to the surface was observed in areas around two wells in the Leroy, Wyoming aquifer storage project. Various well-logging techniques, surveying, sampling and testing methods, tracer studies, computer simulation, and engineering analysis were used to understand the cause of the leakage in order to control and reduce it. The studies showed a correlation between the rate of migration and storage pressures, but could not pinpoint the cause of the problem. It could be related to wellbore problems, existing fractures/faults, and/or other structural imperfections. Gas leakage from the storage formation appeared to be controllable by limiting maximum injection pressures. Gas surface-detector surveys indicated a reduction in the amount of leakage when pressures were lowered. It was concluded that the continuing leak did not substantially affect the operations of the project (Araktigni et al., 1984).

One depleted-reservoir gas-storage project in East Whittier, California had to be abandoned because the stored natural gas was being produced by wells belonging to another company. At the time the permit was granted, the exact dimensions of the storage formation were not known well enough; it extended below a neighboring lease (DOGGR, District 1, pers. comm., 2001).

In the West Montebello oil and gas field, in the Los Angeles area, improperly plugged old wells allowed the migration of natural gas into an overlying zone but not to the surface. The wells that created the problem were plugged. At present the storage project is inactive. Eventually the stored gas might be produced (DOGGR, District 1, pers. comm., 2001).

In the McDonald Island gas storage field, California, a depleted gas reservoir, the operators lost control of an injection/withdrawal well, which then caught fire. After the fire was extinguished, the well was plugged, solving the problem (Pacific Gas & Electric Co., pers. comm., 2000).

In the 1960s and 1970s, a number of water wells in Northern Indiana were affected by the intrusion of natural gas. It seems that the aquifer used for storage was too shallow. Such operation would not be allowed under present regulations. The project had to be abandoned (Indiana Division of Oil and Gas, pers. comm., 2001).

A recent example of an accident related to an underground natural gas operation occurred on January 17, 2001, when natural gas built up under and erupted in and around the city of Hutchinson, Kansas. Explosions killed two people, destroyed downtown businesses, and hundreds of residents had to be evacuated. Several "gas geysers" sprouted around town, throwing a mixture of water, gas, and soil high into the air, and some ignited. Most of the fires were left to burn out. More than 60 wells were drilled to find and vent pockets of gas; only some (23) actually hit gas. The gas may have escaped from a damaged injection/withdrawal well in the Yaggy natural gas storage field (a mined salt-cavern project) located about seven miles northwest of the city. That field, initially developed to store propane gas, has 160 storage caverns at a depth of 150–200 m. It seems that by plugging the damaged well, the source of the gas that found its way to Hutchinson was stopped. An estimated 143 million cubic feet of natural gas have leaked from one of the storage caverns.

Half a year after the accident, questions still lingered about how the leak occurred and the subsurface flowpath followed by the natural gas. It seemed to have migrated laterally through shallow permeable zones (a thin strip of dolomite, about 50 m wide and two feet thick, is suspected), reaching the surface by flowing up old, unplugged wells that had been used for salt-solution mining. No reliable maps showing the location of the abandoned wells exist. To find them, Kansas Geological Survey and Hutchinson City personnel used electromagnetic metal detectors. The wells were plugged as they were found.

In mid-April 2001, an airborne emission spectrometer on a NASA plane flew over the Hutchinson area, looking for the infrared signature of natural gas. At the time of this report, scientists of the Jet Propulsion Laboratory (Pasadena, California) were studying the collected data to determine whether the instrument was able to detect leaks from the air. (The information on the Hutchinson accident was compiled from newspaper articles in *The Hutchinson News* and *The Topeka Capital-Journal.*)

In summary, accidents in underground natural gas storage projects associated with depleted reservoirs and aquifers have been few and were mainly related to faulty well construction and maintenance and the presence of old, improperly plugged abandoned wells. Even though costly, the problems were solved by repairing and plugging the problem wells.

There were instances when leakage occurred because the geology of the site had not been properly characterized, or the pressure in the storage reservoir was too high, allowing the stored gas to migrate vertically and/or horizontally. A carefully designed monitoring program would detect the leaks at an early stage, before a large volume of gas is lost from storage.

The Hutchinson accident was a worst-case scenario. A break in a well casing allowed natural gas to leak from a mined salt cavern used for storage. The gas seems to have migrated over a large distance, flowed through permeable formations, reached the surface (flowing up old, abandoned wells), and then ignited. The existence of those widespread formations and old salt-solution wells was unknown to the operators of the storage facility, the Kansas State Geologic Survey, city personnel, and its inhabitants. It is still not clear how long the leakage occurred.

Only a properly designed, constructed and operated project (one that includes a strict monitoring program), in an area where the geology is well known, will avoid or reduce the possibility of leakage problems in natural gas underground storage fields.

## 5.6. Summary Conclusions and Remarks

Underground natural gas storage projects have been operated successfully in the U.S. for almost 90 years and today, 450 projects store approximately 139 Mt of natural gas in 30 states. The majority of storage projects are in depleted oil and gas reservoirs, but 51 projects are in brine-filled aquifers and 40 are in salt caverns. Experience has shown that there are a number of factors critical to the success of these projects:

- First, it is important to have a site that is adequately characterized (i.e., permeability, thickness and extent of storage reservoir, caprock integrity, geologic structure, lithology, etc.).
- Second, the storage formation should be deep enough to allow sufficiently high gas pressures for the economic success of the operation.
- Third, injection/withdrawal wells must be properly designed, constructed, monitored and maintained.
- Fourth, overpressuring the storage reservoir should be avoided.
- Finally, abandoned wells in and near the project must be located and plugged.

While underground natural gas storage has been used safely and effectively, there have been a number of documented cases where leakage has occurred. In the vast majority of cases, leakage was caused by defective wells (poorly completed or improperly plugged abandoned wells). Over time, as engineering practices have improved and regulatory oversight has grown more stringent, fewer accidents have occurred and modern practices have made underground natural gas storage a safe and effective practice.

Primary regulatory responsibility for protecting the environment and drinking water aquifers from underground gas storage detrimental effects has been given to the states, which have effective regulations for permitting, operating, and monitoring storage fields. Regulations differ from state to state and are tailored to local concerns, such as in Pennsylvania where extra measures are taken to avoid leakage of gas into underground coalmines. In several states with abundant oil, gas, coal and/or mineral resources, a protection (or buffer) zone is established to avoid or reduce the risk of accidents caused by human intrusion.

Monitoring is an important part of the regulatory oversight of these projects. While regulations on monitoring and reporting vary between states, almost all monitoring requirements focus on assuring that the injection/withdrawal wells are not leaking (e.g., pressure measurements and down hole logs such as temperature, pressure, noise/sonic, casing condition logs). Observation wells installed and monitored for the purpose of verifying that gas has not leaked into shallower strata are rarely required; however, a few storage projects have over one hundred wells for this purpose. The use of geophysical techniques for monitoring the gas bubble in the storage formation is unusual.

Depleted oil and gas reservoirs are easier to develop than are aquifer storage projects because the geologic structure and cap rock are usually well characterized from existing wells. Moreover, since the structure is known to have trapped and stored hydrocarbons over geologic time periods, it is likely to be effective for natural gas storage. Standard natural gas reservoir engineering practices are used during the permitting process and storage operations. For aquifer gas storage projects, extensive site characterization is required and well testing methods have been developed specifically for evaluating the permeability and continuity of the cap rock.

In the event that leakage occurs, remediation is possible by producing or venting the gas accumulated in shallower layers, and/or reducing reservoir pressure. In most cases, leakage is caused by the presence of leaking or abandoned wells which should be identified and plugged as soon as possible. Projects may be allowed to continue operation even though some leakage from the primary storage formation occurs. In the case of the Herscher project in Illinois (Figure 5.5), shallow extraction wells are used to capture the gas that leaks from the main storage aquifer.

When an underground natural gas storage site is shut down, as much of the gas as is economically feasible is removed from the storage formation. The injection/withdrawal wells are then plugged and abandoned using prescribed procedures. No long-term monitoring is required after a project has been closed.

# CHAPTER 6. NUCLEAR WASTE DISPOSAL: LESSONS LEARNED FOR $CO_2$ SEQUESTRATION

## 6.1. Introduction

The disposal of nuclear waste in geologic formations has been studied intensely in the U.S. and other countries for the last 20 years. Not only was extensive work done on the science and technology related to repository design and performance assessment, but the regulatory and monitoring aspects have also been considered thoroughly. This section is devoted to summarizing the main experiences and approaches developed in nuclear waste geologic repositories, with the aim of providing insights, lessons, and methodologies useful to the problem of geologic carbon sequestration.

Before getting into details about nuclear waste geologic disposal, we provide perspective by listing the differences and similarities between nuclear waste disposal and $CO_2$ geologic sequestration. The main differences in terms of analogue system considerations are:

- $CO_2$ is not toxic and is hazardous only at abnormal concentrations, whereas nuclear waste, being radioactive, is hazardous even at low concentrations. The toxicity of radioactive waste is also considered to be cumulative, meaning the cumulative effect of low dosage over a period of days or years is harmful, whereas the effects of exposure to elevated concentrations of $CO_2$ is not thought to be cumulative.

- There will be at most only a few sites for nuclear waste geologic disposal in each country of the world. On the other hand, if proven feasible, $CO_2$ sequestration sites would have to be numerous to handle the large volume of $CO_2$ to be sequestered. For nuclear waste, one or two sites will be selected for maximum isolation capability and studied in great detail; for $CO_2$ sequestration, such detailed analysis may not be necessary.

- The safety of nuclear waste disposal underground is enhanced by an engineered barrier system, including waste canisters and the filling and sealing materials to be emplaced around these canisters for increased isolation. For $CO_2$ sequestration, engineered barrier systems will normally be impractical.

A number of areas of similarities or transferable methodologies exist between nuclear waste geologic disposal and $CO_2$ geologic sequestration:

- Both nuclear waste and $CO_2$ geologic storage will require carefully and logically designed procedures for systematic regional surveys and site selection. For example, in the Finnish Nuclear Waste Program (which probably will have the first high-level nuclear waste repository in Europe), a 12-year program (1980–1992) progressed from a nationwide geologic survey to regional studies identifying 327 regional blocks, followed by environmental and geologic studies that led to the identification of 134 investigation areas, and finally the determination of five sites for field investigation (TILA-99, 1999). Similar systematic site screening and selection procedures may be necessary for $CO_2$ geologic sequestration.

- After identifying a potential site, both nuclear waste and $CO_2$ cases would require a carefully laid-out site characterization program to evaluate the site over tens to hundreds of square kilometers. Some of the techniques developed for nuclear waste site characterization over the last 20–30 years may be applicable to the $CO_2$ case. These include hydrological, geophysical, geochemical, and rock-mechanical laboratory and field-testing, as well as data analysis and modeling methods.

- Nuclear-waste-repository performance assessment might also be transferable to $CO_2$ geologic sequestration. For example, the systematic survey of FEP (features, events, and processes) developed in the nuclear waste area may be applicable to the $CO_2$ case. In predicting the performance of $CO_2$ sequestration in geologic formations, we may also take advantage of the advanced numerical models of flow and transport in complex geologic systems that have been developed because of the need for nuclear-waste-repository performance assessment (see, for example, SKI, 1996 and NIREX, 1995).

- The nuclear-waste-repository safety assessment also makes use of concepts such as probabilistic assessment, reasonable expectation, and likelihood of risk. These concepts were accepted, for example, in the WIPP waste repository program. They could also be useful for $CO_2$ sequestration, in which the probability of leakage can be put in a risk-assessment framework.

- Finally, like nuclear waste, $CO_2$ will remain underground for a long time. This requirement raises questions about the ability of flow and transport models to predict behavior well beyond the time over which they have been tested. Natural analogue studies, which can provide information about processes and events on geologic time scales (hundreds to millions of years), and which have been used in nuclear waste disposal investigations, are already being used for $CO_2$ storage investigations as well. The long time horizon for storage also raises issues about creating a legacy for future generations to deal with, concerns about safety in the event of human intrusion, and health, safety and environmental (HSE) liability that extends over many generations, successive land owners, and changing land use patterns.

Rather than providing a broad discussion of experiences from a number of nuclear waste projects worldwide, this section focuses on the history, development, science and technology, and eventual successful opening of a particular underground nuclear waste repository. This is the Waste Isolation Pilot Plant (WIPP) project, which is the first U.S. geologic repository for the permanent disposal of TRU (transuranic) radioactive waste. It is one of only two long-term underground repositories in the world that have been successfully permitted and opened to receive radioactive wastes (the other one being the repository for intermediate-level waste at Forsmark, Sweden). The WIPP facility, located 40 km southeast of Carlsbad, New Mexico and operated by the U.S. Department of Energy, occupies 16 $km^2$ of federal land. The repository is emplaced in a salt deposit 225 million years old, at a depth of 655 m. In 1999, after obtaining the required permits, WIPP opened and began storing TRU waste.

In Section 6.2, we review the history of the WIPP development and the related congressional, regulatory, and legal actions. Then we discuss the broad technical criteria contained in WIPP regulations and radioactive release limits established by the US. Environmental Protection Agency (EPA). Section 6.4 reviews the approach for performance assessment and risk assessment that was used in the WIPP project. The proposed monitoring plans are presented in Section 6.5. Finally, lessons learned, useful scientific and technical methods, and risk-assessment approaches that may be applicable to $CO_2$ sequestration are summarized in Section 6.6.

## 6.2. History of the WIPP Project and Regulatory Process

The Atomic Energy Commission (AEC), which in the early 1950s evolved into the Department of Energy and Nuclear Regulatory Commission, recognized the need for nuclear waste disposal. The AEC asked the National Academy of Sciences (NAS, 1957) to conduct a study of possible approaches for the disposal of radioactive wastes. A panel of the American Institute of Physics also evaluated potential strategies (APS, 1978). A wide range of alternatives was discussed, including geologic storage, ejection into outer space, and subseabed disposal. One outcome of the various discussions was that nuclear waste disposal in geologic formations, particularly with salt as the host rock, appeared to be one of the best options.

Surveys and studies were initiated at a number of salt sites in the U.S., and the Lyons site in Kansas was selected for detailed consideration. However, in 1970, this site was rejected because of the complexity of the site hydrogeology and also because of the presence of existing boreholes that may have compromised its integrity as an isolation facility. Note that the matter of existing or abandoned boreholes that have not been properly sealed has since become a significant issue in selecting sites for isolation of hazardous wastes and remediating sites contaminated by chemical wastes in general.

In 1974, the salt formation at about 600 m depth near Carlsbad, New Mexico, was suggested as a potential site. Site evaluation was initiated with the drilling of a 900 m exploratory borehole. Initial work indicated that the site might be promising, and in 1978, the State of New Mexico established a group to provide technical oversight of the project. The DOE also engaged the NAS for occasional scientific and technical review of the project until it could be successfully implemented.

In 1979, Congress authorized research and development (R&D) at the Carlsbad site, exempted the project from Nuclear Regulatory Commission regulations, and gave oversight to the U.S. Environmental Protection Agency (EPA). Based on this congressional act, in 1982 the first exploratory shaft was constructed at the site, and underground excavation was started to provide opportunities for *in situ* R&D to characterize the site and assess its suitability for nuclear waste storage.

From 1985 through 1989, EPA took a number of steps in establishing the regulatory framework for WIPP, including the 1985 WIPP regulation, Subparts B and C of 40 CFR Part 191, and the determination in 1986 that Resource Conservation and Recovery Act (RCRA) regulation was applicable to WIPP. In 1989, DOE applied to the U.S. Department of the Interior for the withdrawal of 10,240 acres of federal land near Carlsbad for WIPP use, which was finally approved by Congress as the Land Withdrawal Act, signed by the President in 1992.

Parallel to these regulatory steps, R&D at the WIPP site was intensively conducted, with technical review from ad hoc scientific panels and from NAS, as well as regulatory oversight from a number of agencies and interested groups listed below:

US EPA:
- Office of Radiation and Indoor Air (ORIA)
- Region VI Office (Dallas, Texas)
- Office of Solid Waste

State of New Mexico:
- State RCRA and mixed waste programs (authorized by EPA)
- Environmental Department
- Environmental Evaluation Group (EEG)

Others:
- US DOI (land)
- US NRC (transportation)
- Tribes
- Independent groups

**Table 6.1. WIPP history.**

| | |
|---|---|
| 1955–56 | AEC/NAS initiated study on disposal of radioactive waste: recommended salt as host rock |
| 1970 | Initial proposal of Lyons site in Kansas rejected (complex geology, hydrology, existing boreholes) |
| 1974 | Suggestions of Carlsbad site, NM.<br>Initiation of 3000-feet exploratory hole. |
| 1979 | Congress authorized R&D and exempted WIPP from NRC regulation |
| 1982 | First exploratory shaft and underground excavation began |
| 1989 | EPA established WIPP regulations |
| 1989 | DOE applied to DOI for withdrawal of 10,240 acres of federal land for WIPP use |
| 1992 | Congress passed Land Withdrawal Act which was signed by the President |
| 1996 | EPA issued compliance criteria for WIPP |
| 1996 | DOE submitted WIPP Compliance Certification Application CCA |
| 1998 | EPA certified WIPP<br>Law suits |
| 1999 | Various judicial actions<br>WIPP opened, April, 1999 |

**Table 6.2. Congressional, regulatory and legal process.**

| | |
|---|---|
| 1978 | State technical oversight (site selected based on exploratory work 1974/5) |
| 1979 | Congress authorized R&D and designated EPA oversight (exempt from NRC) |
| 1985, 1986 | EPA established WIPP regulation (1985), subparts B and C of 40 CFR Part 191.<br>Applicability of RCRA to WIPP (1986) |
| 1990 | EPA approval for 5-year test plan; EPA authorized New Mexico Environmental Department to regulate mixed waste disposal |
| 1992 | Congress passed WIPP Land Withdrawal Act |
| 1995 | WIPP submitted RCRA-Part B permit application by DOE |
| 1996 | EPA issued WIPP compliance Criteria, February<br>DOE submitted Compliance Certification Application (CCA), Oct. 1996 |
| 1997 1998 | EPA preliminary certification Oct. 1997; many public meetings, 1997–98; Certification May 1998 |
| 1999 | NM and local groups filed law suits; Judicial actions up to April 1999 |
| | Numerous interactions among DOE, state agencies, tribes, EPA, DOI (land), NRC (transportation) and environmental groups. |

In 1995, DOE submitted an RCRA-Part B permit application for WIPP to EPA. In February 1996, EPA issued WIPP compliance criteria, and DOE submitted the WIPP compliance certification application (CCA) in October the same year. EPA issued preliminary certification in October 1997, which also initiated a series of public meetings, consummated by EPA certification in May 1998. This was immediately followed by a number of lawsuits, which were acted on by the courts between May 1998 and April 1999. The WIPP was finally opened to receive radioactive waste in April 1999.

The various steps in the history of WIPP development are summarized in Tables 6.1 and 6.2.

## 6.3. Broad Technical Criteria and Regulatory Limits

The conceptual picture of the WIPP project is the excavation at about 600 m depth of underground tunnels and rooms, in which nuclear wastes are emplaced and sealed. The primary HSE concern results from the degradation of the waste containers over time and the subsequent leakage of radionuclides from the repository, through shallower geological formations, to the biosphere or the accessible environment.

The broad technical criteria issued by EPA (40 CFR Part 194) in 1994 cover five areas:

1. Quality Assurance
2. Use of computer models to simulate WIPP performance
3. Limits on radionuclide releases to specific levels in 10,000 years
4. Measures to reduce the likelihood that the release limits will be exceeded
5. Standards for protecting individuals and groundwater from exposure to radioactive contamination

The first area, quality assurance, indicates EPA's and the public's interest not only in the results of DOE's evaluation of the WIPP site, but also in the traceability of conclusions back to site data and their reproducibility. The second area, the use of computer models, reflects the recognition that the performance of a geologic repository depends on details of the geologic system and on uncertainties of parameters and future scenarios, and that computer models are essential tools to incorporate such complex information and to treat the associated uncertainties.

The third and fifth areas provide requirements on repository performance to ensure public safety. The former is called the containment requirement, which specifies limits on the escape of radionuclides across a specified imaginary subsurface boundary surrounding the repository. The latter is the individual or ground water protection requirement, which specifies the maximum dosage from all possible pathways that may be received by an individual residing at a single geographic point on the surface of the accessible environment or by a drinking-water aquifer.

Fulfillment of both these requirements is to be evaluated on a reasonable-expectation basis. More specifically for the containment requirement, reasonable expectation means that, based on a carefully conducted and documented performance assessment (see next section), the `cumulative release of various radionuclides from the repository to the accessible environment over the next 10,000 years should have a likelihood of less than one part in 10 to exceed the release limits (RL) given in Table 6.3, and of less than one part in 1,000 to exceed ten times these release limits. The "likelihood" is evaluated through calculations of complementary cumulative distribution functions (CCDF), accounting for the ranges of possible scenarios, physical conditions and parameter uncertainties (Cheng and Iles, 1983; Apostolakis, 1990). A typical example is shown in Figure 6.1, which shows the results of two sets of CCDF calculations (labeled CCA and PAVT) for cumulative releases of the radionuclides in Table 6.3 (called total normalized release in the figure), as compared with the EPA limit. The EPA unit on the x-axis is the total of the release limits shown in Table 6.3.

For compliance with the individual and groundwater protection requirement, calculations are required to meet reasonable expectations in the CCDF sense, on the maximum annual dosage. However, DOE later decided to use the worst-case scenarios instead of reasonable expectations for these calculations.

**Table 6.3. The 40 CFR Part 191 release limits for the containment requirements**
(from Table 1 of Appendix A, 40 CFR Part 191).

| **Radionuclide** | **$L_I$*** |
|---|---|
| Americium -241 or -243 | 100 |
| Carbon-14 | 100 |
| Cesium-135, -137 | 1,000 |
| Iodine-129 | 100 |
| Neptunium-237 | 100 |
| P1utonium-238, -239, -240, -242 | 100 |
| Radium-226 | 100 |
| Strontium-90 | 1,000 |
| Technetium-99 | 10,000 |
| Thorium-230, -232 | 10 |
| Tin-126 | 1,000 |
| Uranium-233, -234, -235, -236, -238 | 100 |
| Any other alpha-emitting radionuclide with a half-life greater than 20 years | 100 |
| Any other radionuclide with a half-life greater than 20 years that does not emit alpha particles | 1,000 |

* $L_1$ is the release limit per $10^6$ Ci of transuranium (TRU) waste with half lives greater than 20 years.

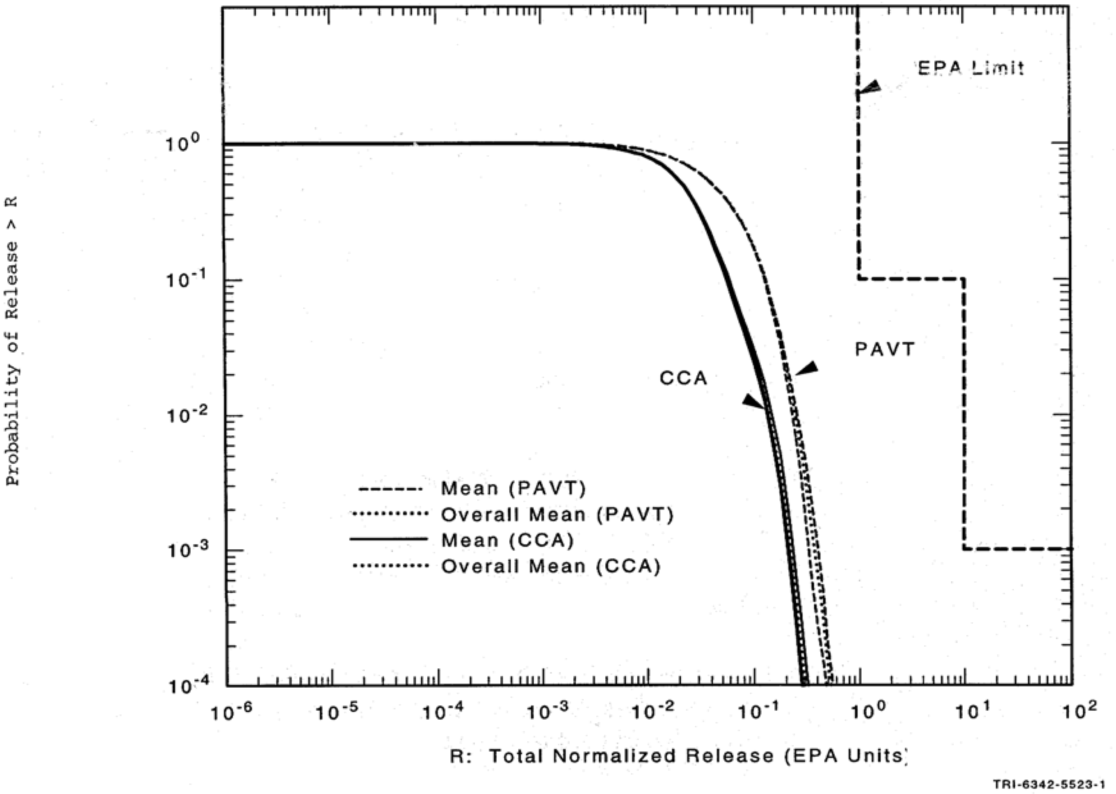

**Figure 6.1. Comparison of mean CCDF (complementary cumulative distribution function) and curves resulting from the performance assessment of the Compliance Certification Application (CCA) and the performance assessment verification test (PAVT) with the EPA release limits (dashed lines). This figure is taken from U.S. DOE (1996).**

## 6.4. Performance Assessment Methodology

To conduct performance assessment of a repository at the WIPP site, DOE was required to make careful field measurements and related laboratory tests to understand the geology, hydrology, hydrogeology and geochemistry of the WIPP disposal system. Extensive measurements and tests were conducted at the site both on land surface and in the underground facility. Background radiation in air, soil, and water were also measured. These data and information were used in the construction of conceptual models and computational models of the site, based on which predictions of repository performance were made for current and future climatological and meteorological conditions. Generally, there were many discussions on the key technical issues and optimal scientific approaches for linking site data to performance assessment (Cook and Tsang, 1990; Tsang et al., 1994).

Three major areas were developed within the performance assessment of the WIPP project, which were later used in a number of other nuclear waste programs in the U.S. and abroad. The first was the development of the FEP (Features, Events, and Processes) framework (Hunter, 1989; Cranwell et al., 1990), which is a formal procedure to identify all relevant features, events, and processes at the site. Here, *features* refer to geologic features, such as stratigraphic layering, faults or fracture zones, and various boundary conditions. *Events* refer to occurrences such as changes in precipitation fluxes, glaciation, seismic activities, and mining enterprises. *Processes* refer to physico-chemical and other processes active at the site. Examples include buoyancy flow of variable-density fluids, coupling of mechanical-stress changes with changes in rock permeability, and chemical-sorption and matrix-diffusion effects. Examples of potentially disruptive events and processes that may occur at the WIPP site are given in Table 6.4.

The FEP framework is a procedure by which the adequacy and comprehensiveness of the relevant FEPs are hopefully assured. By combining these FEPs scenarios are constructed and selected for performance assessment. Through the efforts of the Nuclear Energy Agency (NEA) in Paris and certain national nuclear management agencies such as the Swedish Nuclear Power Inspectorate (SKI) in Stockholm, a list of over 1,200 possible FEPs have been compiled, which include natural, human-induced and repository waste-induced events and processes (Andersson et al., 1989; Stenhouse et al., 1993). The naturally occurring FEPs are used to evaluate what was referred to at WIPP as the "undisturbed performance" (UP) of the repository, and FEPs related to human activities, repository construction and waste emplacement are used to evaluate so-called "disturbed performance" (DP). Then for a given site, all the FEPs are reviewed, screened, and combined. The screening procedure uses three criteria:

1. Probability of occurrence at a given site for the particular FEP under discussion
2. Its impact or consequences
3. Regulatory requirements

The screening must be carried out in a well-documented manner, including formal expert elicitation and peer review panels (Hora and Iman, 1989; Bonano et al., 1990; Ortiz et al., 1991). Note that expert elicitation and peer review are not superficial activities, but carefully structured and documented procedures to obtain the best opinions corresponding to the state-of-knowledge. In the case of WIPP, this procedure was used to screen the 1,200 FEPs down to 900, and then down to 236 natural and human or repository-induced FEPs. Among the natural FEPs, investigators for WIPP identified 70 as relevant, then selected 26 to be included in WIPP performance assessment. WIPP investigators conducted about 300 side studies to develop and document arguments for such screening.

Note that WIPP investigators considered human-induced FEPs to be potentially more damaging to the repository than naturally occurring FEPs. These included (see Table 6.4) mining activities, existing boreholes, future drilling events, and geothermal, oil, and gas developments. On the other hand, the impact of undetected abandoned wells was screened out because of its low probability at the WIPP site. The performance assessment at WIPP did not consider processes and events with a probability of less than one in 10,000 in the next 10,000 years, and this judgment allowed the investigators to screen out volcanic activities, nuclear criticality, formation of new fracture zones caused by permafrost, etc. On the other hand, FEPs such as excavation fracturing, gas generation, salt creep, and leakage through the shaft and tunnel system were included in the performance assessment.

The second element of WIPP performance assessment that has become an example followed by other nuclear waste programs is uncertainty identification and treatment (Zimmerman et al., 1990; NEA, 1987; Iman and Helton, 1991; Doctor, 1989). WIPP investigators identified uncertainties as occurring in four major areas: scenarios, conceptual models, computational models, and parameter values and variability. These are listed in Table 6.5, together with proposed techniques to assess or reduce them. These uncertainties were further evaluated based on whether they were subjective uncertainty or stochastic uncertainty. The former concerns the inability to predict future events; the latter refers to incomplete knowledge of the site parameters and properties.

**Table 6.4. Potentially disruptive events and processes (Cranwell et al., 1990).**

**Natural Events and Processes**

- Celestial Bodies
  - Meteorite Impact
- Surficial Events and Processes
  - Erosion/Sedimentation
  - Glaciation
  - Pluvial Periods
  - Sea-Level Variations
  - Hurricanes
  - Seiches
  - Tsunamis
  - Regional Subsidence or Uplift
  - Mass Wasting
  - Flooding
- Subsurface Events and Processes
  - Diapirism
  - Seismic Activity
  - Volcanic Activity
  - Magmatic Activity
  - Formation of Dissolution Cavities
  - Formation of Interconnected Fracture Systems
    - Faulting

Human-Induced Events and Processes

- Inadvertent Intrusions
  - Explosions
  - Drilling
  - Mining
  - Injection Wells
  - Withdrawal Wells
- Hydrologic Stresses
  - Irrigation
  - Damming of Streams and Rivers
- Repository-and Waste-Induced Events and Processes
  - Caving and Subsidence
  - Shaft and Borehole Seal Degradation
  - Thermally Induced Stress Fracturing in Host Rock
  - Excavation-Induced Stress Fracturing in Host Rock
  - Gas Generation
  - Explosions
  - Nuclear Criticality

**Table 6.5. Techniques for assessing or reducing uncertainty in the WIPP performance assessment (Benram-Howery and Hunter, 1989b).**

| Type of Uncertainty | Technique for Assessing or Reducing Uncertainty |
|---|---|
| Scenarios (Completeness Logic, and Probabilities) | Expert Judgment and Peer Review<br>Quality Assurance |
| Conceptual Models | Expert Judgment and Peer Review<br>Sensitivity Analysis<br>Uncertainty Analysis<br>Quality Assurance |
| Computer Models | Expert Judgment and Peer Review<br>Verification and Validation*<br>Sensitivity Analysis<br>Quality Assurance |
| Parameter Values and Variability | Expert Judgment and Peer Review<br>Data-Collection Programs<br>Sampling Techniques<br>Sensitivity Analysis<br>Uncertainty Analysis<br>Quality Assurance |

*to the extent possible

In WIPP performance assessment, the CCDFs were calculated by first identifying 57 uncertain parameters that were considered important. Then, multiple realizations of these parameters were generated using a Latin Hypercube sampling scheme (Seaholm et al., 1988). For each realization, Monte Carlo random sampling was used over six stochastic variables, which defined times and locations of (for instance) human intrusion events, to generate a series of about 10,000 "futures." Modeling results of radionuclide releases for these "futures" were then used to calculate CCDFs, from which the mean, 10th, and 90th percentiles can be evaluated. These results allow a comparison with regulatory release limits, such as that shown in Figure 6.1.

The third element of performance assessment as part of the WIPP and other national waste geologic storage projects is the advanced numerical modeling techniques that have been developed for simulation of flow and transport in complex geologic media. These may prove to be useful for the performance assessment of $CO_2$ geologic sequestration. They include fracture-network models for media dominated by fractures; stochastic models for media of strongly varying hydraulic properties; and dual-permeability models for media where both fractures and porous matrix play significant roles (see, e.g., Zimmerman, 1990, 1998; NIREX, 1995; SKI, 1996). Furthermore, so-called coupled-process models have also been developed for coupling effects of thermal, hydrological, geochemical, and geomechanical processes to evaluate their effects on flow and transport (Tsang, 1987, 1991, 1999; Stephansson et al., 1996; Xu and Pruess, 1998).

## 6.5. Monitoring Approaches

Although the time period of interest for performance assessment at WIPP is 10,000 years, the planned period of monitoring is much shorter, ranging from 50 to 150 years. This is based on the philosophy that we should not burden future generations with monitoring a repository of waste that the present generation has produced, and that we should design the waste repository carefully enough that it can do without long-term monitoring.

Monitoring may be divided into measurements in the pre-closure stage and the post-closure stage. The former is the period before the nuclear waste repository is filled with waste, while the latter is the period after the repository is full, sealed, and closed. Pre-closure monitoring includes:

- Measurement of properties of backfill materials, such as porosity, permeability, and deformation
- Deformation (salt creep) of roof, wall, and floor of the tunnels containing the waste
- Detection of the initiation and displacement of major brittle features in rock
- Groundwater flow
- Brine quantity, flux, composition and spatial distribution
- Gas quantity and composition

In conducting these measurements and analyzing the data, it is important to know beforehand the expected results and how much deviation would be significant. Significance is based on the effect on performance assessment outcome. This is especially true if the parameter measured is related to the conceptual model of the site. Deviations that should alert responsive actions need to be defined, and appropriate responses need to be planned.

Post-closure monitoring would extend the monitoring time period to 150 years, which includes the 50 years of pre-closure monitoring and 100 years of post-closure measurements. The WIPP project was sensitive to the idea that any such measurements should not adversely affect the integrity of the repository. Thus, for example, no cables connecting the repository to the accessible environment will be used, and methods would emphasize remote sensing and telemetry techniques. The proposed post-closure monitoring methods for WIPP include:

- Groundwater surveillance program, including water levels, flow direction, and chemical composition in an upper formation (the Culebra formation at WIPP site)
- Geomechanical monitoring
- Volatile organic carbon (VOC) emission, which is a function of gas production and creep in the repository
- Land surface subsidence

Concerning groundwater surveillance, the plan is to obtain measurements in 48 wells monthly for approximately thirty years beyond the pre-closure period of 50 years, and further, to take water samples annually from seven wells for analysis. Land subsidence measurements are considered a good non-intrusive performance-confirmation method and are useful in testing conceptual models. Generally, a good initial baseline measurement is needed so that changes can be determined and analyzed for whether they are within an acceptable range. The land-surface benchmark was established in 1996 at the WIPP site, and changes will be measured every 10 years.

In addition to the above monitoring program, measurements on nearby ecological systems will also be conducted periodically. These include surface water, sediments, and soils, and measurement techniques will include radiation monitoring, VOC monitoring, aerial photography, and wild-life monitoring. These will be conducted annually until a number of years after the 50 year pre-closure period.

## 6.6. Lessons Learned and Applications to $CO_2$ Sequestration

In reviewing the history, the regulatory requirements, and some key elements of performance assessment and monitoring planning of the WIPP project, we can identify a number of the lessons learned and methodologies used that could be applicable to $CO_2$ sequestration.

The first lesson is to involve the scientific community, local communities, and the political system in advisory and decision-making roles. For the WIPP project, it was very useful to involve national academies and the scientific community at large right from the beginning. Thus the NAS was invited to give scientific consideration and guidance from WIPP's first conception. Consequently, all through the WIPP project up to its successful conclusion, NAS provided an objective peer-review function. Further, various ad hoc committees from the scientific community were organized to be peer reviewers for various aspects of the project. Along with this, WIPP was also consistently active in international cooperation, which gave credibility to the project. The public, state, tribes, and other interested groups were also encouraged to be involved early in the project history, to review and interact with the project. Though there were still conflicts that had to be decided in court, the open approach made the path forward possible. This is in contrast to the nuclear waste programs in certain countries, where the programs were stopped partly because of ineffective communication with interested parties, and partly because of the attitude of "trust us, we know best" that these programs were perceived to have. In addition, for a project of such large scale and such significant impact on the country, involvement of the Congress, the individual states, and the federal government is to be expected. Early contact with and considerations by responsible congressional and government staff are crucial to eventual project success.

The second lesson is about the role of simulation models, and how probabilistic approaches can be used to build confidence in simulations that extend well beyond the time period over which they have been tested. Like $CO_2$ storage, safe nuclear waste disposal requires understanding the complex, coupled physical-chemical-mechanical processes that will occur over periods of hundreds to thousands of years. Until geologic disposal of nuclear waste was proposed, models that could simulate such behavior were not available. Major effort was devoted to the development and testing of these models, and tremendous progress has been made in building this capability. Nevertheless, for nuclear waste disposal, significant uncertainties remain about the adequacy of such site characterization, the level of understanding of the complex processes involved, and the completeness of the important events included in our simulations. In light of the need to move forward, nuclear waste storage programs around the world have developed and adopted a disciplined approach for dealing with these uncertainties. The Features-Events-Processes (FEP) methodology for identifying and ranking the importance of various attributes of the site, containment approach, and human behavior may provide a useful framework for evaluating geologic storage of $CO_2$. In addition, 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 $CO_2$ storage at a given site. The study and simulation of natural analogues, such as naturally occurring $CO_2$ reservoirs, are useful for demonstrating the ability of simulation models to predict the behavior of analogous systems on the time scales that are meaningful for $CO_2$ storage. Regulatory agencies and the general public are expected to require assurance about the reliability of the simulation models that are used to predict the safety and effectiveness of geologic storage of $CO_2$. Preparing for this requirement by having a documented track record of successful applications of these simulation models – to a wide range of relevant laboratory experiments and field sites – will be helpful in this regard.

Another important lesson to be learned from nuclear waste disposal is that safe and effective storage allows for the possibility that the primary containment structure might leak. In fact, nuclear waste disposal projects in the U.S. acknowledge potential leakage, and their performance is evaluated with the possibility that when the waste container is breached, radionuclides move into the surrounding rocks, and eventually (albeit very slowly) migrate to the accessible environment. A combination of three regulatory requirements is used to ensure human and environmental health under these conditions. First, there are performance requirements on elements of the engineered systems (e.g., canisters). Second, there are requirements on the integrated system (engineered plus geologic system) that limit the release of radionuclides from the repository. And finally, there are requirements that limit the dose to which an individual living at a specified distance from the site would be exposed. This hierarchy of performance requirements may provide a guide for regulating $CO_2$ storage sites where some leakage may also be acceptable. Performance requirements for leakage from $CO_2$-injection wells may be specified in a manner analogous to the engineered systems in a repository. Setting limits on the acceptable leakage rates from the primary storage structure is analogous to setting specifications for maximum permissible leakage from the repository. Also, release of $CO_2$ to the atmosphere could be considered analogous to maximum dose limits for human exposure. Early consideration of this approach may create a helpful framework for HSE risk assessment of $CO_2$ storage in geologic formations.

Finally, similar to nuclear waste storage programs, a carefully designed monitoring effort is needed for $CO_2$ storage. This includes the need for baseline measurements early on in the project, continued monitoring of critical parameters, pre-determination of acceptable parameter ranges, and plans for actions if changes are beyond these acceptable ranges. Current plans for long-term monitoring of nuclear waste disposal sites envision that after the repository performance is confirmed to be within the expected range, monitoring can be stopped. For WIPP, this performance confirmation period is expected to last from 50 to 150 years. A similar concept may also be valuable for geologic storage of $CO_2$. That is, once the performance of the storage site is confirmed to be performing as expected, monitoring could be curtailed or stopped. This is particularly important in light of the long-term nature of $CO_2$ storage projects and the ongoing costs associated with perpetual monitoring.

**Appendices**

# Appendix 1: Data Table and References for Figure 2.2a, Comparison of carbon reservoirs and one-time events

| Reservoirs and One-Time Events | Amount of Carbon $10^6$ tonnes | Amount of $CO_2$ $10^6$ tonnes | Amount of $CO_2$ $10^{12}$ cf at SATP | Amount of $CO_2$ $10^9$ $m^3$ at SATP |
|---|---|---|---|---|
| Total Intermediate and Deep Ocean Carbon Reservoir | 38100000 | 140000000 | 2730000 | 77300000 |
| Total Global Recoverable Fossil Fuel Reserves (Projected) | 4000000 | 14700000 | 285000 | 8110000 |
| Total Terrestrial Systems Carbon Reservoir | 1960000 | 7190000 | 140000 | 3970000 |
| Total Surface Ocean Carbon Reservoir | 1030000 | 3780000 | 73800 | 2090000 |
| Total Global Proven Fossil Fuel Reserves -1999 | 882000 | 3230000 | 63200 | 1790000 |
| Total Atmospheric Carbon Reservoir | 775000 | 2840000 | 55500 | 1570000 |
| Total Global Coal Reserves - 1999 | 691000 | 2530000 | 49500 | 1400000 |
| Total Global Anthropogenic Carbon Emissions 1751-2000 | 290000 | 1060000 | 20800 | 588000 |
| Total US Proven Fossil Fuel Reserves - 1999 | 179000 | 655000 | 12800 | 362000 |
| Total US Coal Reserves - 1998 | 173000 | 634000 | 12400 | 351000 |
| Total Global Crude Oil Reserves - 1999 | 116000 | 424000 | 8290 | 235000 |
| Total Global Natural Gas Reserves - 1999 | 75100 | 275000 | 5380 | 152000 |
| Total US Natural Gas Reserves - 1998 | 3240 | 11900 | 230 | 6570 |
| Total US Crude Oil Reserves - 1998 | 2430 | 8910 | 170 | 4930 |
| Largest Single US Natural Volcanic Carbon Dioxide Reservoir | 140 | 510 | 10 | 280 |
| Total US Natural Gas Storage Capacity - 1999 | 99 | 360 | 7.1 | 200 |
| Active Volcanic Eruptions - Pinatubo 1991 | 12 | 44 | 0.86 | 24 |
| Conversion Reference for 1 MMTC | 1.000 | 3.667 | 0.07163 | 2.028 |
| Lake Nyos - $CO_2$ released in 1986 event | 0.065 | 0.24 | 0.0047 | 0.13 |
| Accidental Release from an Industrial Fire Suppression System | 0.0000007 | 0.0000026 | 0.00000005 | 0.0000014 |

| Reservoirs and One-Time Events | Amount of $CO_2$ $10^9$ cf at critical | Amount of $CO_2$ $10^6$ $m^3$ at critical | Reference |
|---|---|---|---|
| Total Intermediate and Deep Ocean Carbon Reservoir | 10600000 | 300000000 | US DOE (1999) |
| Total Global Recoverable Fossil Fuel Reserves (Projected) | 1110000 | 31400000 | US DOE (1999) |
| Total Terrestrial Systems Carbon Reservoir | 544000 | 15400000 | US DOE (1999) |
| Total Surface Ocean Carbon Reservoir | 286000 | 8100000 | US DOE (1999) |
| Total Global Proven Fossil Fuel Reserves -1999 | 245000 | 6930000 | Compiled from US DOE (2000b) |
| Total Atmospheric Carbon Reservoir | 215000 | 6090000 | US DOE (1999) |
| Total Global Coal Reserves - 1999 | 192000 | 5430000 | US DOE (2000b) |
| Total Global Anthropogenic Carbon Emissions 1751-2000 | 80500 | 2280000 | Est. from Marland et al. (2000) |
| Total US Proven Fossil Fuel Reserves - 1999 | 49600 | 1400000 | Compiled from US DOE (2000a) |
| Total US Coal Reserves - 1998 | 48000 | 1360000 | US DOE (2000a) |
| Total Global Crude Oil Reserves - 1999 | 32100 | 910000 | US DOE (2000b) |
| Total Global Natural Gas Reserves - 1999 | 20800 | 590000 | US DOE (2000b) |
| Total US Natural Gas Reserves - 1998 | 900 | 255000 | US DOE (2000a) |
| Total US Crude Oil Reserves - 1998 | 675 | 19100 | US DOE (2000a) |
| Largest Single US Natural Volcanic Carbon Dioxide Reservoir | 39 | 1100 | Broadhead (1987) |
| Total US Natural Gas Storage Capacity - 1999 | 28 | 780 | US DOE (2000a) |
| Active Volcanic Eruptions - Pinatubo 1991 | 3.3 | 94 | Gerlach et al. (1996) |
| Conversion Reference for 1 MMTC | 0.2776 | 7.861 | Appendix 3 |
| Lake Nyos - $CO_2$ released in 1986 event | 0.18 | 0.51 | Giggenbach (1990) |
| Accidental Release from an Industrial Fire Suppression System | 0.00000019 | 0.0000055 | US DOE (1998) |

## Appendix 2: Data Table and References for Figure 2.2b, Comparison of carbon fluxes and target sequestration rates

| **Carbon Fluxes and Target Sequestration Rates** | **Amount of Carbon** $10^6$ tonnes/yr | **Amount of $CO_2$** $10^6$ tonnes/yr | **Amount of $CO_2$** $10^{12}$ cf/yr at SATP | **Amount of $CO_2$** $10^9$ $m^3$/yr at SATP |
|---|---|---|---|---|
| Annual Carbon Cycling - Atmospheric Exchange | 150000 | 550000 | 10700 | 304000 |
| Annual Net Primary Productivity | 61700 | 226000 | 4420 | 125000 |
| Global Average Annual Anthropogenic Emissions - Early 1990s | 7400 | 27100 | 530 | 15000 |
| US DOE Target Global Sequestration Rate for 2050 | 4000 | 14700 | 287 | 8110 |
| Global Annual Coal Production/Consumption - 1998 | 3190 | 11700 | 228 | 6470 |
| Global Annual Petroleum Consumption - 1998 | 3110 | 11400 | 223 | 6310 |
| Global Annual Crude Oil Production - 1998 | 2830 | 10400 | 203 | 5740 |
| US Annual Anthropogenic Emissions - 1998 | 1500 | 5500 | 107 | 3040 |
| US Annual Emissons from Fossil Fuel Combustion - 1998 | 1470 | 5390 | 105 | 2980 |
| Global Annual Natural Gas Production/Consumption - 1998 | 1200 | 4400 | 86 | 2430 |
| US DOE Target Global Sequestration Rate for 2025 | 1000 | 3670 | 72 | 2030 |
| US Annual Petroleum Consumption - 1998 | 810 | 2960 | 58 | 1640 |
| US Annual Coal Production/Consumption - 1998 | 685 | 2510 | 49 | 1390 |
| Total Annual US Electric Utilities Power Plant Emissions | 550 | 2020 | 39 | 1120 |
| Total Global Annual Human Expired $CO_2$ (6000 x $10^6$ people) | 410 | 1500 | 29 | 830 |
| US Annual Natural Gas Production/Consumption - 1998 | 290 | 1060 | 21 | 590 |
| US Annual Crude Oil Production - 1998 | 265 | 970 | 19 | 535 |
| Total Annual Volcanic Emissions | 42 | 155 | 3.0 | 86 |
| Total Annual Greenhouse Gas Emissions, Royal Dutch Shell - 1999 | 27 | 99 | 1.9 | 55 |
| Total US Annual Human Expired $CO_2$ (300 x $10^6$ people) | 20.5 | 75 | 1.5 | 41 |
| US Annual Average Single Refinery Input - 1999 | 4.3 | 16 | 0.31 | 8.7 |
| Active Volcanic Eruptions - Mt Etna 1975-1987 (No diffuse flux) | 3.6 | 13 | 0.26 | 7.3 |
| Annual Emissions From One 500 MW Coal-Fired Power Plant | 1.3 | 4.8 | 0.093 | 2.6 |
| Conversion Reference for 1 x $10^6$ Metric Tonnes Carbon | 1.000 | 3.667 | 0.07163 | 2.028 |
| Annual Emissions From An Average Refinery - Chevron | 0.56 | 2.05 | 0.040 | 1.14 |
| Annual Emissions From One 500 MW Natural Gas Power Plant | 0.54 | 2.00 | 0.039 | 1.1 |
| Weyburn EOR Project Target Annual Injection Rate | 0.50 | 1.80 | 0.036 | 1.0 |
| Active Volcanic Eruptions - Mt. St. Helens 1980-81 | 0.48 | 1.75 | 0.034 | 0.97 |
| Sleipner Vest Pilot Sequestration Project Annual Injection Rate | 0.27 | 0.99 | 0.019 | 0.55 |
| Annual Emissions From One 500 MW Geothermal Power Plant | 0.16 | 0.60 | 0.012 | 0.33 |
| Mammoth Mtn Average Annual Release Rate 1990-95 | 0.12 | 0.44 | 0.0086 | 0.24 |
| Lake Nyos - Annual $CO_2$ Accumulation 1989-90 | 0.003 | 0.011 | 0.00021 | 0.0061 |
| Single Passenger Car Emissions for 15k mi/yr, 20 mi/gal | 0.0000019 | 0.0000068 | 0.00000013 | 0.0000038 |
| Average Annual Individual Human Expired $CO_2$ | 0.00000007 | 0.00000026 | 0.000000005 | 0.00000014 |

# Appendix 2 cont.: Data Table and References for Figure 2.2b, Comparison of carbon fluxes and target sequestration rates

| **Carbon Fluxes and Target Sequestration Rates** | **Amount of $CO_2$** $10^9$ cf/yr at critical | **Amount of $CO_2$** $10^6$ $m^3$/yr at critical | **Reference** |
|---|---|---|---|
| Annual Carbon Cycling - Atmospheric Exchange | 41600 | 1180000 | US DOE (1999) |
| Annual Net Primary Productivity | 17100 | 485000 | US DOE (1999) |
| Global Average Annual Anthropogenic Emissions - Early 1990s | 2050 | 58200 | US DOE (1999) |
| US DOE Target Global Sequestration Rate for 2050 | 1110 | 31400 | US DOE (1999) |
| Global Annual Coal Production/Consumption - 1998 | 885 | 25100 | US DOE (2000b) |
| Global Annual Petroleum Consumption - 1998 | 860 | 24400 | US DOE (2000b) |
| Global Annual Crude Oil Production - 1998 | 785 | 22200 | US DOE (2000b) |
| US Annual Anthropogenic Emissions - 1998 | 415 | 11800 | US DOE (1999) |
| US Annual Emissons from Fossil Fuel Combustion - 1998 | 410 | 11600 | US EPA (2000d) |
| Global Annual Natural Gas Production/Consumption - 1998 | 330 | 9430 | US DOE (2000b) |
| US DOE Target Global Sequestration Rate for 2025 | 280 | 7860 | US DOE (1999) |
| US Annual Petroleum Consumption - 1998 | 225 | 6340 | US DOE (2000a) |
| US Annual Coal Production/Consumption - 1998 | 190 | 5380 | US DOE (2000a) |
| Total Annual US Electric Utilities Power Plant Emissions | 150 | 4320 | US DOE 2000a |
| Total Global Annual Human Expired $CO_2$ (6000 x $10^6$ people) | 115 | 3220 | Appendix 3 |
| US Annual Natural Gas Production/Consumption - 1998 | 81 | 2280 | US DOE (2000a) |
| US Annual Crude Oil Production - 1998 | 73 | 2080 | US DOE (2000a) |
| Total Annual Volcanic Emissions | 12 | 330 | Gerlach (1992) |
| Total Annual Greenhouse Gas Emissions, Royal Dutch Shell - 1999 | 7.5 | 210 | Shell (2000) |
| Total US Annual Human Expired $CO_2$ (300 x $10^6$ people) | 5.7 | 160 | Appendix 3 |
| US Annual Average Single Refinery Input - 1999 | 1.2 | 34 | US DOE (2000a) |
| Active Volcanic Eruptions - Mt Etna 1975-1987 (No diffuse flux) | 1.0 | 28 | Allard et al. (1991) |
| Annual Emissions From One 500 MW Coal-Fired Power Plant | 0.36 | 10 | Fridleifsson (2001); Barbier (1997) |
| Conversion Reference for 1 x $10^6$ Metric Tonnes Carbon | 0.2776 | 7.861 | Appendix 3 |
| Annual Emissions From An Average Refinery - Chevron | 0.155 | 4.4 | Chevron (2001) |
| Annual Emissions From One 500 MW Natural Gas Power Plant | 0.15 | 4.25 | Fridleifsson (2001); Barbier (1997) |
| Weyburn EOR Project Target Annual Injection Rate | 0.14 | 3.9 | Brown et al. (2001) |
| Active Volcanic Eruptions - Mt. St. Helens 1980-81 | 0.13 | 3.8 | Brantley and Koepenick (1995) |
| Sleipner Vest Pilot Sequestration Project Annual Injection Rate | 0.075 | 2.1 | Kongsjorden et al. (1997) |
| Annual Emissions From One 500 MW Geothermal Power Plant | 0.045 | 1.3 | Fridleifsson (2001); Barbier (1997) |
| Mammoth Mtn Average Annual Release Rate 1990-95 | 0.033 | 0.94 | Farrar et al. (1995) |
| Lake Nyos - Annual $CO_2$ Accumulation 1989-90 | 0.00083 | 0.024 | Evans et al. (1993) |
| Single Passenger Car Emissions for 15k mi/yr, 20 mi/gal | 0.00000051 | 0.000015 | US DOE Fuel Economy Guide 2001 |
| Average Annual Individual Human Expired $CO_2$ | 0.000000019 | 0.00000055 | Appendix 3 |

# Appendix 3: Conversions for Appendices 1 and 2

**Standard Conversions**

SATP = standard ambient temperature and pressure = 25 degC/298.15 degK and 1 atm/760 torr

Density of $CO_2$ at SATP = 1.8080 kg/$m^3$

Density of natural gas at SATP = 0.65688 kg/$m^3$

Density of natural gas at 60 degF and 14.73 psia = 0.68009 kg/$m^3$

14.73 psia = 1 atm

14.4435 $10^{12}$ cf (60 degF, 14.73 psia) or 14.4435 tcf natural gas (methane) = 1 MMTC

7.333 x $10^6$ brl crude oil = 1 MMT crude = 0.8487 MMTC

$10^6$ shtn coal = 1.1023 MMT coal = 0.7716 MMTC

1 MMTC = 3.667 MMT $CO_2$

1 MMTC = 0.07163 x $10^{12}$ cf $CO_2$ (SATP)

1 MMTC = 2.028 x $10^9$ $m^3$ $CO_2$ (SATP)

critical T and P for $CO_2$ are 31.0 degC and 72.878 atm, density = 466.5 kg/$m^3$

1 MMTC = 0.2776 x $10^9$ cf (crit)

1 MMTC = 7.861 x $10^6$ $m^3$ $CO_2$ (crit)

1 metric ton = 1.10231136 short tons, International Energy Annual 1999, Energy Information Agency, US DOE, 2000. www.eia.doe.gov/emeu/iea/tablec1.html ,

1 metric ton = 7.333 barrels crude oil, , International Energy Annual 1999, Energy Information Agency, US DOE, 2000. www.eia.doe.gov/emeu/iea/tablec2.html

U.S. crude oil = 84.87 % carbon by weight, Table B4, Emissions of Greenhouse Gases in the United States 1999, Energy Information Agency, US DOE, 2000. www.eia.doe.gov/oiaf/1605/ggrpt/tblb4.html

Hong, B.D. and E.R. Slatick, Carbon Dioxide Emission Factors for Coal, *Quarterly Coal Report*, January-April 1994, DOE/EIA-0121(94/Q1), Energy Information Administration, US DOE, Washington, DC, Aug 1994. www.eia.doe.gov/cneaf/coal/quarterly/co2_article/co2.html

> The carbon content of coal can be from low in the 60s percent to a high of above 80%. A rough estimate of the average carbon content of coal is 70%

**Reservoirs/Events**

Accidental Release from an Industrial Fire Suppression System, US DOE, 1998.
55 x 100 lbs = 5500 lbs x (1kg/2.20462 lbs) x (1 metric ton/1000 kg) = 2.495 metric tons

Total Global Anthropogenic Carbon Emissions 1751-2000, estimated from Marland et al., 2000.
270 MMTC 1751-1997. Emissions for 1997 were 6.6 MMTC. Estimated emissions were 6.6, 6.6, and 6.7 for 1998, 1999, 2000. 270 MMTC + 6.6 + 6.6 + 6.7 = 290 MMTC for 1751 to 2000.

Total U.S. Natural Gas Storage Capacity – 1999, U.S. DOE 2000, AER 1999, Table 6.7.
6.881 x $10^{12}$ cf nat gas (60 degf, 14.73 psia) x (1 $m^3$/35.31467 cf) x 0.68009 kg/$m^3$ (@ 60 degF, 14.73 psia) x (1 metric ton/1000 kg) x (12 g carbon/16 g natural gas {$CH_4$}) = 99.386 x $10^6$ metric tons carbon = 99.386 MMTC

Total U.S. Crude Oil Reserves -1998, U.S. DOE, 2000, AER 1999, Table 4.10.
21.0 x $10^9$ brls crude oil x (1 MT crude/7.333 brls crude) x (0.8487 MT carbon/1 MT crude) x
1 MMTC/$10^6$ MTC = 2430 MMTC

Total U.S. Natural Gas Reserves including natural gas liquids (assumed to have the same physical properties as crude oil) – 1998, U.S. DOE, 2000, AER 1999, Table 4.10.
164.0 x $10^{12}$ cf nat gas (60 degF, 14.73 psia) x (1$m^3$/35.31467 cf) x (0.68009 kg/$m^3$) x
(1 metric ton/1000 kg) x (12g carbon/16g nat gas) = 2368.7 MMTC
7.5 x $10^9$ brls nat gas liquids x (1 metric ton ngl/7.333 brls) x (0.8487 tons carbon/1 ton ngl) =
868.0 MMTC
Total = 2368.7 + 868.0 = 3240 MMTC

Total Global Natural Gas Reserves 1998, U.S. DOE 2000, IEA 1999, Table 8.1.
5149.6/5210.8 x$10^{12}$ cf. 5200 x $10^{12}$ cf nat gas (60 degF, 14.73 psia) x (1$m^3$/35.31467 cf) x (0.68009 kg/$m^3$) x (1 metric ton/1000 kg) x (12g carbon/16g nat gas) = 75100 MMTC

Total Global Crude Oil Reserves 1998, U.S. DOE 2000, IEA 1999, Table 8.1.
1016.8/981.4 x $10^9$ brls crude. 1000 x $10^9$ brls crude x (1 MT crude/7.333 brls crude) x (0.8487 MT carbon/1 MT crude) x 1 MMTC/$10^6$ MTC = 115740 MMTC

Total U.S. Demonstrated Coal Reserves on 1-Jan-1999, U.S. DOE 2000, AER 1999, Table 4.11.
504.3 x $10^9$ shtn coal => 504300 Mshtn coal x (1 MMT coal/1.1023 Mshtn coal) x 0.70 MMTC/MMT coal = 320250 MMTC

Total U.S. Recoverable Coal Reserves on 1-Jan-1999, U.S. DOE 2000, AER 1999, Table 4.11.
504.3 x $10^9$ shtn coal => 504300 Mshtn coal x (1 MMT coal/1.1023 Mshtn coal) x 0.54 MMT recoverable coal/MMT demonstrated coal x 0.70 MMTC/MMT coal = 172900 MMTC
54% of demonstrated reserves are estimated to be recoverable.

Total Global Recoverable Coal 1998, U.S. DOE, 2000, IEA 1999, Table 8.2.
1088602 Mshtn coal x (1 MMT coal/1.1023 Mshtn) x (0.70 MMTC/MMT coal) = 691300 MMTC

Total U.S. Proven Fossil Fuel Reserves 1998 = 172900 + 3240 + 2430 = 178570 MMTC

Total Global Proven Fossil Fuel Reserves 1998 = 691300 + 115700 + 75100 = 882100 MMTC

**Rates**

Single passenger car emissions for 15,000 mi/yr, 20 mi/gal of gasoline, US DOE Fuel Economy Guide 2001 provided conversion, 1 gal of gasoline = 20 lbs $CO_2$.

(20 lbs $CO_2$/1 gal gasoline) x (1 kg/2.20462 lbs) x (1 metric ton/1000 kg) x (1 gal of gasoline/20 miles) x 15,000 mi/yr = 6.804 metric tons/yr

Lake Nyos annual accumulation 1989-1990, Evans et al., 1993.
$2.6 \times 10^8$ mol $CO_2$/yr x (44.0 g/mol) x (1kg/1000g) x (1 metric ton/1000kg) = $1.144 \times 10^4$ metric tons $CO_2$/yr

Mammoth Mountain Annual Average 1990-95, >100 acre tree-kill area, Farrar et al., 1995.
1200 metric tons/day x 365 days/yr = 438,000 metric tons CO2/yr

Weyburn EOR Project Target Annual Injection Rate, Brown et al., 2001.
5000 metric tons $CO_2$/day x 365 days/yr = 1.83 x 10E6 metric tons $CO_2$/yr

Active Volcanic Eruptions – Mt. St. Helens 1980-1981, Brantley and Koepenick, 1995.
($0.04 \times 10^{12}$ mol $CO_2$/yr) x 44.0 g/mol x 1 MMT $CO_2$/$10^{12}$ g $CO_2$= 1.76 MMT $CO_2$/yr

Active Volcanic Eruptions – Mt. Etna 1984-1985, Allard et al., 1991.
13 Tg $CO_2$/yr x 1 MMT $CO_2$/Tg $CO_2$ = 13 MMT $CO_2$/yr

Total Annual Volcanic Emissions, Gerlach, 1992.
3-4 x $10^{12}$ mol $CO_2$/yr x 44 g/mol x 1 metric ton/$10^6$ g = 132-176 x $10^6$ metric tons of $CO_2$ = 132-176 MMT $CO_2$/yr ; approximate average = 155 MMT $CO_2$/yr = 42.3 MMTC/yr

Annual Emissions from One 500 MW Power Plant, Barbier 1997, Fridleifsson 2001.
Geothermal, approx median = 136 kg $CO_2$/MW-hr x (1metric ton/$10^3$ kg) x 500 MW x 24 hr/day x 365 days/yr = 596,000 metric tons $CO_2$/yr
Natural Gas, 453 kg/MW-hr → 1,984,000 metric tons $CO_2$/yr
Coal, 1042 kg/MW-hr → 4,564,000 metric tons $CO_2$/yr

Annual Emissions From an Average Refinery, Chevron personal communication.
5600 tons $CO_2$/day x (1 ton carbon/3.667 tons $CO_2$) x 365 days/yr = 557000 tons carbon/yr = 0.56 MMTC/yr

U.S. Annual Average Single Refinery Input – 1999, U.S. DOE 2000, AER 1999, Table 5.8, 5.9
16.11 Mbrls crude total/day x (1 metric ton crude/7.333 brls) x (0.8487 metric tons carbon/1 metric ton crude) x 365 days/yr x (1/159 refineries) = 4.2802 MMTC/yr/refinery

U.S. Annual Crude Oil Production – 1998, U.S. DOE 2000, AER, 1999, Table 5.1.
6.25 Mbrl crude/day x (1 metric ton/7.333 brls) x (365 day/yr) x (0.8487 tons carbon/1 ton crude) = 264.025 MMTC/yr

Approximate U.S. Annual Natural Gas Production/Consumption, 1998, U.S. DOE, 2000, AER 1999, Table 6.1.
Production = $18.71 \times 10^{12}$ cf nat gas (60 degF, 14.73 psia)/yr x (1 $m^3$/35.31467 cf) x 0.68009 kg/$m^3$ (@ 60 degF, 14.73 psia) x (1 metric ton/1000 kg) x (12 g carbon/16 g nat gas {$CH_4$}) = 270.230 MMTC
Consumption = $21.26 \times 10^{12}$ cf nat gas/yr = 307.060 MMTC/yr
Approximate average = 290 MMTC/yr

Approximate U.S. Annual Coal Consumption/Production, 1998, U.S. DOE 2000, AER 1999, Table 7.1.
Production = 1117.5 Mshtn coal/yr x (1 MMT coal/1.1023 Mshtn coal) x (0.70 MMT carbon/MMT coal) = 709.65 MMTC/yr
Consumption = 1040.1 Mshtn coal/yr = 660.50 MMTC/yr
Approximate average = 685 MMTC/yr

U.S. Annual Petroleum Consumption 1998, U.S. DOE, 2000, AER 1999, Table 5.1.
18.92 Mbrl/day x 365 day/yr x (1 MMT petroleum/7.333 Mbrl) x (12 g carbon/14 g petroleum) = 807 MMTC/yr

Approximate Global Annual Gas Production/Consumption, Table 1.3 and Table 2.4, U.S. DOE 1999, IEA 1998

Production = 82.96 x$10^{12}$ cf nat gas (60 degF, 14.73 psia)/yr x (1 $m^3$/35.31467 cf) x (0.68009 kg/$m^3$) x (1 metric ton/1000 kg) x (12 g carbon/16 g nat gas) = 1198 MMTC

Consumption = 82.19 x $10^{12}$/yr= 1187 MMTC/yr

Approximately 1200 MMTC/yr

U.S. Annual Anthropogenic Emissions – 1998, U.S. DOE, 2000, AER 1999, Table 12.1.

5483.9 MMT $CO_2$ x (1 MMTC/3.667 MMT $CO_2$) = 1495.5 MMTC/yr

Global Annual Crude Oil Production, U.S. DOE 1999, IEA 1998, Table 2.2.

66,972,000 brls crude/day x (365 days/yr) x (1 metric ton/7.333 brls crude) x (0.8487 metric tons carbon/metric ton crude) = 2830 MMTC/yr

Global Annual Petroleum Consumption, U.S. DOE 1999, IEA 1998, Table 1.2.

73,643,000 brls petroleum/day x (365 days/yr) x (1 metric ton/7.333 brls crude) x (0.8487 metric tons carbon/ metric ton crude) = 3110/yr

Global Annual Coal Consumption/Production 1998, U.S. DOE 1999, IEA 1998, Table 1.4 and Table 2.5.

5013.47 Mshtns and 5042.69 Mshtons. 5025 Mshtns x (1 MMT coal/1.1023 Mshtn) x (0.70 MMTC/MMT coal) = 3190 MMTC/yr

**Back of the Envelope (BOE) Calculations for Annual Carbon Dioxide Production Rate in Humans**

1) For one person:

$$1\text{ breath} \times \frac{0.5\text{ L air }(25\ ^{o}\text{C, 1 atm})}{\text{breath}} \times \frac{3.5\text{ parts }CO_2}{100\text{ parts air}} \times \frac{1\text{ mol }CO_2}{24.465\text{ L }CO_2\ (25\ ^{o}\text{C, 1 atm})} \times \frac{44\text{ g }CO_2}{1\text{ mol }CO_2} \times$$

$$\frac{1\text{ kg }CO_2}{1000\text{ g }CO_2} \times \frac{1\text{ metric tonne }CO_2}{1000\text{ kg }CO_2} \times \frac{15\text{ breaths}}{1\text{ minute}} \times \frac{60\text{ minutes}}{1\text{ hour}} \times \frac{24\text{ hours}}{1\text{ day}} \times \frac{365\text{ days}}{1\text{ year}} =$$

0.25 metric tonnes of $CO_2$ per person per year

2) Total US Annual Human Expired $CO_2$ = $\frac{0.25\text{ metric tonnes of }CO_2}{\text{year x person}}$ x $\underline{300\ (10^6)}$ people =

75 x $10^6$ metric tonnes of $CO_2$

3) Total Global Annual Human Expired $CO_2$ = $\frac{0.25\text{ metric tonnes of }CO_2}{\text{year x person}}$ x 6000 ($10^6$) people =

1500 x $10^6$ metric tonnes of $CO_2$

## Appendix 4: Data Table and References for Figure 2.6, Comparison of ambient concentrations of $CO_2$ and risks of exposure

| OCCURRENCE | CONCENTRATION | PARTIAL | PRESSURE | REFERENCE |
|---|---|---|---|---|
| | in % | in atm | in torr | |
| Annual Average Atmospheric - Glacial Maximum | 0.018% | 0.00018 | 0.14 | IPCC (1995) |
| Annual Average Atmospheric - >200 yrs ago | 0.028% | 0.00028 | 0.21 | IPCC (1995) |
| Annual Average Atmospheric - in 2000 | 0.037% | 0.00037 | 0.28 | CDIAC (2000) |
| Normal Ventilation - IAQ Exposure Limit | 0.10% | 0.001 | 0.76 | CGA (1997); ASHRAE(1999) |
| Projected Atmospheric during Cretaceous - 75 Mya | 0.15% | 0.0015 | 1.14 | Est.from Berner and Lasaga (1989) |
| Controlled Atmosphere Greenhouse Enrichment | 0.15% | 0.0015 | 1.14 | Average from Mastalerz (1977) |
| Occupational Exposure - Avg Daily 8hr Limit | 0.50% | 0.005 | 3.8 | NIOSH/OSHA (1981); ACGIH (1999) |
| Soil Gas - Aerated/Normal | 1.0% | 0.010 | 7.6 | Est. from Farrar et al. (1995) |
| Occupational Exposure - Avg Short Term 15 Min. Limit | 3.0% | 0.030 | 23 | NIOSH/OSHA (1981); ACGIH (1999) |
| Breathing Rate Doubles | 3.0% | 0.030 | 23 | Est. from NIOSH (1976) |
| Exhaled Breath - Normal | 3.5% | 0.035 | 27 | Campbell (1999) |
| Occupational Exposure - Maximum Limit | 4.0% | 0.040 | 30 | NIOSH (1994a) |
| Headache, Dyspnea, and Dizziness | 4.0-7.0% | 0.04-0.07 | 30-53 | Est from NIOSH (1976); CGA (1997) |
| Exhaled Breath - Strenuous Exercise | 5.0% | 0.05 | 38 | Est. from Campbell (1999) |
| Severe Headache and Mental Confusion | 7.0-10% | 0.07-0.10 | 53-76 | Est. from NIOSH (1976); CGA (1997) |
| Exhaust from Internal Combustion Engine – Diesel* | (8) 2-12% | (0.08) 0.02-0.12 | (61) 15-91 | Est. from Heywood (1988) |
| Lowest Published Lethal Concentration - 5 Min. Exp | 9.0% | 0.09 | 68 | SIRI (2001) |
| Soil Gas - Poorly Aerated/Waterlogged | 10.0% | 0.10 | 76 | Est. from Amundson and Davidson (1990) |
| Exhaust from Internal Combustion Engine – Gasoline* | (12) 8-14% | (0.12) 0.08-0.14 | (91) 61-106 | Est from Heywood (1988) |
| Unconscious Within Minutes | 10-15% | 0.10-0.15 | 76-114 | Est from NIOSH (1976); CGA (1997) |
| Unconscious and Convulsions Within Minutes | 15-25% | 0.15-0.25 | 114-190 | Est from NIOSH (1976); CGA (1997) |
| Soil Gas - Tree Die-Off From Volcanic Release | 20% | 0.2 | 152 | Est from Farrar et al. (1995) |
| Death Within Minutes | 30% | 0.3 | 228 | Est from NIOSH (1976); CGA (1997) |
| Effective Control of Food Rot Fungi | 30% | 0.3 | 228 | Est from Tian et al. (2001) |
| Effective Control of Insect Pests in Food Storage | 40% | 0.40 | 304 | Est from Annis and Morton (1997) |
| Mars Atmosphere | 95% | 0.006 | 4.3 | www.zepa.net/astro/planets.html |
| Venus Atmosphere | 96% | 91 | 69200 | www.zepa.net/astro/planets.html |

* Combustion estimates are highly variable. The values from Heywood (1988) are rough averages read from a graph.

Est. = estimated

## Appendix 5: Applications of $CO_2$

*Beverage Carbonation*
The characteristic tingle and fizz of carbonated beverages results from the interaction of $CO_2$ and $H_2O$ molecules in beverage solutions.

*Fire Protection*
$CO_2$ is widely used in fire extinguishers for both hand held and fixed systems. It is also used in "blanketing" to displace oxygen to prevent combustion. A major advantage of $CO_2$ is its cleanliness.

*Enhanced Recovery of Petroleum Products*
$CO_2$ is used in various processes of oil and natural gas well stimulation to enhance productivity.

*Molded Product Deflashing*
Molded products, especially rubber compounds, often have undesirable flashings where mold sections were joined. $CO_2$ is used to cool and embrittle the flashings in preparation of mechanical removal, saving the high cost of hand trimming and buffing.

*pH Control of Waste Water*
One of the critical aspects of effluent disposal is its degree of alkalinity. $CO_2$ is one of the safest, cleanest and most economical means of reducing the pH of waste water.

*Foam Expansion*
The use of $CO_2$ as an expanding agent in polyurethane foams eliminates the use of volatile organic compounds and chlorofluorocarbons to provide a safe, low cost alternative to these harmful chemicals.

*Shielded Arc Welding*
$CO_2$ vapor is used to displace oxygen at the point of contact in arc welding. Speed, efficiency, quality and cost factors have stimulated wide use of this application in the Welding Industry.

*Low Temperature Grinding*
$CO_2$ is added to heat sensitive materials in grinding operations for heat removal to prevent product softening or melting.

*Aerosol Propellant*
$CO_2$ is a cost effective alternative pressure medium in many non-water based aerosol products, eliminating the use of hazardous solvents and chlorofluorocarbons.

*Recarbonation of Potable Water*
As a result of typical municipal potable water softening operations, the pH level of the water is raised which results in a chemically unstable water condition. The application of $CO_2$ (recarbonation) establishes a chemical balance and minimizes mineral deposits in the water distribution system.

*Purging and Inerting*
Fuel tanks, pipelines and other containers with explosive or combustible vapors must be purged prior to some types of maintenance and/or change in usage. $CO_2$ is an effective method for purging vessels of many unwanted vapors.

*Foundry Core Hardening*
As an alternative to the conventional process of baking foundry cores, $CO_2$ is used in conjunction with a treated (silica) sand to form high quality cores resulting in time and energy savings.

*Chemical Reactant*
$CO_2$ is used in the production of various carbonate compounds, in controlling pH and in many other processes involving chemical reactions.

*IQF Freezing*
Cooling and freezing operations are integrated into high speed production lines with $CO_2$ tunnel and spiral freezers. Advantages include reduction of cold storage space, bacteria retardation, greater refrigeration efficiency, enhanced product quality and more efficient space utilization.

*Shrink Fitting*
Machined metal products such as bushings, collars and seats which require a "tight fit" can be easily assembled by cooling with dry ice.

*Refrigeration in Mixing & Blending*
$CO_2$ injection reduces heat buildup induced by blade friction in mixing and blending of meat products and firms it in preparation of the forming process. Semi-automatic operation reduces manpower and minimizes space requirements.

*Low Temperature Testing*
$CO_2$ is used as a refrigerant for testing products by simulating ambient temperatures down to -109.8 r;F. $CO_2$ is easily stored, readily available and can be piped for automatic operation.

*Pest Control in Stored Grain*
Fumigating coffee, tea, tobacco and grains with $CO_2$ has been successful in controlling insects in storage. $CO_2$ provides a safe, clean alternative to environmentally hazardous fumigants.

*Greenhouse Atmosphere Enrichment*
$CO_2$ is an essential raw material used by green plants in photosynthesis. Increasing the amount of $CO_2$ available to plants can greatly increase plant growth and yields.

*In-Transit Refrigeration of Processed Foods*
Perishable processed foods can be refrigerated with $CO_2$ during processing, enabling direct loading onto trucks and sustained safe temperatures during mechanical refrigeration temperature pull-down. Valuable freezer space is conserved and risk of spoilage is minimized. $CO_2$ can also be used in limited applications as the sole refrigerant.

*In-Flight Food Refrigeration*
$CO_2$ in its solid form (Dry Ice) is used to refrigerate In-flight Modules by the Airline Industry. Alternative methods are not as reliable or cost effective.

*Non-Destructive Cleaning*
$CO_2$ cleaning utilizes dry ice to remove contaminants from most surfaces, greatly reducing waste products and the need for chemical solvents, sand, water and other media.

*Modified Atmosphere Packaging*
Packaging perishable food products with $CO_2$ greatly extends the product shelf life by limiting the growth of aerobic microorganisms. Other benefits include reduced development of rancidity and odors, and better color retention.

# Occupational Health Guideline for Carbon Dioxide

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula: $CO_2$
- Synonyms: Carbonic acid gas; "Dry Ice"; $CO_2$
- Appearance and odor: Primarily a colorless, odorless gas; however, it can be a liquid or a solid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon dioxide is 5000 parts of carbon dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9000 milligrams of carbon dioxide per cubic meter of air ($mg/m^3$). NIOSH has recommended that the permissible exposure limit be changed to 10,000 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 30,000 ppm averaged over a 10-minute period. The NIOSH Criteria Document for Carbon Dioxide should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon dioxide can affect the body if it is inhaled. Solid carbon dioxide (dry ice) and compressed carbon dioxide gas from a cylinder can affect the body if it comes in contact with the eyes, skin, or mouth.

- **Effects of overexposure**

Inhaling carbon dioxide may cause rapid breathing, rapid beating of the heart, headache, sweating, shortness of breath, dizziness, mental depression, visual disturbances, shaking, unconsciousness, and death. Skin, eye, or mouth contact with solid carbon dioxide (dry ice) may cause frostbite. Similar effects may occur from carbon dioxide as it is being released from a cylinder.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon dioxide.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to carbon dioxide at potentially hazardous levels.

- **Summary of toxicology**

Carbon dioxide gas is an asphyxiant, a potent respiratory stimulant, and both a stimulant and depressant of the CNS. Respiratory volume is doubled at 4% $CO_2$ and redoubled at 5%. Increases in heart rate and blood pressure have been noted at 7.6% and dyspnea, headache, dizziness, and sweating occur if exposure at that level is prolonged. At 10% and above, prolonged exposure can result in unconsciousness. Above 11%, unconsciousness occurs in 1 minute or less. Numerous human fatalities have occurred after persons entered fermentation vats, wells, and silos where oxygen had been largely replaced by carbon dioxide. Exposure to very high concentrations, 25 to 30%, may cause convulsions. Carbon dioxide at room temperature will not injure the skin, but frostbite may result from contact with the solid or the liquid phases.

## CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44
2. Boiling point (760 mm Hg): −78.5 C (−109 F) (sublimation point)
3. Specific gravity (water = 1): 1.02 (liquid)
4. Vapor density (air = 1 at boiling point of carbon dioxide): 1.52
5. Melting point: −78.5 C (-109 F ) (sublimation point)
6. Vapor pressure at 20 C (68 F): Greater than 1

---

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

**U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES**
Public Health Service    Centers for Disease Control
National Institute for Occupational Safety and Health

**U.S. DEPARTMENT OF LABOR**
Occupational Safety and Health Administration

atmosphere

7. Solubility in water, g/100 g water at 20 C (68 F): 0.14

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with chemically active metals such as sodium, potassium, or hot titanium may cause fire.
3. Hazardous decomposition products: None
4. Special precautions: Liquid or solid carbon dioxide will attack some forms of plastics, rubber, and coatings. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that carbon dioxide is an odorless gas.
2. Irritation Levels: Grant states that "carbon dioxide at high concentration in air causes a stinging sensation in the eyes, nose, and throat. . . ."
3. Evaluation of Warning Properties: Since carbon dioxide has no odor, and since no quantitative information is available relating its irritant effects of to air concentrations, this gas has been treated as a material with poor warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon dioxide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of carbon dioxide in a gas sampling bag, followed by gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon dioxide may be used. An analytical method for carbon dioxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with solid carbon dioxide or from contact with vessels containing carbon dioxide.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon dioxide may occur and control methods which may be effective in each case:

| Operation | Controls |
|---|---|
| Liberation from fermentation in manholes, mine floors, wells, shipwells, brewery vats, garbage dumps, and fruit storage facilities | General dilution ventilation; local exhaust ventilation; personal protective equipment |

| Operation | Controls |
|---|---|
| Use in cooling and refrigerating for storage, preparation and transfer of foods; use as an inert gas in fire extinguishers; for protection of flammable materials during manufacture; in shielded arc welding; and in canned food production | General dilution ventilation; local exhaust ventilation; personal protective equipment |
| Use as an inert pressure medium for aerosol packaging; pressure spraying, spray painting, gas-operated firearms, purging tanks and pipelines, inflating liferafts, manufacture of plastic foam | General dilution ventilation; local exhaust ventilation; personal protective equipment |
| Use in manufacture of carbonated beverages | General dilution ventilation; local exhaust ventilation; personal protective equipment |
| Use as a neutralizing agent in textile processing and treatment of leather hides; use as shattering agent for coal mining; in fracturing and acidizing treatment of oil and gas wells | General dilution ventilation; local exhaust ventilation; personal protective equipment |
| Use during water treatment for neutralizing alkaline waste waters; carbonating water to prevent scaling; use for chemical synthesis and pH control in manufacture of urea, asprin, carbonates and bicarbonates, beer, and sugar | General dilution ventilation; local exhaust ventilation; personal protective equipment |
| Use in miscellaneous operations for enrichment of greenhouse air, antiseptic, industrial solvent extraction, medical use, in foundries, cement curing, and in animal slaughter | General dilution ventilation; local exhaust ventilation; personal protective equipment |

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid carbon dioxide (dry ice) or carbon dioxide as it is being released from a cylinder gets into the eyes, get medical attention.

- **Skin or Mouth Exposure**

If solid carbon dioxide (dry ice) or carbon dioxide as it is being released from a cylinder comes in contact with the skin or mouth, stop the exposure immediately. If frostbite has occurred, get medical attention.

- **Breathing**

If a person breathes in large amounts of carbon dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If carbon dioxide is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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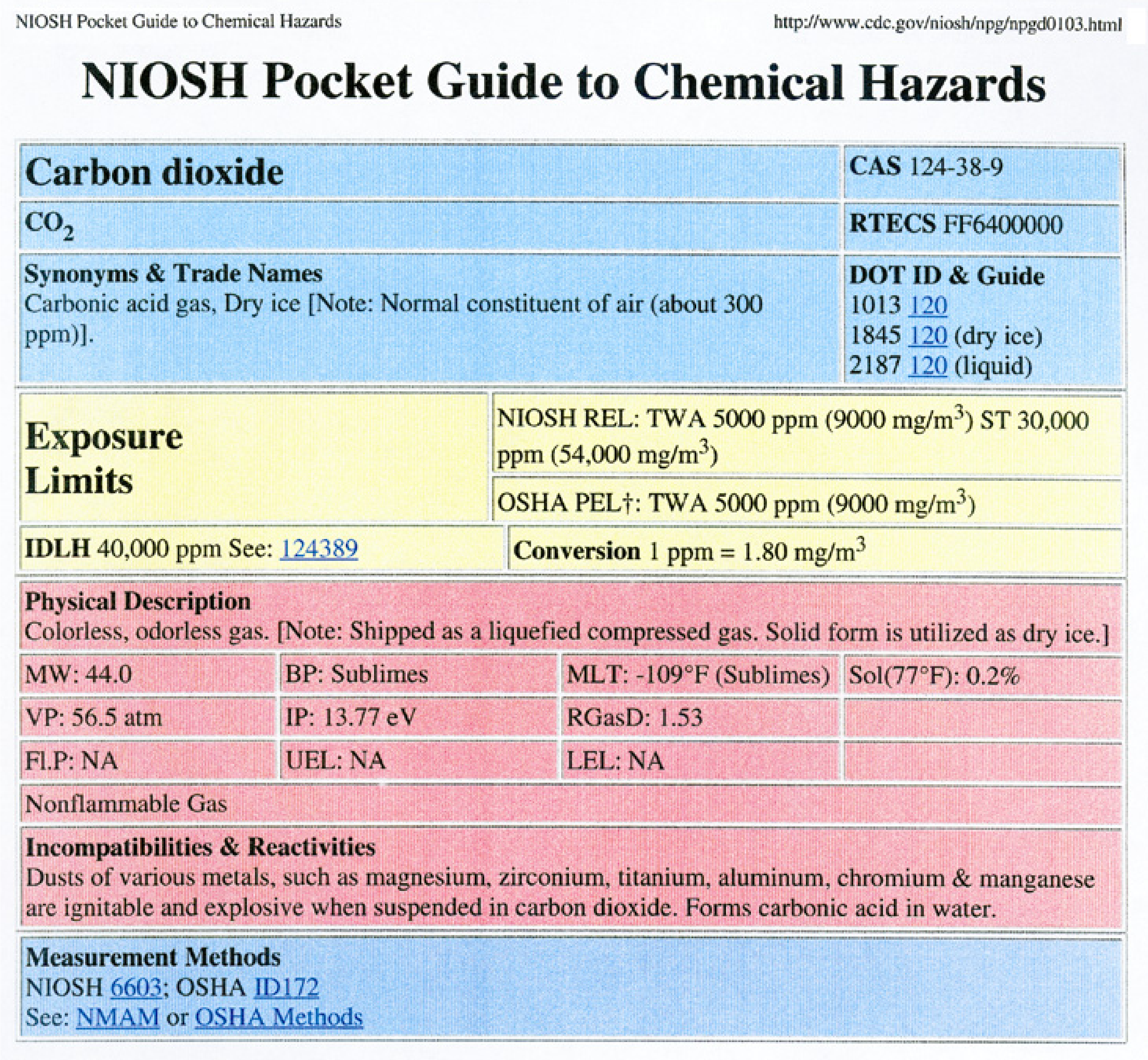
## RESPIRATORY PROTECTION FOR CARBON DIOXIDE

| **Condition** | **Minimum Respiratory Protection* Required Above 5000 ppm** |
|---|---|
| Gas Concentration | |
| 50,000 ppm or less | Any supplied-air respirator.<br>Any self-contained breathing apparatus. |
| Greater than 50,000 ppm or entry and escape from unknown concentrations | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.<br>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode. |
| Fire Fighting | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. |
| Escape | Any escape self-contained breathing apparatus. |

*Only NIOSH-approved or MSHA-approved equipment should be used.

Appendix 7



NIOSH Pocket Guide to Chemical Hazards http://www.cdc.gov/niosh/npg/npgd0103.html

# NIOSH Pocket Guide to Chemical Hazards

| | |
|---|---|
| **Carbon dioxide** | **CAS** 124-38-9 |
| $CO_2$ | **RTECS** FF6400000 |
| **Synonyms & Trade Names**<br>Carbonic acid gas, Dry ice [Note: Normal constituent of air (about 300 ppm)]. | **DOT ID & Guide**<br>1013 120<br>1845 120 (dry ice)<br>2187 120 (liquid) |

| | |
|---|---|
| **Exposure Limits** | NIOSH REL: TWA 5000 ppm (9000 mg/$m^3$) ST 30,000 ppm (54,000 mg/$m^3$)<br>OSHA PEL†: TWA 5000 ppm (9000 mg/$m^3$) |
| **IDLH** 40,000 ppm See: 124389 | **Conversion** 1 ppm = 1.80 mg/$m^3$ |

**Physical Description**
Colorless, odorless gas. [Note: Shipped as a liquefied compressed gas. Solid form is utilized as dry ice.]

| | | | |
|---|---|---|---|
| MW: 44.0 | BP: Sublimes | MLT: -109°F (Sublimes) | Sol(77°F): 0.2% |
| VP: 56.5 atm | IP: 13.77 eV | RGasD: 1.53 | |
| Fl.P: NA | UEL: NA | LEL: NA | |

Nonflammable Gas

**Incompatibilities & Reactivities**
Dusts of various metals, such as magnesium, zirconium, titanium, aluminum, chromium & manganese are ignitable and explosive when suspended in carbon dioxide. Forms carbonic acid in water.

**Measurement Methods**
NIOSH 6603; OSHA ID172
See: NMAM or OSHA Methods

**Personal Protection & Sanitation**
Skin: Frostbite
Eyes: Frostbite
Wash skin: No recommendation
Remove: No recommendation
Change: No recommendation
Provide: Frostbite

**First Aid** (See procedures)
Eye: Frostbite
Skin: Frostbite
Breathing: Respiratory support

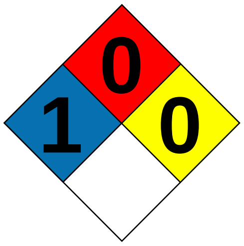
**Respirator Recommendations** NIOSH/OSHA
Up to 40,000 ppm: (APF = 10) Any supplied-air respirator/(APF = 50) Any self-contained breathing apparatus with a full facepiece
Emergency or planned entry into unknown concentrations or IDLH conditions: (APF = 10,000) Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode/(APF = 10,000) Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus
Escape: Any appropriate escape-type, self-contained breathing apparatus

**Exposure Routes** inhalation, skin and/or eye contact (liquid/solid)

**Symptoms** Headache, dizziness, restlessness, paresthesia; dyspnea (breathing difficulty); sweating, malaise (vague feeling of discomfort); increased heart rate, cardiac output, blood pressure; coma; asphyxia; convulsions; frostbite (liquid, dry ice)

**Target Organs** respiratory system, cardiovascular system

See also: INTRODUCTION See ICSC CARD: 0021



# CARBON DIOXIDE

UN 1013
UN 2187
UN 1845

Shipping Name: UN 1013 Carbon dioxide
UN 2187 Carbon dioxide, refrigerated liquid
UN 1845 Carbon dioxide, solid *or* Dry ice

Other Names: Carbonic acid anhydride
Carbonic anhydride
Carbonic acid gas
Dry ice

## Hazards:

- Replaces oxygen in enclosed areas leading to possible asphyxiation
- Odor is not a reliable indicator of the presence of toxic amounts of gas
- Container may BLEVE when exposed to fire
- Contact with solid may cause frostbite
- Gas is heavier than air and will collect and stay in low areas

## Awareness and Operational Level Training Response:

- Stay upwind and uphill
- Determine the extent of the problem
- Isolate the area of release or fire and deny entry
- For container exposed to fire evacuate the area in all directions because of the risk of BLEVE
- Notify local health and fire officials and pollution control agencies

## Description:

- Colorless gas, white solid (dry ice) or cryogenic liquid
- Odorless
- Solid sinks in water, liquid floats on the surface of water; is insoluble in water
- Nonflammable
- Gas is heavier than air and will collect and stay in low areas
- Solid or liquid form will produce large amounts of vapor

## Operational Level Training Response:

RELEASE, NO FIRE:

- Stop the release if it can be done safely from a distance
- Ventilate confined area if it can be done without placing personnel at risk

FIRE:

- Material does not burn; fight surrounding fire with an agent appropriate for the burning material
- DO NOT APPLY WATER to cryogenic liquid containers; if cryogenic liquid containers are exposed to direct flame or elevated temperatures for prolonged times, withdraw immediately to a secure location
- Cool exposed noncryogenic containers with large quantities of water from unattended equipment or remove intact containers if it can be done safely
- If cylinders are exposed to excessive heat from fire or flame contact, withdraw immediately to a secure location

## First Aid:

- Provide Basic Life Support/CPR as needed
- Decontaminate the victim as follows:
    - Inhalation - remove the victim to fresh air and give oxygen if available
- Seek medical attention
- Frostbite - warm injured area in very warm water

**CAS: 124-38-9**

Appendix 9

# GUIDE 120 GASES - INERT (INCLUDING REFRIGERATED LIQUIDS)

## POTENTIAL HAZARDS

### HEALTH

- Vapors may cause dizziness or asphyxiation without warning.
- Vapors from liquefied gas are initially heavier than air and spread along ground.
- Contact with gas or liquefied gas may cause burns, severe injury and/or frostbite.

### FIRE OR EXPLOSION

- **Non-flammable gases.**
- Containers may explode when heated.
- Ruptured cylinders may rocket.

## PUBLIC SAFETY

- **CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.**
- Isolate spill or leak area immediately for at least 25 meters (80 feet) in all directions.
- Keep unauthorized personnel away.
- Stay upwind.
- Many gases are heavier than air and will spread along ground and collect in low or confined areas (sewers, basements, tanks).
- Keep out of low areas.
- Ventilate closed spaces before entering.

### PROTECTIVE CLOTHING

- Wear positive pressure self-contained breathing apparatus (SCBA).
- Structural firefighters 'protective clothing will only provide limited protection.
- Always wear thermal protective clothing when handling refrigerated/cryogenic liquids or solids.

### EVACUATION

**Large Spill**

- Consider initial downwind evacuation for at least 100 meters (330 feet).

**Fire**

- If tank, rail car or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

# GASES - INERT (INCLUDING REFRIGERATED LIQUIDS)

# GUIDE 120

## EMERGENCY RESPONSE

### FIRE

- Use extinguishing agent suitable for type of surrounding fire.
- Move containers from fire area if you can do it without risk.
- Damaged cylinders should be handled only by specialists.

**Fire involving Tanks**

- Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
- Cool containers with flooding quantities of water until well after fire is out.
- Do not direct water at source of leak or safety devices; icing may occur.
- Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
- ALWAYS stay away from tanks engulfed in fire.

### SPILL OR LEAK

- Do not touch or walk through spilled material.
- Stop leak if you can do it without risk.
- Use water spray to reduce vapors or divert vapor cloud drift. Avoid allowing water runoff to contact spilled material.
- Do not direct water at spill or source of leak.
- If possible, turn leaking containers so that gas escapes rather than liquid.
- Prevent entry into waterways, sewers, basements or confined areas.
- Allow substance to evaporate.
- Ventilate the area.

**CAUTION: When in contact with refrigerated/cryogenic liquids, many materials become brittle and are likely to break without warning.**

### FIRST AID

- Move victim to fresh air.
- Call 911 or emergency medical service.
- Apply artificial respiration if victim is not breathing.
- Administer oxygen if breathing is difficult.
- Clothing frozen to the skin should be thawed before being removed.
- In case of contact with liquefied gas, thaw frosted parts with lukewarm water.
- Keep victim warm and quiet.
- Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves.

# International Chemical Safety Cards

## CARBON DIOXIDE

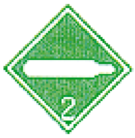
**ICSC: 0021**

National Institute for Occupational Safety and Health

NIOSH

Carbonic acid gas
Carbonic anhydride
$CO_2$
Molecular mass: 44.0

ICSC # 0021
CAS # 124-38-9
RTECS # FF6400000
UN # 1013



| TYPES OF HAZARD/ EXPOSURE | ACUTE HAZARDS/ SYMPTOMS | PREVENTION | FIRST AID/ FIRE FIGHTING |
|---|---|---|---|
| FIRE | Not combustible. | | In case of fire in the surroundings: all extinguishing agents allowed. |
| EXPLOSION | Containers may burst in the heat of a fire! | | In case of fire: keep cylinder cool by spraying with water. Combat fire from a sheltered position. |
| EXPOSURE | | | |
| •INHALATION | Dizziness. Headache. Elevated blood pressure. Tachycardia. | Ventilation. | Fresh air, rest. Artificial respiration if indicated. Refer for medical attention. |
| •SKIN | ON CONTACT WITH LIQUID: FROSTBITE. | Cold-insulating gloves. Protective clothing. | ON FROSTBITE: rinse with plenty of water, do NOT remove clothes. Refer for medical attention. |
| •EYES | On contact with liquid: frostbite. | Safety goggles, or face shield. | First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor. |
| •INGESTION | | | |

| SPILLAGE DISPOSAL | STORAGE | PACKAGING & LABELLING |
|---|---|---|
| Ventilation. NEVER direct water jet on liquid (extra personal protection: self-contained breathing apparatus). | Fireproof if in building. Cool. | R:<br>S:<br>UN Hazard Class: 2.2 |

**SEE IMPORTANT INFORMATION ON BACK**

**ICSC: 0021**

Prepared in the context of cooperation between the International Programme on Chemical Safety & the Commission of the European Communities (C) IPCS CEC 1999. No modifications to the International version have been made except to add the OSHA PELs, NIOSH RELs and NIOSH IDLH values.

# International Chemical Safety Cards

## CARBON DIOXIDE

**ICSC: 0021**

**IMPORTANT DATA**

**PHYSICAL STATE; APPEARANCE:**
ODOURLESS, COLOURLESS, COMPRESSED LIQUEFIED GAS.

**PHYSICAL DANGERS:**
The gas is heavier than air and may accumulate in low ceiling spaces causing deficiency of oxygen. Build up of static electricity can occur at fast flow rates and may ignite any explosive mixtures present. Free-flowing liquid condenses to form extremely cold dry ice.

**CHEMICAL DANGERS:**
The substance decomposes on heating above 2000°C producing toxic carbon monoxide. Reacts violently with strong bases and alkali metals. Various metal dusts such as magnesium, zirconium, titanium, aluminium, chromium and manganese are ignitable and explosive when suspended and heated in carbon dioxide.

**OCCUPATIONAL EXPOSURE LIMITS:**
TLV: 5000 ppm; 9000 mg/m$^3$ (as TWA); 30,000 ppm; 54,000 mg/m$^3$ (as STEL) (ACGIH 1994-1995).
MAK: 5000 ppm; 9000 mg/m$^3$ (1993).
OSHA PEL: TWA 5000 ppm (9000 mg/m$^3$)
NIOSH REL: TWA 5000 ppm (9000 mg/m$^3$) ST 30,000 ppm (54,000 mg/m$^3$)
NIOSH IDLH: 40,000 ppm

**ROUTES OF EXPOSURE:**
The substance can be absorbed into the body by inhalation.

**INHALATION RISK:**
On loss of containment this liquid evaporates very quickly causing supersaturation of the air with serious risk of suffocation when in confined areas.

**EFFECTS OF SHORT-TERM EXPOSURE:**
Inhalation of high concentrations of this gas may cause hyperventilation and unconciousness. Rapid evaporation of the liquid may cause frostbite.

**EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:**
The substance may have effects on the metabolism.

**PHYSICAL PROPERTIES**

Sublimation point: -79°C
Solubility in water, ml/100 ml at 20°C: 88
Vapour pressure, kPa at 20°C: 5720
Relative vapour density (air = 1): 1.5

**ENVIRONMENTAL DATA**

**NOTES**

Carbon dioxide is given off by many fermentation processes (wine, beer, etc.) and is a major component of flue gas. High concentrations in the air cause a deficiency of oxygen with the risk of unconsciousness or death. Check oxygen content before entering area. No odour warning if toxic concentrations are present. Turn leaking cylinder with the leak up to prevent escape of gas in liquid state. Other UN classification numbers for transport are: UN 1845 carbon dioxide, dry ice; UN 2187 carbon dioxide refrigerated liquid.

Transport Emergency Card: TEC (R)-11-1 (in cylinders); 11-2 (refrigerated gas)

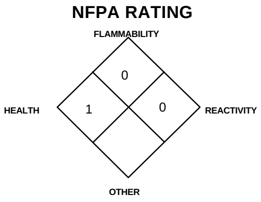
## ADDITIONAL INFORMATION

**ICSC: 0021** **CARBON DIOXIDE**

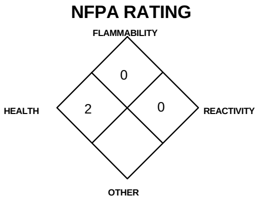
(C) IPCS, CEC, 1999

| | |
|---|---|
| **IMPORTANT LEGAL NOTICE:** | Neither NIOSH, the CEC or the IPCS nor any person acting on behalf of NIOSH, the CEC or the IPCS is responsible for the use which might be made of this information. This card contains the collective views of the IPCS Peer Review Committee and may not reflect in all cases all the detailed requirements included in national legislation on the subject. The user should verify compliance of the cards with the relevant legislation in the country of use. The only modifications made to produce the U.S. version is inclusion of the OSHA PELs, NIOSH RELs and NIOSH IDLH values. |

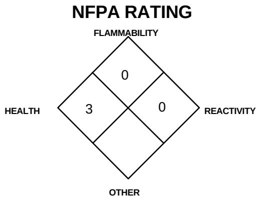
**CARBON DIOXIDE GAS**



**CARBON DIOXIDE SOLID**



**CARBON DIOXIDE LIQUEFIED**



# MATERIAL SAFETY DATA SHEET

*Prepared to U.S. OSHA, CMA, ANSI and Canadian WHMIS Standards*

## PART I *What is the material and what do I need to know in an emergency?*

### 1. PRODUCT IDENTIFICATION

CHEMICAL NAME; CLASS: **CARBON DIOXIDE - $CO_2$, GASEOUS**
**CARBON DIOXIDE - $CO_2$, CRYOGENIC**
**CARBON DIOXIDE - $CO_2$, SOLID**
Document Number: 001013

PRODUCT USE: For general analytical/synthetic chemical uses.

SUPPLIER/MANUFACTURER'S NAME: AIRGAS INC.
ADDRESS: 259 N. Radnor Chester Road
Suite 100
Radnor, PA 19087-5283

BUSINESS PHONE: 1-610-687-5253
EMERGENCY PHONE: CHEMTREC: 1-800-424-9300
International: 703-527-3887 (Call Collect)

DATE OF PREPARATION: May 20, 1996
FOURTH REVISION: January 22, 1999

### 2. COMPOSITION and INFORMATION ON INGREDIENTS

| CHEMICAL NAME | CAS # | mole % | EXPOSURE LIMITS IN AIR | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | ACGIH | | OSHA | | IDLH ppm | OTHER ppm |
| | | | TLV ppm | STEL ppm | PEL ppm | STEL ppm | | |
| Carbon Dioxide | 124-38-9 | > 99.8 | 5000 | 30,000 | 5000<br>10,000 (Vacated 1989 PEL) | 30,000 (Vacated 1989 PEL) | 40,000 | DFG-MAK: 5000<br>NIOSH REL TWA: 5000 ST: 30000 ppm |
| Maximum Impurities | | < 0.2 | None of the trace impurities in this mixture contribute significantly to the hazards associated with the product. All hazard information pertinent to this product has been provided in this Material Safety Data Sheet, per the requirements of the OSHA Hazard Communication Standard (29 CFR 1910.1200) and State equivalent standards. | | | | | |

NE = Not Established C = Ceiling Limit. See Section 16 for Definitions of Terms Used.

NOTE: All WHMIS required information is included. It is located in appropriate sections based on the ANSI Z400.1-1993 format.

## 3. HAZARD IDENTIFICATION

Carbon Dioxide Gas and Cryogenic Liquid

**EMERGENCY OVERVIEW**: Carbon Dioxide is a colorless gas, or a colorless, cryogenic liquid. At low concentrations, both the gas and the liquid are odorless. At higher concentrations Carbon Dioxide will have a sharp, acidic odor. The liquid boils rapidly at standard temperatures and pressures. At concentrations between 2 and 10%, Carbon Dioxide can cause nausea, dizziness, headache, mental confusion, increased blood pressure and respiratory rate. If the gas concentration reaches 10% or more, suffocation and death can occur within minutes. Contact with the cold gas can cause freezing of exposed tissue. Moisture in the air could lead to the formation of carbonic acid which can be irritating to the eyes. All forms of Carbon Dioxide are non-combustible. Carbon Dioxide is heavier than air and should not be allowed to accumulate in low lying areas.

### CARBON DIOXIDE GAS

**HAZARDOUS MATERIAL INFORMATION SYSTEM**

| | | |
|---|---|---|
| HEALTH | (BLUE) | 1 |
| FLAMMABILITY | (RED) | 0 |
| REACTIVITY | (YELLOW) | 0 |
| PROTECTIVE EQUIPMENT | | B |

| EYES | RESPIRATORY | HANDS | BODY |
|---|---|---|---|
|  | See Section 8 |  | See Section 8 |

For routine industrial applications

### CARBON DIOXIDE LIQUEFIED

**HAZARDOUS MATERIAL INFORMATION SYSTEM**

| | | |
|---|---|---|
| HEALTH | (BLUE) | 3 |
| FLAMMABILITY | (RED) | 0 |
| REACTIVITY | (YELLOW) | 0 |
| PROTECTIVE EQUIPMENT | | X |

| EYES | RESPIRATORY | HANDS | BODY |
|---|---|---|---|
|  | See Section 8 |  | See Section 8 |

For routine industrial applications

**See Section 16 for Definition of Ratings**

SYMPTOMS OF OVEREXPOSURE BY ROUTE OF EXPOSURE: The most significant route of overexposure for this gas is by inhalation. The following paragraphs describe symptoms of exposure by route of exposure.

INHALATION: Carbon Dioxide is an asphyxiant and a powerful cerebral vasodilator. If the concentration of Carbon Dioxide reaches 10% or more, suffocation can occur rapidly. Inhalation of concentrations between 2 and 10% can cause nausea, dizziness, headache, mental confusion, increased blood pressure and respiratory rate. Carbon Dioxide initially stimulates respiration and then causes respiratory depression. Inhalation of low concentrations (3-5%) have no known permanent harmful effects. Symptoms in humans at various levels of concentration are as follows:

| **CONCENTRATION** | **SYMPTOMS OF EXPOSURE** |
|---|---|
| 1%: | Slight increase in breathing rate. |
| 2%: | Breathing rate increases to 50% above normal; exposure cause headache, tiredness. |
| 3%: | Breathing increases to twice normal rate and becomes labored. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate. |
| 4-5%: | Breathing increases to approximately four times normal rate, symptoms of intoxication become evident and slight choking may be felt. |
| 5-10%: | Characteristic sharp odor noticeable. Very labored breathing, headache, visual impairment and ringing in the ears. Judgment may be impaired, followed by loss of consciousness. |
| 50-100%: | Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation. |

High concentrations of this gas can also cause an oxygen-deficient environment. However, the asphyxiating properties of Carbon Dioxide will be reached before oxygen-deficiency is a factor.

## 3. HAZARD IDENTIFICATION (Continued)

OTHER POTENTIAL HEALTH EFFECTS: Contact of the cold gas with the skin can lead to frostbite or dermatitis (red, cracked, irritated skin), depending upon concentration and duration of exposure. Contact of the cold gas with the eyes can cause pain, redness, burns, and severe exposure could cause blindness. Symptoms of frostbite include change in skin color to white or grayish-yellow. The pain after contact with cold gas can quickly subside. Moisture in the air could lead to the formation of carbonic acid, which can be irritating to the eyes.

HEALTH EFFECTS OR RISKS FROM EXPOSURE: An Explanation in **Lay Terms**. Overexposure to Carbon Dioxide may cause the following health effects:

**ACUTE**: Inhaling high concentrations of Carbon Dioxide can lead to coma or death. At low concentrations, inhalation of Carbon Dioxide can cause nausea, dizziness, visual disturbances, shaking, headache, mental confusion, sweating, increased heartbeat, and elevated blood pressure and respiratory rate. High concentrations of the gas in air may cause eye irritation or damage.

**CHRONIC**: Reversible effects on the acid-base balance in the blood, blood pressure, and circulatory system may occur after prolonged exposure to elevated Carbon Dioxide levels.

**TARGET ORGANS:** Respiratory system, cardiovascular system, eyes.

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## Carbon Dioxide Solid

**EMERGENCY OVERVIEW**: Solid Carbon Dioxide (dry ice), is a white, opaque solid which releases colorless, gas. This solid sublimates to gas quickly at standard temperatures and pressures, forming a fog in air. As a result, the main hazards associated with Carbon Dioxide are related to Carbon Dioxide gas formation and the cold temperature of the solid and evolved gas. At concentrations between 2 and 10%, Carbon Dioxide can cause nausea, dizziness, headache, mental confusion, increased blood pressure and respiratory rate. If the gas concentration reaches 10% or more, suffocation and death can occur within minutes. Contact with the solid can cause freezing of exposed tissue. Moisture in the air could lead to the formation of carbonic acid which can be irritating to the eyes. Carbon Dioxide is heavier than air and should not be allowed to accumulate in low lying areas.

### CARBON DIOXIDE SOLID

**HAZARDOUS MATERIAL INFORMATION SYSTEM**

| | |
|---|---|
| HEALTH (BLUE) | 2 |
| FLAMMABILITY (RED) | 0 |
| REACTIVITY (YELLOW) | 0 |
| PROTECTIVE EQUIPMENT | B |

| EYES | RESPIRATORY | HANDS | BODY |
|---|---|---|---|
| 🥽 | See Section 8 | 🧤 | See Section 8 |

For routine industrial applications

**See Section 16 for Definition of Ratings**

SYMPTOMS OF OVEREXPOSURE BY ROUTE OF EXPOSURE: The most significant routes of overexposure for Carbon Dioxide are by inhalation of Carbon Dioxide gas, and skin or eye contact with the solid or gas. Symptoms of such exposure are as follows:

INHALATION: Carbon Dioxide is an asphyxiant and a powerful cerebral vasodilator. If the concentration of Carbon Dioxide reaches 10% or more, suffocation can occur rapidly. Inhalation of concentrations between 2 and 10% can cause nausea, dizziness, headache, mental confusion, increased blood pressure and respiratory rate. Carbon Dioxide initially stimulates respiration and then causes respiratory depression. Inhalation of low concentrations (3-5%) have no known permanent harmful effects. Symptoms in humans at various levels of concentration are as follows:

| **CONCENTRATION** | **SYMPTOMS OF EXPOSURE** |
|---|---|
| 1%: | Slight increase in breathing rate. |
| 2%: | Breathing rate increases to 50% above normal; exposure causes headache, tiredness. |
| 3%: | Breathing increases to twice normal rate and becomes labored. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate. |
| 4-5%: | Breathing increases to approximately four times normal rate, symptoms of intoxication become evident; slight choking may be felt. |
| 5-10%: | Labored breathing, headache, visual impairment, ringing in the ears, impaired judgment, followed by loss of consciousness. |
| 50-100%: | Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation. |

## 3. HAZARD IDENTIFICATION (Continued)

INHALATION (Continued): High concentrations of this gas can also cause an oxygen-deficient environment. However, the asphyxiating properties of Carbon Dioxide will be reached before oxygen-deficiency is a factor.

OTHER POTENTIAL HEALTH EFFECTS: Contact with solid Carbon Dioxide can cause frostbite to skin, eyes, and other exposed tissue. Contact of the cold gas generated from the solid with the skin can lead to frostbite or dermatitis (red, cracked, irritated skin), depending upon concentration and duration of exposure. Contact of the cold gas with the eyes can cause pain, redness, burns, and severe exposure could cause blindness. Symptoms of frostbite include change in skin color to white or grayish-yellow. The pain after contact with cold gas or solid can quickly subside. Moisture in the air could lead to the formation of carbonic acid, which can be irritating to the eyes.

HEALTH EFFECTS OR RISKS FROM EXPOSURE: An Explanation in **Lay Terms**. Overexposure to Carbon Dioxide may cause the following health effects:

**ACUTE**: Contact with solid Carbon Dioxide or cold gas can cause frostbite to skin, eyes, and other exposed tissue. Carbon Dioxide gas evolved from the sublimation of the solid is an asphyxiant and a powerful cerebral vasodilator. Inhaling high concentrations of Carbon Dioxide can lead to coma or death. At low concentrations, inhalation of Carbon Dioxide can cause nausea, dizziness, visual disturbances, shaking, headache, mental confusion, sweating, increased heartbeat, and elevated blood pressure and respiratory rate. High concentrations of the gas in air may cause eye irritation or damage.

**CHRONIC**: There are currently no known adverse health effects associated with chronic exposure to solid Carbon Dioxide or the gas which is generated by sublimation.

**TARGET ORGANS:** Respiratory system, cardiovascular system, eyes.

# PART III *How can I prevent hazardous situations from occurring?*

## 4. FIRST-AID MEASURES

**RESCUERS SHOULD NOT ATTEMPT TO RETRIEVE VICTIMS OF EXPOSURE TO THIS PRODUCT WITHOUT ADEQUATE PERSONAL PROTECTIVE EQUIPMENT. At a minimum, Self-Contained Breathing Apparatus Personal Protective equipment should be worn.**

Remove victim(s) to fresh air, as quickly as possible. Trained personnel should administer supplemental oxygen and/or cardio-pulmonary resuscitation, if necessary. Only trained personnel should administer supplemental oxygen.

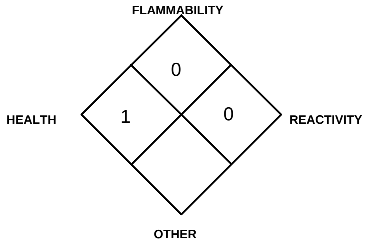
In case of frostbite, place the frostbitten part in warm water. DO NOT USE HOT WATER. If warm water is not available, or is impractical to use, wrap the affected parts gently in blankets. Alternatively, if the fingers or hands are frostbitten, place the affected area in the armpit, Encourage victim to gently exercise the affected part while being warmed. Seek immediate medical attention.

Victim(s) must be taken for medical attention. Rescuers should be taken for medical attention, if necessary. Take copy of label and MSDS to physician or other health professional with victim(s).

## 5. FIRE-FIGHTING MEASURES

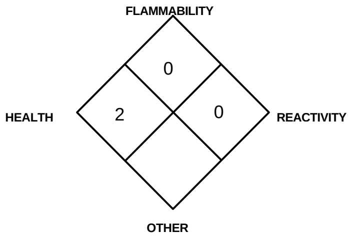
**CARBON DIOXIDE GAS**

**NFPA RATING**



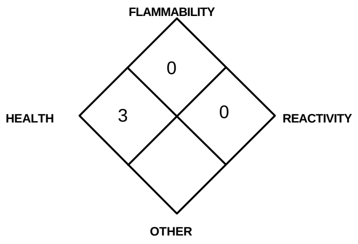
**CARBON DIOXIDE SOLID**

**NFPA RATING**



**CARBON DIOXIDE LIQUEFIED**

**NFPA RATING**



**See Section 16 for Definition of Ratings**

FLASH POINT: Not Applicable.

AUTOIGNITION TEMPERATURE: Not Applicable.

FLAMMABLE LIMITS (in air by volume, %): Lower: Not Applicable.
Upper: Not Applicable.

## 5. FIRE-FIGHTING MEASURES (Continued)

FIRE EXTINGUISHING MATERIALS: Carbon Dioxide is commonly used as an extinguishing agent, and therefore, should not present a problem when trying to control a blaze. Use extinguishing media appropriate for surrounding fire.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Carbon Dioxide does not burn; however, containers, when involved in fire, may rupture or burst in the heat of the fire. Dusts of various reactive metals (e.g.: magnesium, zircon, titanium alloys), are readily ignited and explode in the presence of Carbon Dioxide. Mixtures of solid Carbon Dioxide with sodium and potassium alloys are impact sensitive and explode violently. In the presence of moisture, cesium oxide ignites on contact with Carbon Dioxide. Metal acetylides or hydrides will also ignite or explode.

Explosion Sensitivity to Mechanical Impact: Not sensitive, except as noted above.
Explosion Sensitivity to Static Discharge: Not Sensitive.

SPECIAL FIRE-FIGHTING PROCEDURES: Structural fire-fighters must wear Self-Contained Breathing Apparatus and full protective equipment. Move fire-exposed cylinders if it can be done without risk to firefighters. Otherwise, cool containers with hose stream and protect personnel. Withdraw immediately in case of rising sounds from venting safety device or any discoloration of tanks due to the fire.

## 6. ACCIDENTAL RELEASE MEASURES

SPILL AND LEAK RESPONSE: Uncontrolled releases should be responded to by trained personnel using pre-planned procedures. Proper protective equipment should be used. In case of a spill, clear the affected area and protect people. Minimum Personal Protective Equipment should be **Level B: protective clothing, mechanically-resistant gloves and Self-Contained Breathing Apparatus**. Locate and seal the source of the leaking gas.

Allow the gas, which is heavier than air, to dissipate. Monitor the surrounding area for Carbon Dioxide and oxygen levels. Colorimetric tubes are available for Carbon Dioxide. The levels of Carbon Dioxide must be below those listed in Section 2 (Composition and Information on Ingredients) and the atmosphere must have at least 19.5 percent oxygen before personnel can be allowed in the area without Self-Contained Breathing Apparatus. Attempt to close the main source valve prior to entering the area. If this does not stop the release (or if it is not possible to reach the valve), allow the gas to release in-place or remove it to a safe area and allow the gas to be released there.

**RESPONSE TO CRYOGENIC RELEASE:** Clear the affected area and allow the liquid to evaporate and the gas to dissipate. After the gas is formed, follow the instructions provided in the previous paragraph. If the area must be entered by emergency personnel, SCBA, Kevlar gloves, and appropriate foot and leg protection must be worn.

**RESPONSE TO SOLID RELEASE:** Pick-up and immediately place solid pieces of dry ice in an appropriate, thermally-insulated, vented container. Alternatively, allow the solid to sublimate and the gas which is generated to dissipate.

# PART III *How can I prevent hazardous situations from occurring?*

## 7. HANDLING and STORAGE

WORK PRACTICES AND HYGIENE PRACTICES: As with all chemicals, avoid getting Carbon Dioxide IN YOU. Do not eat or drink while handling chemicals. Be aware of any signs of dizziness, fatigue, or any exposure symptom described in Section 3 (Hazard Identification); exposures to fatal concentrations of Carbon Dioxide could occur without any significant warning symptoms.

STORAGE AND HANDLING PRACTICES: Cylinders should be stored in dry, well-ventilated areas away from sources of heat. Containers of Carbon Dioxide can present significant safety hazards. Store containers away from heavily trafficked areas and emergency exits. Store containers away from process and production areas, away from elevators, building and room exits or main aisles leading to exits. Containers should be stored in dry, well-ventilated areas away from sources of heat, ignition and direct sunlight. Protect containers against physical damage. Isolate from other non-compatible chemicals (refer to Section 10, Stability and Reactivity).

SPECIAL PRECAUTIONS FOR HANDLING GAS CYLINDERS: Protect cylinders against physical damage. Store in cool, dry, well-ventilated, fireproof area, away from flammable materials and corrosive atmospheres. Store away from heat and ignition sources and out of direct sunlight. Do not store near elevators, corridors or loading docks. Do not allow area where cylinders are stored to exceed 52°C (125°F). Use only storage containers and equipment (pipes, valves, fittings to relieve pressure, etc.) designed for the storage of Solid, Gaseous or Liquefied Carbon Dioxide. Do not store containers where they can come into contact with moisture.

## 7. HANDLING and STORAGE (Continued)

SPECIAL PRECAUTIONS FOR HANDLING GAS CYLINDERS (Continued): Cylinders should be stored upright and be firmly secured to prevent falling or being knocked over. Cylinders can be stored in the open, but in such cases, should be protected against extremes of weather and from the dampness of the ground to prevent rusting. Never tamper with pressure relief devices in valves and cylinders. Liquefied Carbon Dioxide must be stored and handled under positive pressure or in a closed system to prevent the infiltration and solidification of air or other gases. The following rules are applicable to situations in which cylinders are being used:

**Before Use:** Move cylinders with a suitable hand-truck. Do not drag, slide or roll cylinders. Do not drop cylinders or permit them to strike each other. Secure cylinders firmly. Leave the valve protection cap in-place (where provided) until cylinder is ready for use.

**During Use:** Use designated CGA fittings and other support equipment. Do not use adapters. Do not heat cylinder by any means to increase the discharge rate of the product from the cylinder. Use check valve or trap in discharge line to prevent hazardous backflow into the cylinder. Do not use oils or grease on gas-handling fittings or equipment.

**After Use:** Close main cylinder valve. Replace valve protection cap (where provided). Mark empty cylinders “EMPTY”.

**NOTE:** Use only DOT or ASME code containers. In the event of an electrical discharge, Carbon Dioxide gas will produce carbon monoxide and oxygen. Close valve after each use and when empty. Cylinders must not be recharged except by or with the consent of owner.

SPECIAL PRECAUTIONS FOR HANDLING PRESSURIZED CONTAINERS OF LIQUID CARBON DIOXIDE: Cold liquids can present significant safety hazards. Never allow any unprotected part of the body to touch uninsulated pipes or vessels which contain cold fluids. The extremely cold metal of the container will cause moist flesh to stick fast and tear when one attempts to withdraw from it. The following rules are applicable to work situations in which liquid containers are being used.

Check all hoses and transfer equipment before filing them with the liquid. Replace any worn or cut hoses prior to use. Liquid Carbon Dioxide is extremely cold and is under pressure. A leak will result in the formation of “Dry Ice” particles which will be forcibly ejected from the system, possibly injuring the operator. A complete hose failure can result in a large release of Carbon Dioxide and violent movement of the hose and associated equipment, which may cause severe injury or death. Special care must be taken when depressurizing and disconnecting hoses. Releasing the contents of a liquid-filled line to atmospheric pressure may result in the formation of a solid dry ice plug in the line. This plug will prevent further removal of the liquid behind the plug, resulting in either an unexpected, rapid release of Carbon Dioxide as the line warms, or the catastrophic failure of the line as the liquid warms behind the plug. Sufficient vapor pressure must be applied and maintained behind the liquid before opening a discharge valve. This action will prevent the depressurization of the liquid to the point of solid formation before it exits the line.

High-pressure containers for liquid product are equipped with pressure relief devices to control internal pressure. Under normal conditions, these containers will periodically vent small amounts of product. Some metals such as carbon steel may become brittle at low temperatures and will easily fracture. Prevent entrapment of liquid in closed systems or piping without pressure relief devices.

SPECIAL PRECAUTIONS FOR HANDLING OF SOLID CARBON DIOXIDE: Do not handle solid Carbon Dioxide with bare hands. Use heavy gloves or dry ice tongs. Handle blocks of dry ice carefully, as injuries can occur if one is accidentally dropped on the feet. Never store dry ice in a standard refrigerator, cooler, or freezer designed for food storage. Containers of solid Carbon Dioxide should be stored upright and be firmly secured to prevent falling or being knocked-over. Containers should be vented, to prevent the build-up of Carbon Dioxide gas. Carbon Dioxide sublimates at -78.5°C (-109.3°F); containers should be thermally insulated and kept at the lowest possible temperature to maintain the solid and avoid generation of Carbon Dioxide gas. Storage containers and equipment used with Carbon Dioxide should not be located in sub-surface or enclosed areas, unless engineered to maintain a concentration of Carbon dioxide below the TLV (TLV = 5000 ppm in the event of a release. Solid consignment of dry ice in a gas-tight vessel can lead to catastrophic failure of the vessel by over-pressurization. Storage of dry ice should never occur in a gas-tight container.

PROTECTIVE PRACTICES DURING MAINTENANCE OF CONTAMINATED EQUIPMENT: Follow practices indicated in Section 6 (Accidental Release Measures). Make certain application equipment is locked and tagged-out safely. Purge gas handling equipment with inert gas (e.g., Nitrogen) before attempting repairs.

## 8. EXPOSURE CONTROLS - PERSONAL PROTECTION

VENTILATION AND ENGINEERING CONTROLS: Use with adequate ventilation. Carbon Dioxide accumulates in low-lying areas with limited air movement. Natural or mechanical ventilation should be available in the worker's breathing zone to prevent levels of Carbon Dioxide above exposure limits (see Section 2, Composition and Information on Ingredients). Local exhaust ventilation is preferred, because it prevents dispersion of this gas into the work place by eliminating it at its source. Areas of Carbon Dioxide use should be engineered to remove vapor from the lowest possible level and exhaust vapor to a well-ventilated area or to the outside. Carbon Dioxide levels should be monitored to assure levels are maintained below the TLV. If appropriate, install automatic monitoring equipment to detect the levels of Carbon Dioxide and of oxygen.

RESPIRATORY PROTECTION: Maintain Carbon Dioxide levels below those listed in Section 2 (Composition and Information on Ingredients) and oxygen levels above 19.5% in the workplace. Use supplied air respiratory protection if Carbon Dioxide levels are above the IDLH (40,000 ppm) or during emergency response to a release of this product. If respiratory protection is required, follow the requirements of the Federal OSHA Respiratory Protection Standard (29 CFR 1910.134), or equivalent State standards. Respiratory selection guidelines from NIOSH for Carbon Dioxide are provided on the following page for further information on respiratory protection.

| CONCENTRATION | RESPIRATORY EQUIPMENT |
|---|---|
| UP TO 40,000 ppm: | Supplied Air Respirator (SAR); or full-facepiece Self-Contained Breathing Apparatus (SCBA). |
| EMERGENCY OR PLANNED ENTRY INTO UNKNOWN CONCENTRATIONS OR IDLH CONDITIONS: | Positive pressure, full-facepiece SCBA; or positive pressure, full-facepiece SAR with an auxiliary positive pressure SCBA. |
| ESCAPE: | Escape-type SCBA. |
| NOTE: | The IDLH concentration for Carbon Dioxide is 40,000 ppm. |

EYE PROTECTION: Splash goggles, face-shields or safety glasses. Face-shields must be worn when using cryogenic Carbon Dioxide.

HAND PROTECTION: Wear mechanically-resistant gloves when handling cylinders of Carbon Dioxide. Recommended use of low-temperature protective gloves (e.g. insulated polyvinyl chloride or insulated nitrile) when working with containers of Liquefied Carbon Dioxide.

BODY PROTECTION: Use body protection appropriate for task. Transfer of large quantities under pressure may require protective equipment appropriate to protect employees from splashes of liquefied product, as well provide sufficient insulation from extreme cold.

## 9. PHYSICAL and CHEMICAL PROPERTIES

GAS DENSITY @ 21°C (70°F) and 1 atm: 0.1144 lb/ft$^3$ (1.833 kg/m$^3$)
LIQUID DENSITY @ 21.1°C (70°F) and 838 psig (5778 kPa): 47.35 lb/ft$^3$ (761.3 kg/m$^3$)
SOLID DENSITY @ -78.5°C (-109.3°F): 97.59 lb/ft$^3$ (1569 kg/m$^3$)
SPECIFIC GRAVITY (gas) @ 21°C (70°F): 1.52
SPECIFIC GRAVITY (solid) @ 0°C (32°F): 1.54
VAPOR PRESSURE (psia): 844.7
SOLUBILITY IN WATER @ 20°C (68°F): 0.90%
ODOR THRESHOLD: Not applicable.
EXPANSION RATIO: Not applicable.
BOILING POINT @ 1 atm (sublimation point): -78.5°C (-109.3°F)
COEFFICIENT WATER/OIL DISTRIBUTION: Not applicable.
EVAPORATION RATE (nBuAc = 1): Not applicable
FREEZING POINT: -56.6°C (-69.9°F)
SPECIFIC VOLUME (ft$^3$/lb): 8.8
pH @ 1 atm: 3.7 (carbonic acid)
TRIPLE POINT @ 60.4 psig (416 kPa): -56.6°C (-69.9°F)

APPEARANCE AND COLOR: Carbon dioxide is a colorless to opaque, white solid; a colorless gas; or a colorless cryogenic liquid. All forms of Carbon Dioxide are odorless at low concentrations. At high concentrations, Carbon Dioxide will have a sharp, acidic odor.

HOW TO DETECT THIS SUBSTANCE (warning properties): The odor is not a good warning property, as the asphyxiation properties of Carbon Dioxide may present a hazard before the odor at high concentrations is readily detectable. In terms of leak detection for the gas, fittings and joints can be painted with a soap solution to detect leaks, which will be indicated by a bubble formation. In conditions of high humidity, the solid form of Carbon Dioxide may release visible vapors.

## 10. STABILITY and REACTIVITY

STABILITY: Normally stable.

DECOMPOSITION PRODUCTS: Carbon Dioxide gas in an electrical discharge yields carbon monoxide and oxygen. In the presence of moisture, Carbon Dioxide will form carbonic acid.

## 10. STABILITY and REACTIVITY (Continued)

MATERIALS WITH WHICH SUBSTANCE IS INCOMPATIBLE: Carbon Dioxide will ignite and explode when heated with powdered aluminum, beryllium, cerium alloys, chromium, magnesium-aluminum alloys, manganese, thorium, titanium, and zirconium. In the presence of moisture, Carbon Dioxide will ignite with cesium oxide. Metal acetylides will also ignite and explode on contact with Carbon Dioxide.

HAZARDOUS POLYMERIZATION: Will not occur, however Carbon Dioxide acts to catalyze the polymerization of acryladehyde and aziridine.

CONDITIONS TO AVOID: Avoid exposing cylinders of Carbon Dioxide to extremely high temperatures, which could cause the cylinders to rupture or burst. Do not store the solid form of Carbon Dioxide in gas-tight containers, which could also cause over-pressurization and rupture of the container.

# PART IV *Is there any other useful information about this material?*

## 11. TOXICOLOGICAL INFORMATION

TOXICITY DATA: Carbon Dioxide is an asphyxiant gas, which has physiological effects at high concentrations. The following toxicological data are available for Carbon Dioxide.

LCLo (inhalation, human) = 9 pph/5 minutes.
LCLo (inhalation, mammal) = 90000 ppm/5 minutes.
TCLo (inhalation, rat) = 6 pph/24 hours; reproductive and teratogenic effects.

SUSPECTED CANCER AGENT: Carbon Dioxide is not found on the following lists: FEDERAL OSHA Z LIST, NTP, CAL/OSHA, IARC, and therefore is not considered to be, nor suspected to be a cancer-causing agent by these agencies.

IRRITANCY OF PRODUCT: Contact with rapidly expanding gases can cause frostbite and damage to exposed skin and eyes. Due to the formation of carbonic acid, this gas mixture can be slightly irritating to contaminated eyes.

SENSITIZATION OF PRODUCT: Carbon Dioxide is not a sensitizer after prolonged or repeated exposures.

REPRODUCTIVE TOXICITY INFORMATION: Listed below is information concerning the effects of Carbon Dioxide on the human reproductive system.

Mutagenicity: Carbon Dioxide is not expected to cause mutagenic effects in humans.
Embryotoxcity: Carbon Dioxide has not been reported to cause embryotoxic effects; see next paragraph for information.
Teratogenicity: Carbon Dioxide is not expected to cause teratogenic effects in humans. Clinical studies involving test animals exposed to high concentrations of Carbon Dioxide indicate teratogenic effects (e.g., cardiac and skeletal malformations, stillbirths).
Reproductive Toxicity: Carbon Dioxide is not expected to cause adverse reproductive effects in humans. Studies involving test animals exposed to high concentrations of Carbon Dioxide indicate reproductive effects (e.g. changes in testes).

*A mutagen is a chemical which causes permanent changes to genetic material (DNA) such that the changes will propagate through generation lines. An embryotoxin is a chemical which causes damage to a developing embryo (i.e. within the first eight weeks of pregnancy in humans), but the damage does not propagate across generational lines. A teratogen is a chemical which causes damage to a developing fetus, but the damage does not propagate across generational lines. A reproductive toxin is any substance which interferes in any way with the reproductive process.*

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE: Disorders involving the “Target Organs” (see Section 3, Hazard Information) may be aggravated by Carbon Dioxide overexposure.

RECOMMENDATIONS TO PHYSICIANS: Treat symptoms and reduce overexposure.

BIOLOGICAL EXPOSURE INDICES (BEIs): Currently, Biological Exposure Indices (BEIs) are not applicable for Carbon Dioxide.

## 12. ECOLOGICAL INFORMATION

ENVIRONMENTAL STABILITY: Carbon Dioxide occurs naturally in the atmosphere. The gas will be dissipated rapidly in well-ventilated areas. The following environmental data are applicable to Carbon Dioxide.

**CARBON DIOXIDE:** Food chain concentration potential: None. Biological Oxygen Demand: None

EFFECT OF MATERIAL ON PLANTS or ANIMALS: Any adverse effect on animals would be related to Carbon Dioxide overexposure and oxygen-deficient environments. No adverse effect is anticipated to occur to plant-life, except for frost produced in the presence of rapidly expanding gases.

EFFECT OF CHEMICAL ON AQUATIC LIFE: The following aquatic toxicity data are available for Carbon Dioxide.

**CARBON DIOXIDE:**
Aquatic toxicity: 100-200 mg/l/no time specified/various organisms/fresh water.
Waterfowl toxicity: Inhalation 5-8%, no effect.

## 13. DISPOSAL CONSIDERATIONS

PREPARING WASTES FOR DISPOSAL: Waste disposal must be in accordance with appropriate Federal, State, and local regulations. Return cylinders with any residual product to Airgas Inc. Do not dispose of locally.

## 14. TRANSPORTATION INFORMATION

THIS MATERIAL IS HAZARDOUS AS DEFINED BY 49 CFR 172.101 BY THE U.S. DEPARTMENT OF TRANSPORTATION.

**For Carbon Dioxide Gas:**
PROPER SHIPPING NAME: Carbon dioxide
HAZARD CLASS NUMBER and DESCRIPTION: 2.2 (Non-Flammable Gas)
UN IDENTIFICATION NUMBER: UN 1013
PACKING GROUP: Not applicable.
DOT LABEL(S) REQUIRED: Non-Flammable Gas
NORTH AMERICAN EMERGENCY RESPONSE GUIDEBOOK NUMBER (1996): 120

**For Carbon Dioxide Liquefied:**
PROPER SHIPPING NAME: Carbon dioxide, refrigerated liquid
HAZARD CLASS NUMBER and DESCRIPTION: 2.2 (Non-Flammable Gas)
UN IDENTIFICATION NUMBER: UN 2187
PACKING GROUP: Not applicable.
DOT LABEL(S) REQUIRED: Non-Flammable Gas
NORTH AMERICAN EMERGENCY RESPONSE GUIDEBOOK NUMBER (1996): 120

**For Carbon Dioxide, Solid:**
PROPER SHIPPING NAME: Carbon dioxide, solid ***or*** Dry ice
HAZARD CLASS NUMBER and DESCRIPTION: 9 (Miscellaneous Dangerous Goods)
UN IDENTIFICATION NUMBER: UN 1845
PACKING GROUP: III
DOT LABEL(S) REQUIRED: None
NORTH AMERICAN EMERGENCY RESPONSE GUIDEBOOK NUMBER (1996): 120

MARINE POLLUTANT: Carbon Dioxide is not classified by the DOT as a Marine Pollutant (as defined by 49 CFR 172.101, Appendix B).

TRANSPORT CANADA TRANSPORTATION OF DANGEROUS GOODS REGULATIONS: THIS MATERIAL IS CONSIDERED AS DANGEROUS GOODS. Use the above information for the preparation of Canadian Shipments.

## 15. REGULATORY INFORMATION

U.S. SARA REPORTING REQUIREMENTS: Carbon Dioxide is not subject to the reporting requirements of Sections 302, 304 and 313 of Title III of the Superfund Amendments and Reauthorization Act.

U.S. SARA THRESHOLD PLANNING QUANTITY: There are no specific Threshold Planning Quantities for Carbon Dioxide (solid, gaseous or liquid form). The default Federal MSDS submission and inventory requirement filing threshold of 10,000 lbs (4,540 kg) therefore applies, per 40 CFR 370.20.

U.S. CERCLA REPORTABLE QUANTITY (RQ): Not applicable.

CANADIAN DSL/NDSL INVENTORY STATUS: Carbon Dioxide is listed on the DSL Inventory.

U.S. TSCA INVENTORY STATUS: Carbon Dioxide is on the TSCA Inventory.

OTHER U.S. FEDERAL REGULATIONS: Not applicable.

U.S. STATE REGULATORY INFORMATION: Carbon Dioxide is covered under the following specific State regulations:

**Alaska - Designated Toxic and Hazardous Substances**: Carbon Dioxide.
**California - Permissible Exposure Limits for Chemical Contaminants:** Carbon Dioxide.
**Florida - Substance List:** Carbon Dioxide.
**Illinois - Toxic Substance List:** Carbon Dioxide.
**Kansas - Section 302/313 List:** No.
**Massachusetts - Substance List:** Carbon Dioxide.
**Michigan - Critical Material Register:** No.
**Minnesota - List of Hazardous Substances:** Carbon Dioxide.
**Missouri - Employer Information/Toxic Substance List:** Carbon Dioxide.
**New Jersey - Right to Know Hazardous Substance List:** Carbon Dioxide.
**North Dakota - List of Hazardous Chemicals, Reportable Quantities:** No.
**Pennsylvania - Hazardous Substance List:** Carbon Dioxide.
**Rhode Island - Hazardous Substance List:** Carbon Dioxide.
**Texas - Hazardous Substance List:** No.
**West Virginia - Hazardous Substance List:** Carbon Dioxide.
**Wisconsin - Toxic and Hazardous Substances:** Carbon Dioxide.

CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT (PROPOSITION 65): Carbon Dioxide is not on the California Proposition 65 lists.

## 15. REGULATORY INFORMATION (Continued)

LABELING: **CARBON DIOXIDE GAS:**

**CAUTION:** LIQUID AND GAS UNDER PRESSURE.
CAN CAUSE RAPID SUFFOCATION.
CAN INCREASE RESPIRATION AND HEART RATE.
MAY CAUSE FROSTBITE.
Avoid breathing gas.
Store and use with adequate ventilation.
Do not get liquid in eyes, on skin or clothing.
Cylinder temperature should not exceed 125°F (52°C).
Use equipment rated for cylinder pressure.
Close valve after each use and when empty.
Use in accordance with the Material Safety Data Sheet.

**NOTE:** Suck-back into cylinder may cause rupture.
Always use a back flow preventative device in piping.

**FIRST-AID**: **IF INHALED**, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.
**IN CASE OF FROSTBITE,** obtain immediate medial attention.
DO NOT REMOVE THIS PRODUCT LABEL.

**CARBON DIOXIDE, LIQUEFIED:**

**ALWAYS KEEP CONTAINER IN UPRIGHT POSITION.**

**WARNING:** COLD LIQUID AND GAS UNDER PRESSURE.
CAN INCREASE RESPIRATION AND HEART RATE.
MAY CAUSE FROSTBITE.
Avoid breathing gas.
Store and use with adequate ventilation.
Do not get liquid in eyes, on skin or clothing.
For liquid withdrawal, wear face shield and gloves.
Do not drop. Use hand truck for container movement.
Close valve after each use and when empty.
Use in accordance with the Material Safety Data Sheet.

**FIRST-AID**: **IF INHALED**, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.
**IN CASE OF FROSTBITE,** obtain medical treatment immediately.
DO NOT REMOVE THIS PRODUCT LABEL.

**CARBON DIOXIDE, SOLID:**

**ALWAYS KEEP CONTAINER IN UPRIGHT POSITION.**

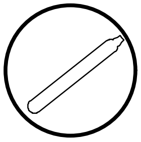
**WARNING:** EXTREMELY COLD SOLID WHICH SUBLIMATES TO GAS RAPIDLY.
GAS CAN INCREASE RESPIRATION AND HEART RATE.
GAS CAN CAUSE RAPID SUFFOCATION.
CAN CAUSE FROSTBITE.
Avoid breathing gas.
Store and use with adequate ventilation.
Do not get solid in eyes, on skin or clothing.
For handling solid, wear face shield and gloves.
Use in accordance with the Material Safety Data Sheet.

**FIRST-AID**: **IF INHALED**, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

**IN CASE OF FROSTBITE,** obtain medical treatment immediately.

DO NOT REMOVE THIS PRODUCT LABEL.

CANADIAN WHMIS SYMBOLS: **Class A: Compressed Gas**



# 16. OTHER INFORMATION

**PREPARED BY:**

CHEMICAL SAFETY ASSOCIATES, Inc.
9163 Chesapeake Drive, San Diego, CA 92123-1002
619/565-0302

The information contained herein is based on data considered accurate. However, no warranty is expressed or implied regarding the accuracy of these data or the results to be obtained from the use thereof. AIRGAS, Inc. assumes no responsibility for injury to the vendee or third persons proximately caused by the material if reasonable safety procedures are not adhered to as stipulated in the data sheet. Additionally, AIRGAS, Inc. assumes no responsibility for injury to vendee or third persons proximately caused by abnormal use of the material even if reasonable safety procedures are followed. Furthermore, vendee assumes the risk in his use of the material.

# DEFINITIONS OF TERMS

A large number of abbreviations and acronyms appear on a MSDS. Some of these which are commonly used include the following:

**CAS #**: This is the Chemical Abstract Service Number which uniquely identifies each constituent. It is used for computer-related searching.

**EXPOSURE LIMITS IN AIR:**

**ACGIH** - American Conference of Governmental Industrial Hygienists, a professional association which establishes exposure limits. **TLV -** Threshold Limit Value - an airborne concentration of a substance which represents conditions under which it is generally believed that nearly all workers may be repeatedly exposed without adverse effect. The duration must be considered, including the 8-hour Time Weighted Average **(TWA)**, the 15-minute Short Term Exposure Limit, and the instantaneous Ceiling Level **(C)**. Skin absorption effects must also be considered.

**OSHA** - U.S. Occupational Safety and Health Administration. **PEL -** Permissible Exposure Limit - This exposure value means exactly the same as a TLV, except that it is enforceable by OSHA. The OSHA Permissible Exposure Limits are based in the 1989 PELs and the June, 1993 Air Contaminants Rule (Federal Register: 58: 35338-35351 and 58: 40191). Both the current PELs and the vacated PELs are indicated. The phrase, "Vacated 1989 PEL," is placed next to the PEL which was vacated by Court Order.

**IDLH -** Immediately Dangerous to Life and Health **-** This level represents a concentration from which one can escape within 30-minutes without suffering escape-preventing or permanent injury. **The DFG - MAK** is the Republic of Germany's Maximum Exposure Level, similar to the U.S. PEL. **NIOSH** is the National Institute of Occupational Safety and Health, which is the research arm of the U.S. **O**ccupational **S**afety and **H**ealth **A**dministration (**OSHA**). NIOSH issues exposure guidelines called **R**ecommended **E**xposure **L**evels (**REL**s). When no exposure guidelines are established, an entry of **NE** is made for reference.

**HAZARD RATINGS:**

**HAZARDOUS MATERIALS IDENTIFICATION SYSTEM:** Health Hazard: **0** (minimal acute or chronic exposure hazard); **1** (slight acute or chronic exposure hazard); **2** (moderate acute or significant chronic exposure hazard); **3** (severe acute exposure hazard; onetime overexposure can result in permanent injury and may be fatal); **4** (extreme acute exposure hazard; onetime overexposure can be fatal). Flammability Hazard: **0** (minimal hazard); **1** (materials that require substantial pre-heating before burning); **2** (combustible liquid or solids; liquids with a flash point of 38-93°C [100-200°F]); **3** (Class IB and IC flammable liquids with flash points below 38°C [100°F]); **4** (Class IA flammable liquids with flash points below 23°C [73°F] and boiling points below 38°C [100°F]. Reactivity Hazard: **0** (normally stable); 1 (material that can become unstable at elevated temperatures or which can react slightly with water); **2** (materials that are unstable but do not detonate or which can react violently with water); **3** (materials that can detonate when initiated or which can react explosively with water); **4** (materials that can detonate at normal temperatures or pressures).

**NATIONAL FIRE PROTECTION ASSOCIATION:** Health Hazard: **0** (material that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible materials); **1** (materials that on exposure under fire conditions could cause irritation or minor residual injury); **2** (materials that on intense or continued exposure under fire conditions could cause temporary incapacitation or possible residual injury); **3** (materials that can on short exposure could cause serious temporary or residual injury); **4** (materials that under very short exposure causes death or major residual injury).

**NATIONAL FIRE PROTECTION ASSOCIATION (Continued):** Flammability Hazard and Reactivity Hazard: Refer to definitions for "Hazardous Materials Identification System".

**FLAMMABILITY LIMITS IN AIR**:

Much of the information related to fire and explosion is derived from the National Fire Protection Association (**NFPA**). Flash Point - Minimum temperature at which a liquid gives off sufficient vapors to form an ignitable mixture with air. Autoignition Temperature: The minimum temperature required to initiate combustion in air with no other source of ignition. LEL - the lowest percent of vapor in air, by volume, that will explode or ignite in the presence of an ignition source. UEL - the highest percent of vapor in air, by volume, that will explode or ignite in the presence of an ignition source.

**TOXICOLOGICAL INFORMATION:**

Possible health hazards as derived from human data, animal studies, or from the results of studies with similar compounds are presented. Definitions of some terms used in this section are: **$LD_{50}$** - Lethal Dose (solids & liquids) which kills 50% of the exposed animals; **$LC_{50}$** - Lethal Concentration (gases) which kills 50% of the exposed animals; **ppm** concentration expressed in parts of material per million parts of air or water; **$mg/m^3$** concentration expressed in weight of substance per volume of air; **mg/kg** quantity of material, by weight, administered to a test subject, based on their body weight in kg. Data from several sources are used to evaluate the cancer-causing potential of the material. The sources are: **IARC** - the International Agency for Research on Cancer; **NTP** - the National Toxicology Program, **RTECS** - the Registry of Toxic Effects of Chemical Substances, **OSHA** and **CAL/OSHA**. IARC and NTP rate chemicals on a scale of decreasing potential to cause human cancer with rankings from 1 to 4. Subrankings (2A, 2B, etc.) are also used. Other measures of toxicity include **TDLo**, the lowest dose to cause a symptom and **TCLo** the lowest concentration to cause a symptom; **TDo**, **LDLo**, and **LDo**, or **TC**, **TCo**, **LCLo**, and **LCo**, the lowest dose (or concentration) to cause lethal or toxic effects. **BEI** - Biological Exposure Indices, represent the levels of determinants which are most likely to be observed in specimens collected from a healthy worker who has been exposed to chemicals to the same extent as a worker with inhalation exposure to the TLV. Ecological Information: EC is the effect concentration in water.

**REGULATORY INFORMATION:**

This section explains the impact of various laws and regulations on the material. **EPA** is the U.S. Environmental Protection Agency. **WHMIS** is the Canadian Workplace Hazardous Materials Information System. **DOT** and **TC** are the U.S. Department of Transportation and the Transport Canada, respectively. Superfund Amendments and Reauthorization Act **(SARA)**; the Canadian Domestic/Non-Domestic Substances List **(DSL/NDSL)**; the U.S. Toxic Substance Control Act **(TSCA)**; Marine Pollutant status according to the **DOT**; the Comprehensive Environmental Response, Compensation, and Liability Act **(CERCLA or Superfund)**; and various state regulations.

**CARBON DIOXIDE** **Effective Date: 2000**

# MATERIAL SAFETY DATA SHEET

## 1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

| | |
|---|---|
| **PRODUCT NAME:** | Carbon Dioxide |
| **CHEMICAL NAME:** | Carbon Dioxide |
| **CHEMICAL FAMILY:** | Acid Anhydride |
| **FORMULA:** | $CO_2$ |
| **SYNONYMS:** | Carbonic Anhydride, Carbonic acid gas, Carbon Anhydride, Carbon dioxide USP, Dry Ice |

**NAME AND ADDRESS:** **TELEPHONE:** **Emergency Phone:**

**Routine information call:**

**|USE:|** Various, beverage carbonation, expendable refrigerant, pH control, fire suppression, controlled atmospheres, pressurizing solvent medium, grain fumigation, supercritical extraction, medical respiratory therapy mixtures, chemical reactant.

## 2. COMPOSITION/INFORMATION ON INGREDIENTS

| INGREDIENT NAME/ /CAS NUMBER | PERCENTAGE | OSHA PEL-TWA | ACGIH TLV-TWA | ACGIH TLV-STEL |
|---|---|---|---|---|
| CARBON DIOXIDE/124-38-9 | >99% | 5000ppm | 5000ppm | 30000ppm |

**|$LD_{50}$:|** None **|$LC_{50}$:|** None

## 3. HAZARDS IDENTIFICATION

**EMERGENCY OVERVIEW**

**CAUTION!** High pressure liquid and gas
Can cause rapid suffocation.
Can increase respiration and heart rate.
Solid and liquid may cause frostbite.
Avoid breathing the gas.
Self-contained breathing apparatus may be required by rescue workers.

**POTENTIAL HEALTH EFFECTS INFORMATION:**

**ROUTES OF EXPOSURE:**

**INHALATION:** Carbon dioxide is an asphyxiant and a powerful cerebral vasodilator. Inhaling large quantities causes rapid circulatory insufficiency leading to coma and death. **High concentrations of carbon dioxide can asphyxiate quickly without warning with no possibility of self-rescue regardless of the oxygen concentration.** Concentrations of 10% or more can produce unconsciousness or death. Lower concentrations may cause headache, sweating, rapid breathing, increased heartbeat, shortness of breath, dizziness, mental depression, visual disturbances, and shaking. Repeated inhalation of low (3% to 5%) concentrations have no known irreversible effects.

**EYE CONTACT:** Contact with solid, liquid or cold vapor can cause freezing of tissue.

**SKIN CONTACT**: Contact with solid, liquid or cold vapor can cause frostbite. Frostbite effects are a change in the color of the skin to gray or white, possibly followed by blistering.

**|SKIN ADSORPTION:|** Not applicable

**|INGESTION:|** Ingestion of solid will cause internal frostbite effects.

**CHRONIC EFFECTS:** None established

**MEDICAL CONDITIONS AGGRAVATED BY OVEREXPOSURE:** None

**OTHER EFFECTS OF OVEREXPOSURE:** Damage to retinal ganglion cells and central nervous system may occur.

**CARCINOGENICITY:** Carbon dioxide is not listed by NTP, OSHA, or IARC.

## 4. FIRST AID MEASURES

**INHALATION:** Persons suffering from overexposure should be removed to fresh air. If victim is not breathing, administer artificial respiration. If breathing is difficult, administer oxygen. Obtain prompt medical attention.

**EYE CONTACT:** Contact with solid, liquid or cold vapor can cause freezing of tissue. Gently flush eyes with lukewarm water. Obtain medical attention immediately.

**SKIN CONTACT:** Contact with solid, liquid or cold vapor can cause frostbite. Immediately warm affected area with lukewarm water not to exceed 105 °F (41 °C). Do not apply direct heat to affected area. Loosely apply dry, sterile, bulky dressings to protect area from infection and further injury. Get medical attention.

**INGESTION OF SOLID:** Drink lukewarm water. Get medical attention promptly.

**NOTES TO PHYSICIAN:** There is no specific antidote. Treatment of overexposure should be directed at the control of symptoms and the clinical condition.

## 5. FIRE FIGHTING MEASURES

**FLASH POINT:** Not applicable **AUTOIGNITION:** Nonflammable

**FLAMMABLE LIMITS IN AIR BY VOLUME:**

**LOWER:** Not applicable **UPPER:** Not applicable

**EXTINGUISHING MEDIA:** Carbon dioxide is nonflammable and does not support combustion. Carbon dioxide is an extinguishing agent for Class B and C fires, but should not be used on Class D fires. Use extinguishing media appropriate for the surrounding fire.

**SPECIAL FIRE FIGHTING INSTRUCTIONS:** Evacuate personnel from danger area. If possible, without risk, remove carbon dioxide cylinders from fire area or cool with water. Self-contained breathing apparatus may be required for rescue workers.

**UNUSUAL FIRE AND EXPLOSION HAZARDS:** Upon exposure to intense heat or flame a cylinder or bulk container may vent rapidly and/or rupture violently. Most containers are designed to vent contents when exposed to elevated temperatures. Pressure in a container can build up due to heat and it may rupture if pressure relief devices should fail to function. See Section 10 for more information.

**HAZARDOUS COMBUSTION PRODUCTS:** None known

**|SENSITIVITY TO STATIC DISCHARGE:|** None

**|SENSITIVITY TO MECHANICAL IMPACT:|** None, except as noted above

## 6. ACCIDENTAL RELEASE MEASURES

**STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED:**

**CYLINDERS**: Evacuate all personnel from the affected area until the area is checked to ensure carbon dioxide levels below the exposure limits. Shut off the source of carbon dioxide, if possible without risk. Ventilate enclosed areas or remove cylinders to a well-ventilated open area. If leaking from cylinder or its valve, contact your supplier. The cylinder or valve may be very cold after a rapid release of product. Handle the cylinder carefully with leather gloves. Carbon dioxide solid may form and remain in the cylinder until it is warmed.

**BULK CONTAINERS**: Evacuate all personnel from the affected area until the area is checked to ensure carbon dioxide levels below the exposure limits. Shut off the source of carbon dioxide, if possible without risk. Ventilate enclosed areas. If leaking from a container valve, contact your supplier. Carbon dioxide solid may form and remain in the container until it is warmed. This must only be done by qualified personnel.

**DRY ICE (SOLID)**: Evacuate all personnel from the affected area until the area is checked to ensure carbon dioxide levels below the exposure limits. Ventilate enclosed areas or remove the solid to a well-ventilated open area secure from contact by passers-by. Handle the solid only with cold-resistant gloves and clothing.

## 7. HANDLING AND STORAGE

**PRECAUTIONS TO BE TAKEN IN STORAGE:** Store and use with adequate ventilation. Storage containers and equipment should not be located in sub-surface or enclosed areas, unless engineered to maintain a concentration of carbon dioxide below the exposure limits in the event of a release. Relief valves should be vented to a well-ventilated external location. Cylinders should be stored upright with their valve protection cap in place and firmly secured to prevent falling or being knocked over. Protect cylinders from physical damage; do not drag, roll, slide or drop. Do not allow storage area temperatures to exceed 125 °F (52 °C). Full and empty cylinders should be segregated. Use a first-in, first-out inventory system to prevent full containers from being stored for long periods of time. Solid carbon dioxide (dry ice) should be stored in insulated containers with loose fitting covers that allow the evolved gas to escape. Store in a well-ventilated area to prevent accumulation of carbon dioxide vapors above the exposure limits.

**PRECAUTIONS TO BE TAKEN IN HANDLING:**

**CYLINDERS:** Use a suitable hand truck for cylinder movement. Never attempt to lift a cylinder by its valve protection cap. Never apply flame or localized heat directly to any part of the cylinder. High temperature may cause damage to cylinder and/or premature failure of the pressure relief device, which will result in venting of the cylinder contents. If user experiences any difficulty operating the cylinder valve, discontinue use and contact supplier. Never insert an object (e.g., wrench, screwdriver, pry bar, etc.) into valve cap openings. Doing so may damage the valve, causing a leak to occur. Use an adjustable strap wrench to remove over-tight or rusted caps. Never strike an arc on a compressed gas cylinder or make a cylinder a part of an electrical circuit.

**LIQUID:** Wear protective clothing, insulated gloves, and protective eye glasses or face shields when transferring liquid carbon dioxide. Use a suitable four-wheel hand truck for container movement. Check all hoses and transfer equipment before filling them with liquid. Replace any worn or cut hoses before use. Liquid carbon dioxide is extremely cold and under pressure. A leak will result in the formation of solid particles, which will be forcibly ejected from the system, possibly injuring the operator. A complete hose failure can result in a large carbon dioxide spill and violent movement of the hose and associated equipment, which may cause severe injury or death. Special care must be taken when depressurizing and disconnecting hoses. Releasing the contents of a liquid-filled line to atmospheric pressure may result in the formation of a solid dry ice plug in the line. This will prevent further removal of the liquid behind the plug, resulting in either an unexpected rapid release as it warms, or the catastrophic failure of the line as the liquid warms behind the plug. Sufficient vapor pressure must be applied and maintained behind the liquid before opening a discharge valve. This will prevent the depressurization of the liquid to the point of solid formation before it exits the line.

**SOLID:** Direct contact with solid carbon dioxide (dry ice) should be avoided. Wear appropriate clothing, safety shoes and insulated gloves. Do not ingest solid carbon dioxide. Wear protective eye glasses or shields when cutting dry ice.

For additional precautions in using carbon dioxide see Section 16, Other Information.

## 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

**ENGINEERING CONTROLS:**

**VENTILATION:** Natural or mechanical to prevent accumulation in worker's breathing zone above exposure limits. (See Section 2.) Carbon dioxide levels should be monitored to assure levels below exposure limits regardless of oxygen levels. Remove vapor from the lowest possible level and exhaust to a well-ventilated outdoor area. Carbon dioxide accumulates in low-lying areas and areas with limited air movement.

**RESPIRATORY PROTECTION (SPECIFY TYPE):**

**General Use:** None required

**Emergency Use:** Self-contained breathing apparatus (SCBA) or positive pressure air line and escape bottle with mask are to be used in oxygen-deficient atmospheres and areas with high carbon dioxide concentrations. Air purifying respirators will not provide protection. See 29 CFR 1910.134 for NIOSH/MSHA warnings/instructions for respirator selection.

**PROTECTIVE GLOVES:** Work gloves are recommended when handling cylinders. Leather and/or insulated gloves impervious to cold should be worn when handling liquid or solid carbon dioxide.

**EYE PROTECTION:** Safety glasses are recommended when handling cylinders, vapor or liquid transfers, and solid carbon dioxide. Face shields are recommended for liquid transfer operations.

**OTHER PROTECTIVE EQUIPMENT:** Safety shoes with metatarsal protection are recommended when handling cylinders or dry ice blocks. Protective clothing as required to avoid skin contact.

## 9. PHYSICAL AND CHEMICAL PROPERTIES

**MOLECULAR WEIGHT:** 44.01

**BOILING POINT (1 atm):** Not applicable at 1 atm - see Sublimation

**SPECIFIC GRAVITY (Air=1):** At 70 °F (21.1 °C) and 1 atm: 1.522

**FREEZING POINT/MELTING POINT:** Not applicable at 1 atm - see Sublimation

**SUBLIMATION TEMPERATURE:** -109.3 °F (-78.5 °C) at 1 atm

**TRIPLE POINT:** -69.9 °F (-56.6 °C) at 60.4 psig (416 kPa)

**VAPOR PRESSURE (at 70 °F (21.1 °C)):** 838 psig (5778 kPa)

**GAS DENSITY (at 70 °F (21.1 °C) and 1 atm):** 0.114 lb/ft$^3$ (1.833 kg/m$^3$)

**LIQUID DENSITY (at 70 °F (21.1 °C) and 838 psig (5778 kPa):** 47.35 lb/ft$^3$ (761.338 kg/m$^3$)

**SOLID DENSITY (at -109.3 °F (-78.5 °C), 1 atm):** 97.59 lb/ft$^3$ (1569 kg/m$^3$)

**EVAPORATION RATE (Butyl Acetate=1):** Not applicable

**SOLUBILITY IN WATER:** 0.90 Vol/Vol at 68 °F (20 °C)

**EXPANSION RATIO (at 70 °F (21.1 °C):** 8.741 ft$^3$ /lb (solid to gas)

**[pH]:** 3.7 at 1 atm (for carbonic acid)

**APPEARANCE, ODOR AND STATE:** Colorless and odorless gas. A slightly acid gas, it is felt by some persons to have a slightly pungent odor and biting taste. Clear, colorless volatile liquid. Odorless white solid.

**[COEFFICIENT OF WATER/OIL DISTRIBUTION]:** Not applicable

**[ODOR THRESHOLD]:** Odorless

## 10. STABILITY AND REACTIVITY

| | |
|---|---|
| **STABILITY:** | Stable |
| **CONDITIONS TO AVOID:** | None |
| **INCOMPATIBILITY (Materials to Avoid):** | None. Carbon dioxide will react with alkaline materials to form carbonates and bicarbonates. |

**REACTIVITY:**

**A) HAZARDOUS DECOMPOSITION PRODUCTS:** Carbon monoxide and oxygen at temperatures above 3000 °F (1648.9 °C).

**B) HAZARDOUS REACTION CONDITIONS:** Dusts of various metals (e.g., magnesium, zircon, titanium alloys), are readily ignited and explode in the presence of Carbon Dioxide. Mixtures of solid Carbon Dioxide with sodium and potassium alloys are impact sensitive and explode violently. In the presence of moisture, cesium oxide ignites on contact with Carbon Dioxide. Metal acetylides or hydrides will also ignite or explode.

**C) HAZARDOUS POLYMERIZATION:** Will not occur.

**D) GENERAL:** Carbon dioxide will react with alkaline materials to form carbonates and bicarbonates.

## 11. TOXICOLOGICAL INFORMATION

Carbon dioxide is an asphyxiant. It initially stimulates respiration and then causes respiratory depression. High concentrations result in narcosis. Symptoms in humans are as follows:

| EFFECT | CONCENTRATION |
|---|---|
| Slight increase in breathing rate. | 1% |
| Breathing rate increases to 50% above normal level. | 2% |
| Prolonged exposure can cause headache, tiredness. | |
| Breathing increases to twice normal rate and becomes labored. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate. | 3% |
| Breathing increases to approximately four times normal rate, symptoms of intoxication become evident and slight choking may be felt. | 4% to 7% |
| Characteristic sharp odor noticeable. Very labored breathing, headache, visual impairment and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness. | 7% to 15% |
| Unconsciousness occurs more rapidly above the 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation or severe acidosis. | Above 15% |

| | | | |
|---|---|---|---|
| **[IRRITANCY OF MATERIAL]:** | None | **[SENSITIZATION TO MATERIAL]:** | None |
| **[REPRODUCTIVE EFFECTS]:** | None | | |
| **[TERATOGENICITY]:** | None | **[MUTAGENICITY]:** | None |
| **[SYNERGISTIC MATERIALS]:** | None | | |

## 12. ECOLOGICAL INFORMATION

No adverse ecological effects are expected. Carbon dioxide does not contain any Class I or Class II ozone depleting chemicals (40 CFR Part 82). Carbon dioxide is not listed as a marine pollutant by DOT (49 CFR Part 171).

## 13. DISPOSAL CONSIDERATIONS

**WASTE DISPOSAL METHOD:**

**CYLINDERS**: Do not attempt to dispose of residual or unused quantities. Return containers to the supplier. For **emergency disposal**, secure the cylinder and slowly discharge gas to the atmosphere in a well-ventilated area or outdoors.

**BULK CONTAINERS**: Do not attempt to dispose of residual or unused quantities. Contact supplier for disposal. For **emergency disposal**, slowly discharge gas to the atmosphere in a well-ventilated area or outdoors.

**DRY ICE (SOLID)**: Do not attempt to dispose of residual or unused quantities. Return containers to the supplier. Handle the solid only with cold-resistant gloves and clothing. For **emergency disposal**, allow solid carbon dioxide to sublime to a well-ventilated area that is away from general traffic and secure from accidental contact.

## 14. TRANSPORT INFORMATION

GAS

**DOT/IMO/IATA Shipping Name:** Carbon Dioxide

**Hazard Class:** 2.2 (Nonflammable gas)

**Identification Number:** UN1013 **|PIN|:** 1013

**Shipping Label:** Nonflammable gas

**Placard:** Nonflammable gas

**REFRIGERATED LIQUID**

**DOT/IMO/IATA Shipping Name:** Carbon Dioxide, Refrigerated Liquid

**Hazard Class:** 2.2 (Nonflammable gas)

**Identification Number:** UN2187 **|PIN|:** 2187

**Shipping Label:** Nonflammable Gas

**Placard:** Nonflammable gas

**SOLID**

**DOT/IMO/IATA Shipping Name:** Carbon Dioxide, Solid or Dry Ice

**Hazard Class:** 9

**Identification Number:** UN1845 **|PIN|:** 1845

**Shipping Label:** No label required for highway shipment. If shipped by air or water, use a Class 9 label.

**Placard:** No placard required for domestic highway shipment.

**PRODUCT REPORTABLE QUANTITY (RQ):** None

**SPECIAL SHIPPING INFORMATION:** Cylinders should be transported in a secure upright position in a well-ventilated truck. The transportation of compressed gas cylinders in automobiles or in closed-body vehicles can present serious safety hazards and should be discouraged.

## 15. REGULATORY INFORMATION

The following information concerns selected regulatory requirements potentially applicable to this product. Not all such requirements are identified. Users of this product are responsible for their own regulatory compliance on a federal, state [provincial], and local level.

**U.S. FEDERAL REGULATIONS:**

**EPA - ENVIRONMENTAL PROTECTION AGENCY**

**CERCLA:** Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (40 CFR Parts 117 and 302):

Reportable Quantity (RQ): None

**SARA:** Superfund Amendment and Reauthorization Act

**SECTIONS 302/304:** Requires emergency planning on threshold planning quantities (TPQ) and release reporting based on reportable quantities (RQ) of EPA's extremely hazardous substances (40 CFR Part 355).

| | |
|---|---|
| Extremely Hazardous Substances: | None |
| Threshold Planning Quantity (TPQ): | None |

**SECTIONS 311/312:** Requires submission of material safety data sheets (MSDSs) and chemical inventory reporting with identification of EPA defined hazard classes (CFR 40 Part 370). The hazard classes for this product are:

| | | | |
|---|---|---|---|
| IMMEDIATE: | Yes | PRESSURE: | Yes |
| DELAYED: | No | REACTIVITY: | No |
| | | FIRE: | No |

**SECTION 313:** Requires submission of annual reports of release of toxic chemicals that appear in 40 CFR Part 372.

Carbon dioxide does not require reporting under Section 313.

**40 CFR PART 68:** Risk Management for Chemical Accidental Release. Requires the development and implementation of risk management programs at facilities that manufacture, use, store, or otherwise handle regulated substances in quantities that exceed specified thresholds.

Carbon dioxide is not listed as a regulated substance.

**TSCA:** Toxic Substance Control Act: Carbon dioxide is listed on the TSCA inventory.

**OSHA - OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION:**

**29 CFR 1910.119:** Process Safety Management of Highly Hazardous Chemicals. Requires facilities to develop a process safety management program based on Threshold Quantities (TQ) of highly hazardous chemicals as listed in Appendix A.

Carbon dioxide is not listed in Appendix A as a highly hazardous chemical.

**FDA - FOOD AND DRUG ADMINISTRATION**

**29 CFR 184.1240:** Generally recognized as safe (GRAS) as a direct human food ingredient when used as a leavening agent, processing aid, propellant, aerating agent and gas.

**Food Chemicals Codex IV**, Carbon Dioxide Monograph defines qualifications for use in foods.

**Carbon dioxide USP** is regulated by FDA as a prescription drug.

**[CANADIAN REGULATIONS:]**

[Controlled Product Hazard Class A. This MSDS has been prepared in compliance with Controlled Product Regulations.]

## 16. OTHER INFORMATION

**SPECIAL PRECAUTIONS:** Use piping and equipment adequately designed to withstand pressures to be encountered. Use a check valve or other protective apparatus in any line or piping from the cylinder to prevent reverse flow. Discharge of liquid carbon dioxide lines to atmospheric pressure will result in formation of solid dry ice, which may cause blockage of the liquid line.

**SPECIAL SHIPPING INFORMATION:** Cylinders should be transported in a secure upright position in a well-ventilated truck. The transportation of compressed gas cylinders in automobiles or in closed-body vehicles can present serious safety hazards and should be discouraged.

**MIXTURES:** When two or more gases or liquefied gases are mixed, their hazardous properties may combine to create additional, unexpected hazards. Obtain and evaluate the safety information for each component before you produce the mixture. Consult an Industrial Hygienist or other trained person when you make your safety evaluation of the end product. Remember, gases and liquids have properties that can cause serious injury or death.

**OTHER INFORMATION:**

| NFPA RATINGS: | | HMIS RATINGS: | |
|---|---|---|---|
| **GAS** | | | |
| HEALTH | = 1 | HEALTH | = 1 |
| FLAMMABILITY | = 0 | FLAMMABILITY | = 0 |
| INSTABILITY | = 0 | REACTIVITY | = 0 |
| SPECIAL | = SA (CGA recommends this to designate a simple asphyxiant.) | | |
| **LIQUID** | | | |
| HEALTH | = 3 | HEALTH | = 3 |
| FLAMMABILITY | = 0 | FLAMMABILITY | = 0 |
| INSTABILITY | = 0 | REACTIVITY | = 0 |
| SPECIAL | = SA (CGA recommends this to designate a simple asphyxiant.) | | |
| **SOLID** | | | |
| HEALTH | = 2 | HEALTH | = 2 |
| FLAMMABILITY | = 0 | FLAMMABILITY | = 0 |
| INSTABILITY | = 0 | REACTIVITY | = 0 |
| SPECIAL | = SA (CGA recommends this to designate a simple asphyxiant.) | | |

**STANDARD VALVE CONNECTIONS FOR U.S. AND CANADA:**

| | |
|---|---|
| **THREADED:** | CGA 320 |
| **PIN-INDEXED YOKE:** | CGA 940 (Medical Use) |
| **ULTRA HIGH INTEGRITY:** | 716 |

Use the proper CGA connections; DO NOT USE ADAPTERS.

Further information about carbon dioxide is available in the following pamphlets published by: Compressed Gas Association Inc. (CGA), 1725 Jefferson Davis Highway, Suite 1004, Arlington, VA 22202. Telephone: (703) 412-0900.

| | |
|---|---|
| G-6 | *Carbon Dioxide* |
| G-6.1 | *Standard for Low Pressure Carbon Dioxide Systems at Customer Sites* |
| G-6.2 | *Commodity Specification for Carbon Dioxide* |
| G-6.3 | *Carbon Dioxide Cylinder Filling and Handling Procedures* |
| G-6.5 | *Standard for Small Stationary Carbon Dioxide Systems* |
| G-6.6 | *Standard for Elastomer Type Bulk Transfer Hose* |
| P-7 | *Standard for the Requalification of Cargo Tank Hose* |
| P-14 | *Accident Prevention in Oxygen-Rich and Oxygen-Deficient Atmospheres* |
| SB-2 | *Oxygen-Deficient Atmospheres* |
| AV-1 | *Safe Handling and Storage of Compressed Gases* |
| AV-7 | *Characteristics and Safe Handling of Carbon Dioxide* |
| HB | *Handbook of Compressed Gases* |

**[PREPARED BY]:**

Compressed Gas Association
1725 Jefferson Davis Highway, Suite 1004
Arlington, VA 22202
703 - 412 - 0900

**Appendix 13: Sensors Magazine Buyer's Guide 2001 – www.sensorsmag.com**

Companies that sell $CO_2$ sensors

AIM, Air Instruments & Measurements Inc
Advanced Photonics International Inc
Alpha Omega Instruments Corp
Analytical Industries Inc
Analytical Technology Inc
Applied Technologies Inc
Bi Ra Systems Inc
CEA Instruments Inc
Campbell Scientific (Canada) Corp
Campbell Scientific Inc
Canongate Technology Inc
Columbus Instruments
CompuDAS
Controle Analytique Inc
Cosa Instrument Corp
Detcon Inc
Dexter Research Ctr Inc
Dickson Co
Digital Control Systems Inc
Draeger Safety Inc
Duke-River Engineering Company
ENMET Corp
Electro-Optical Systems Inc
Figaro USA Inc
Flowmetrics Inc
Gas Tech Inc
General Monitors
GlobalSpec.com
Hi-Tech Inc
Horiba Instruments Inc
Industrial Process Measurement Inc
Industrial Scientific Corp
International Sensor Technology
Irdam Co
J & J Instruments, LLC
LI-COR Inc
Labtech Corp
MSA Sensors
Melles Griot
Micro Probes
Microelectrodes Inc
Misonix Inc
Nova Analytical Systems Inc
ORB Analytical Co
Oakton Instrument
Pall Corp
RKI Instruments
Rel-Tek Corp
Ritron Inc
Rosemount Analytical Inc
SICK Inc
SRI International
Scott Specialty Gases
Sensor Electronics Corp
Servomex Transducers
Siemens Energy & Automation Inc
Sierra Monitor Corp
Telaire
Testo Inc
Thermal Instrument Co
Vaisala Inc
Valtronics
Yokogawa Corp of America
Zellweger Analytics Inc

## Appendix 14

## Opposition to Off-Site Deep Well Injection Disposal Facilities

### *Vickery, Ohio*

Ohio Liquid Disposal, a subsidiary of Chemical Waste Management (CWM), in turn a subsidiary of Waste Management Inc. (WMI), has operated a waste storage, treatment, and disposal facility at Vickery, Ohio, since the late 1970s. Disposal includes the injection of hazardous waste into the Mount Simon sandstone, approximately 2,800 ft below the surface. Since the start of operations, CWM has been the subject of numerous legal actions (Cray 1991). Of these, the most significant relates to the discovery, in 1983, of leakage from their deep wells into formations other than those specified for injection. Ohio EPA and WMI, the parent company, settled in 1984 with a consent agreement that included $10 M in fines and an additional $10 M in costs to bring the facilities in compliance. The following year, in 1985, the EPA filed a lawsuit against CWM for selling heating oil contaminated with PCBs and for illegal storage of PCB and dioxin contaminated waste in open lagoons. A $2.5 M penalty was levied in settlement, and CWM was required to clean up the open lagoons, at an estimated cost of $20 M. In 1990, a civil action against CWM, originally filed in 1982, was settled out of court, when CWM agreed to pay $15 M to local property owners and their attorneys. The settlement relieved CWM of any claims relating to future subsurface, off-site migration of wastes from permitted deep wells, and restricted plaintiffs, their heirs, and successors from impeding deep well injection operations, or oppose or object to pending or future requests for approval or permitting, provided that there is no fundamental change in the nature of operations at the site. At present, organized opposition to the operation of the Vickery facility is muted, primarily because the out-of-court settlement in 1990 largely inhibits such activity.

In 1997, CWM sought a variance of their permit to inject hazardous waste from Ohio EPA, as a result of changes in the land disposal restrictions (40 CFR Parts 148, 261, 268, 271), promulgated on May 12, 1997, which set ban dates for a number of hazardous waste codes. A revised permit, allowing CWM to continue injection of these wastes, was issued in October 1997 (USEPA 1997, Ohio EPA 1997). Subsequently, in May 2000, Ohio EPA asserted that there was “no known threat to any underground source of drinking water from waste being injected into waste for disposal at Vickery Environmental, Inc. (VEI)… (formerly known as Waste Management of Ohio)” (Ohio EPA 2000).

### *Winona, Texas*

In 1981, Gibraltar Chemical Resources, Inc. opened a deep well injection facility, consisting of two wells, for the disposal of hazardous wastes, a hazardous fuel blending operation, and a solvent recovery facility adjacent to the community of Winona, near Tyler, Texas. The facility, sold to American Ecology Environmental Services Corporation in 1994, received truck delivered hazardous waste from various suppliers throughout the region. There is anecdotal information of numerous incidents of releases of toxic airborne pollutants from the facility. Despite these incidents, strict enforcement was lax, and protests from the local community were largely ignored for lack of an effective voice and the poverty of its members. However, the situation changed dramatically in 1991, when Phyllis Glazer, the owner of a 2,200 acre ranch in the neighborhood, and well endowed with a legacy from her late father, took note after an explosion and release of noxious clouds of pollutants at the facility (M.O.S.E.S. 2001). Galvanized by her perception that the facility’s operation was the cause of numerous adverse health conditions among local residents, she organized Mothers Organized to Stop Environmental Sins (M.O.S.E.S) to fight on behalf of the interests of Winona’s residents. As a possible consequence, the Texas Attorney General’s office filed a lawsuit in 1992 demanding that the Company comply with the Texas Clean Air Act, for which the company was fined $1.1 M. In January of the following year, an accident at the plant caused a release of hydrogen bromide into the atmosphere. As a consequence, Glazer took legal action to pressure the TNRCCto close the plant. In the fall of 1993, Gibraltar management failed to report a chemical accident until the day after it occurred, thereby providing TNRCC with the basis for ordering Gibraltar temporarily to stop receiving hazardous waste (Maclean and Puchalsky 1994). She also pressured EPA to follow federal regulations. (One of the injection wells was missing 800 ft of cement casing around the well and was operating in conflict with 40 CFR section 145.1 [USEPA 1993, Sanjour 1997)). Her lawyers also filed a federal lawsuit alleging violation of the Texas Clean Air Act. Through the gathering of evidence documenting pollution and health effects, and by community and legal activism, she eventually forced the operators to close the facility in 1997. However, the wells were subsequently re-permitted to allow cleanup operations to proceed (Van Voorhees 2001).

Lawsuits are currently pending, including a multimillion-dollar federal lawsuit against Glazer and her family by American Ecology, claiming a conspiracy to destroy the company, and a $200 M class action lawsuit against American Ecology by local residents.

*Romulus, Michigan*

A 4,500 ft deep injection well for the disposal of hazardous wastes was completed by Environmental Disposal Systems, Inc. (EDS) in 1993, close to a residential neighborhood in Romulus, Michigan, a community of 24,000. According to Domino (1999), the discovery of the existence of this well by local citizens lead to the formation of a citizen group, Romulus Environmentalists Care About People (RECAP). This group actively campaigned against the operation of the well and EDS's planned construction of a second deep injection disposal well in the community. They expressed concern over the potential volume of truck traffic bringing in the estimated 96 million gallons of hazardous waste annually (19,200 p.a.), the lack of funds to regulate the facility, the potential of the facility to attract other facilities, the proximity of the existing well to a residential neighborhood, and the adverse impact on property values (Marra 1994). The adversarial process has evolved from discussion at public hearings and city council meetings, mass mailings of letters, and investigations into the financial structure of EDS to legal action. In consequence of a legal challenge by the city of Romulus, a district court placed an injunction on the further use of the existing EDS well, but found that EDS' state and federal permits overrode local authority to regulate use of the well for waste disposal. EDS, in turn sued the city of Romulus for $1M in damages for lost future earnings from the well, which led to a ruling in favor of the city.

Meanwhile, Michigan lawmakers have proposed regulations that would apply more stringent regulations to injection wells, where owners would be required to operate under Michigan's hazardous materials Act (HMA). Under HMA, public hearings would be required during the well-siting process and regular inspections of the well after it becomes operational. However, a 1997 request by a State Legislator to the Michigan Department of Environmental Quality (MDEQ) to consider increasing random inspections of deep well injection facilities from two to six per annum, and to fine violators of federal or state regulations while on site, was not acted upon.

From the above brief histories, it is evident that off-site facilities can be the focus of undesired local hostility, which can eventually lead to court or out-of-court settlements. The litigation is of concern to the CMA, which, as the final outcome, might eventually adversely affect continuing deep underground injection operations elsewhere in the United States. Sutherland (1999) cites David Mentall, manager of environmental issues and UIC staff executive for CMA: "We have no concern from a regulatory point of view with these wells, but there are a number of civil action suits pending which we are very concerned could possibly set an astronomical monetary effect precedent."

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