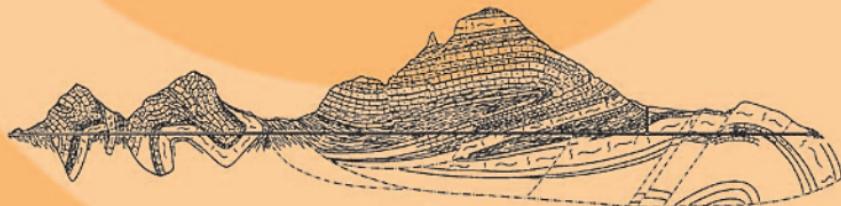


Hazardous Gases Underground

Applications to Tunnel Engineering



Barry R. Doyle

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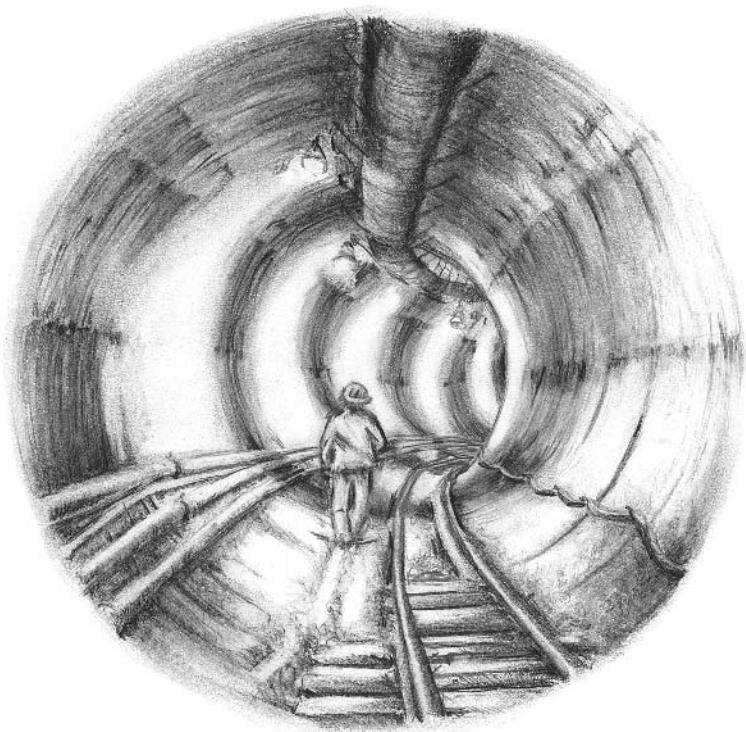
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Preface

Natural gases are a commonly acknowledged hazard to construction of tunnels, shafts, and underground chambers. Gases from the ground can mix with air in the excavation to form an atmosphere that can explode, or can irritate, poison, or asphyxiate the occupants. Encounters with gases usually result in costly delays. Tragic accidents are rare but persistent in underground construction, and proclaim our lack of understanding of this geologic hazard. Current civil engineering and engineering geology literature does not provide enough information on the nature of gases underground, or guidance toward avoiding potential problems.

Gases are poorly understood within the underground construction industry for several reasons. Few excavations encounter gases in the ground in amounts that can generate a hazardous atmosphere, so gases are not a subject of routine interest in subsurface exploration programs. Gases occur in a wide variety of geologic conditions, so experience from one project might not be readily applied to others. Gases are generated by complex biological and geochemical processes generally not familiar to underground construction professionals. Finally, encounters with gases often entail unanticipated, negative consequences—experiences that project participants are not inclined to recount in publication.

In contrast to its peripheral standing in the underground construction industry, gas is a subject of considerable research in environmental remediation, petroleum exploration, coal science, and geothermal energy development. Workers in these fields study the most productive sources of gas underground. They examine how gases are generated, how they move through the ground, how they come to reside, and how they can be detected. Their collective knowledge can explain the occurrence of hazardous concentrations of gas at the depths at which underground civil works are constructed. Much relevant information has been acquired only within the last few years.

This text incorporates information from the aforementioned fields into solu-

tion of the gas problem in underground construction. It is intended to describe, for civil engineers, engineering geologists, and geologists, the occurrence of potentially hazardous concentrations of gases in the ground. Understanding gas will enable investigators to assess the risk associated with gas prior to excavation, an essential step toward timely implementation of sound gas control measures. This text deals primarily with controlling gas during the construction process, but the implications for the design of permanent underground facilities are clear.

A number of people assisted in the preparation of this text. Specialists in various fields reviewed major portions of the draft, to improve the text's accuracy and clarity and to bring their own indispensable experiences to the task. Their names are shown in the list of principal reviewers. Others contributed project records, reviewed project case histories, translated technical papers written in non-English publications, and provided other assistance. In particular, I would like to acknowledge the contributions of Michael J. Barcelona, Steven B. Fradkin, Hisato Hayashi, Raymond W. Henn, Klaus Herkt, Romeo S. Jurani, Ann G. Kim, Van E. Komurka, Richard J. Proctor, Dudley D. Rice, and Ronald R. Skabo. The efforts of all contributors are very much appreciated. Frontispiece artwork is by Holly VanAntwerp.

Barry R. Doyle

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1

The Hazardous Nature of Gases Underground

INTRODUCTION

Gases are common constituents of the underground environment, along with soils, rocks, and water. Natural gases present underground originate from the atmosphere, the mantle, bacterial decomposition of organic matter, thermal decomposition of organic and inorganic compounds, and geochemical reactions. Gases are usually widely dispersed in low concentrations, but under some geologic conditions are abundant. Gases can be a hazard to construction of underground civil works such as tunnels, shafts, and underground chambers. Gases tend to be drawn into excavations by geostatic, hydrostatic, and barometric pressure reductions associated with the excavation. Gases from the ground may mix with air in the excavation to generate an explosive, toxic, or asphyxiating atmosphere.

An excavation in gassy ground can be safely made by controlling the atmosphere, by 1) preventing hazardous concentrations of gas from accumulating, 2) eliminating potential ignition sources in the presence of combustible gas, and 3) sounding the alarm to evacuate in the event that gas concentrations approach hazardous levels. Atmosphere control measures include ventilation, gas monitoring, use of explosion-proof electrical equipment, and hazard awareness training for workers. Accidents due to gas have occurred where control measures were allowed to lapse even briefly.

Excavations are seldom overcome by rapid inflows of gas. Hazardous atmospheres more commonly develop from low inflows coincident with deficient atmosphere control measures. Most accidents and financial losses attributed to gas are a consequence of errors made in developing and maintaining control measures, originating from a lack of awareness of the nature of gases underground. An understanding of the nature of gas enables underground construction professionals to make excavations safer, by making control measures more reliable. To this end this text explains:

- How potentially hazardous gases are generated
- How gases migrate and become trapped underground
- How gases enter excavations
- How to identify geologic environments that may retain gas
- How to detect gases in the ground, and to assess the risk associated with them

Gases considered hazardous to underground construction are methane, hydrogen sulfide, and carbon dioxide, which are generated by natural biologic and geologic processes; and gasoline vapors, which are associated with leaks from underground storage tanks and pipelines. These gases can enter an excavation in the near-surface underground, and within a matter of minutes can explode, or can irritate, poison, or asphyxiate the occupants. The term *near-surface underground* is used throughout this text to refer to depths within which civil works are normally constructed, a maximum of about 1000 m. Gases generated within an excavation by use of internal combustion engines and explosives are not addressed in this text. Conditions at great depth and pressure routinely encountered in mining and petroleum exploration are also not addressed. An overview of radon is included in this chapter. In nearly all geologic situations encountered in civil works tunneling, normal ventilation will control radon, making it unnecessary to pay specific attention to this gas. However, radon in an unventilated work space can pose a hazard to workers subjected to long-term exposure.

The text is organized as follows: Chapter 1 describes hazardous properties of each of the subject gases; Chapters 2 through 8 describe generation, behavior, and environment of the natural gases methane, hydrogen sulfide, and carbon dioxide; Chapter 9 describes gasoline vapors; and Chapter 10 describes methods and objectives of an exploration program to identify hazardous gases underground. Units of measure, physical quantities, and miscellaneous constants and terms applied throughout the text are summarized in Appendix A. Data tables are presented in Appendix B. Principles of physical chemistry of gases and vapors, of fundamental importance to behavior of gases in the ground and in excavations, are presented in Appendix C. The reference lists at the end of each chapter are an avenue to more detailed study that may be necessary to address specific project issues.

The study of gas inflows to excavations is a challenging problem, considering that it draws from the fields of human toxicology, physical chemistry, organic chemistry, environmental microbiology, coal science, petroleum science, geothermal science, physical geology, environmental remediation, and industrial ventilation. Establishing an appropriate level of detail in which to address these matters has been most difficult. The level of detail presented here was developed from studies of numerous incidences of gas inflows to tunnels and shafts, some of which are described in following chapters. The text is intended to provide a thorough understanding of the fundamentals of gas generation and behavior underground, and a basis for performing more detailed work where appropriate. As with most geotechnical problems, assessing gas inflows to excavations is not a precise exercise but a matter of recognizing a range of possibilities and identifying controlling variables.

OUR VULNERABILITY TO CONTAMINANT GASES

The gaseous composition of our atmosphere has remained relatively constant since the ascent of land plants 350 million years ago (Kasting 1993). Man's evolution in this stable atmosphere has left us poorly equipped for change in the availability or composition of the air we breathe. If deprived of oxygen, the human body can sustain itself for 5 minutes without permanent damage, and dies after 8 minutes. Our respiratory system includes physiological defense mechanisms to protect us from airborne microorganisms, viruses, and inert particulate matter but not contaminant gases. Gases present in inhaled air enter the bloodstream within a matter of seconds.

The body comes into intimate contact with the atmosphere in the lungs. The lungs provide a surface area of up to about 90 m^2 for exchange of gases between the atmosphere and the blood (Benjamin 1996). This exchange of gases occurs in the alveoli, minute air chambers that cluster around the smallest air passages of the lungs. The alveoli are defined by delicate partitions of tissue a mere two cells thick, partitions that also form capillary blood vessels. Gases held in the alveoli and in blood moving through capillary vessels equilibrate almost instantly across these partitions.

Respiration is regulated by the respiratory nerve center located at the base of the brain. This nerve center monitors carbon dioxide and oxygen concentrations in blood leaving the lungs, and adjusts the volume and rate of respiration accordingly. The nerve center is sensitive to small changes in carbon dioxide concentration, and to large and sustained decreases in oxygen concentration (Revoir and Bien 1997, p. 26). To promote a stable concentration of these gases in blood leaving the lungs, air entering the alveoli is drawn from a reservoir of stable, conditioned air stored in the larger passages of the lungs. This *stationary air* occupies a volume of about 3 L. With each breath, about 0.3 L of *tidal air*

mixes with stationary air to maintain a nearly constant composition of 15% oxygen and 5.5% carbon dioxide in the reservoir (Henderson and Haggard 1943, p. 27–28).

HAZARDOUS PROPERTIES OF GASES

The particular hazard or hazards posed by any gas depends on its chemical properties. A combustible gas in an enclosed space can explode; a physiologically inert gas can displace oxygen, causing asphyxiation; a toxic gas absorbed into body tissues can disrupt normal physical processes. The hazards of methane, hydrogen sulfide, carbon dioxide, and gasoline vapors are summarized in Table 1-1.

Detection of gas in an excavation atmosphere, in excess of allowable limits, disrupts normal work activities as a matter of procedure. In this text, concentrations of gas that exceed allowable limits are defined as hazardous. Allowable limits for airborne contaminants vary internationally among agencies that establish or enforce them. Allowable limits for the subject hazardous gases, as established by ACGIH and OSHA (two U.S. organizations), are shown in Table 1-2. ACGIH is the *American Conference of Governmental Industrial Hygienists*. ACGIH is an organization of government and independent practitioners of industrial hygiene, occupational and environmental health, and occupational safety (Plog, Niland, and Quinlan 1996). ACGIH issues frequently updated recommendations for exposure limits for toxic chemicals. OSHA is the *Occupational Safety and Health Administration*, a U.S. government agency that enforces safety standards applicable to private employers. OSHA exposure limits for toxic chemicals may differ from ACGIH recommended limits.

References are made in Table 1-2 to *threshold limit values* (TLVs) for contaminant gases. Threshold limits are set at contaminant levels to which nearly all workers may be exposed daily, without physical stress or impaired health. The *threshold limit value-time-weighted average* (TLV-TWA), as defined by

Table 1-1 Hazards of Gases Found Underground

Gas	Nature of hazard		
	Combustion/ explosion	Simple asphyxiant	Toxic
Methane	×	×	
Hydrogen sulfide			×
Carbon dioxide		×	
Gasoline vapors	×		×

Table 1-2 Maximum Allowable Concentrations of Hazardous Gases and Vapors in Air

Chemical	Concentration	
Methane		1% (20% LEL) ^a
Hydrogen sulfide	TWA = 10 ppmv	STEL = 15 ppmv
Carbon dioxide	TWA = 0.5%	STEL = 3%
Gasoline vapors	TWA = 300 ppmv	STEL = 500 ppmv
Benzene	TWA = 10 ppmv	

^a OSHA 1999, 29 CFR 1926.800.j.l.ix.

Toxic exposure limits as recommended by ACGIH.

TWA is time-weighted average for 40-h workweek.

STEL is short-term exposure limit for 15-min exposure.

LEL is lower explosive limit.

Source: Plog et al. 1996, App. B, except as noted.

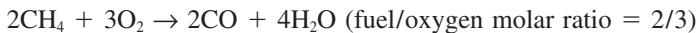
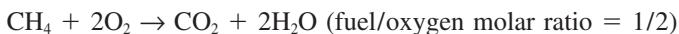
ACGIH, is a time-weighted average exposure for a normal 8-hour workday and 40-hour workweek. The *threshold limit value–short-term exposure limit* (TLV-STEL) is a 15-minute time-weighted average exposure. Both limits apply concurrently. For more information on exposure limits, refer to a text on industrial hygiene (for example, Plog, Niland, and Quinlan 1996).

Methane

Methane (CH_4) is the most familiar hazardous gas, and the most destructive. Methane is generated underground by bacterial decomposition of organic matter in anaerobic environments, and by thermal decomposition of organic matter during coalification and petroleum generation.

Methane is combustible in air in concentrations from 5.0% to 15.0% by volume. In this text, the term *combustible* is defined as “capable of propagating a flame freely.” A 5% concentration of methane in air is referred to as the *lower explosive limit*, or *LEL*. A 15% concentration is the *upper explosive limit*, or *UEL*. Methane concentrations above the UEL, though not combustible, are still dangerous because dilution of the mixture with fresh air will lower the concentration into the combustible range. A combustible concentration of methane can be ignited by a weak spark (electrical, frictional, or static), which produces a high temperature for a very short duration. The minimum spark energy necessary for methane ignition is 0.30 mJ (Kuchta 1985). Ordinary electrical equipment and even some static electrical discharges produce much higher spark energies. A combustible concentration of methane can also be ignited by a hot surface or an open flame. The lowest temperature necessary to ignite methane, the *autoignition temperature*, is 630°C.

Ignition of a combustible concentration of methane causes the following reactions:



These reactions are highly exothermic, and once initiated are self-propagating. Heat from the reaction causes the gas volume to expand, by a factor of about five in underground conditions. Flame temperatures depend on pressure developed within the combustion zone; temperatures of 1000°C or higher can be expected. Speed of the advancing flame front varies but may reach hundreds of meters per second. In a confined space such as a tunnel, ignition of a combustible gas mixture can drive a destructive pressure pulse far beyond the combustion zone (Nagy 1981). Depletion of oxygen and formation of carbon monoxide within the combustion zone generates a condition as deadly as the heat and physical violence of the explosion (Humphrey 1960). Carbon monoxide is a chemical asphyxiant that interferes with the oxygen-carrying capacity of the blood.

Methane also acts as a simple asphyxiant. It can cause an oxygen-deficient atmosphere in an unventilated, enclosed space by displacing normal air and reducing the oxygen concentration of the CH₄-air mixture. Methane at 7% concentration in air reduces oxygen concentration to the OSHA allowable minimum of 19.5%; methane at 71% reduces oxygen to a fatally low 6%; the relationship is linear. Methane cannot be detected by the physical senses. It is odorless, and it does not react chemically with body tissues.

Hydrogen Sulfide

Hydrogen sulfide (H₂S) in the near-surface underground usually originates from bacterial decomposition of organic matter in anaerobic environments. It can also occur in geothermal systems, where it originates from magma degassing and thermal metamorphism.

Hydrogen sulfide in low concentrations has a characteristic odor of rotten eggs. The odor is strongly offensive at concentrations as low as about 5 ppmv. At concentrations above 100 ppmv, the gas quickly paralyzes the olfactory nerves, and the sense of odor disappears. This can give the false impression that exposure to the gas was transient. Persons exposed to high concentrations have reported no apparent odor (Robinson, Camp, and Chamberlain 1942; National Research Council 1978, p. 56).

Hydrogen sulfide is a toxic hazard. This somewhat water-soluble gas is absorbed on moist surfaces, causing tissue inflammation. In low concentrations (50 ppmv), hydrogen sulfide is an irritant of the eyes and entire respiratory tract. Prolonged exposure to moderate concentrations (250 ppmv) causes the alveolar membranes to exude fluids that interfere with the normal exchange of gases. This

irritation may cause only minor pain (Revoir and Bien 1997, p. 44). The principal symptom is asphyxia, which becomes apparent hours after exposure, and may lead to suffocation. Inhalation of high concentrations of hydrogen sulfide (1000 ppmv) paralyzes the respiratory nerve center, which can lead to suffocation. Physical collapse may occur without warning (National Research Council 1978, p. 47–51; Deng 1992). The effects of hydrogen sulfide on the body are summarized in Table 1-3. Symptoms may appear at lower hydrogen sulfide concentrations during physical exertion.

Hydrogen sulfide is combustible in air at concentrations from 4.3% to 46%, far above the 1000 ppmv (0.1%) concentration that causes respiratory system paralysis. Natural gases containing hydrogen sulfide in combustible concentrations occur rarely in deep petroleum reservoirs. It is highly unlikely that combustible concentrations of hydrogen sulfide could reach civil works excavations in the near-surface underground.

Carbon Dioxide

Carbon dioxide (CO_2) is generated underground by bacterial decomposition of organic matter in aerobic environments. It also occurs in geothermal systems, where it originates from magma degassing, from thermal decomposition of carbonates, and from dissolution reactions between acid waters and carbonates. Carbon dioxide underground is common but infrequently destructive. Most bacterially generated carbon dioxide occurs within a few meters of the ground surface, and few underground construction projects are sited in geothermal fields. Nevertheless, carbon dioxide has injured or killed underground workers.

Carbon dioxide is classified as a simple asphyxiant in occupational medicine literature; it can displace normal air and reduce the oxygen concentration

Table 1-3 Effects of Exposure to Hydrogen Sulfide

Concentration (ppmv)	Effects
0.003–0.02	Approximate threshold for odor
3–10	Obvious offensive odor
50–100	Serious eye irritation, respiratory tract irritation
100–200	Loss of smell
250–500	Fluid buildup in lungs, imminent threat to life
500	Anxiety, headache, dizziness, excessively rapid respiration, amnesia, unconsciousness
500–1000	Immediate collapse, irregular heartbeat, neural paralysis, respiratory paralysis leading to death

Source: Adapted from Reiffenstein et al. 1992.

Table 1-4 Effects of Exposure to Carbon Dioxide

Concentration (%)	Effects
5	Perceptible increased respiration
6–10	Shortness of breath, headache, dizziness, sweating, restlessness
10–15	Impaired coordination, abrupt muscular contractions
20–30	Loss of consciousness, convulsions

Source: Adapted from Hathaway et al. 1991, p. 139.

of the CO₂-air mixture. Carbon dioxide is a powerful stimulant to respiration; its presence in inspired air in excess of the normal concentration of about 360 ppmv (0.036%) causes the rate of breathing to increase. This response becomes pronounced when the concentration of carbon dioxide in inspired air approaches the normal concentration in stationary air in the lungs, about 5.5%. The effects of breathing elevated levels of carbon dioxide in air are summarized in Table 1-4. Symptoms may appear at lower carbon dioxide concentrations during physical exertion.

Gasoline Vapors

Gasoline is a common contaminant in the near-surface underground in cities and towns. It usually enters the subsurface from leaks in underground storage tanks and piping at automotive service station sites. Liquid gasoline easily migrates through permeable soils and rocks above the water table. Gasoline that flows into an excavation will quickly volatilize into the atmosphere.

The most serious hazard from gasoline is from explosion of vapors. Gasoline vapors are combustible in air in concentrations from about 1.4% (LEL) to 7.6% (UEL) (Cole 1994, Tbl. 3-3). Autoignition temperatures for combustible concentrations of gasoline vapors range from 280° to 456°C (Sax and Lewis 1989, p. 1795). Ignition of a combustible concentration of gasoline vapors releases about 5400 to 5900 kJ mol⁻¹ of heat energy, compared to about 800 kJ mol⁻¹ for methane (Bolz and Tuve 1973).

Gasoline vapors pose a toxic hazard. Exposure to low concentrations can irritate the eyes and upper respiratory tract. Vapors can enter the body through the alveoli, and exposure to high concentrations can depress the central nervous system, leading to cardiac arrest. A concentration of 5000 ppmv (0.5%) can be lethal (Weaver 1992). The effects of breathing gasoline vapors are summarized in Table 1-5.

Gasoline also poses a toxic hazard from exposure to benzene vapors. Liquid gasoline contains the hydrocarbon benzene in concentrations of up to about 3.5% (wt.; Table 9-3). Benzene has a higher solubility in water than other gasoline

Table 1-5 Effects of Exposure to Gasoline Vapors

Concentration (ppmv)	Effects
0.25	Approximate threshold for odor.
500	Moderate eye irritation.
900	Nose and throat irritation.
1000	Drowsiness, dizziness, nausea, and numbness.
5000–16000	Irregular heartbeat leading to cardiac arrest.

Source: Adapted from Sittig 1991 and Weaver 1992.

hydrocarbons, so it can make up a disproportionate amount of hydrocarbons in solution in groundwater contaminated with gasoline. These hydrocarbons are released as vapors with inflow of contaminated groundwater to an excavation. Benzene is metabolized in the body to other substances that can disrupt blood cell formation in bone marrow and can cause leukemia (Andrews and Snyder 1993). Benzene is considerably more toxic than other gasoline hydrocarbons. The odor threshold for benzene is about 4 to 5 ppmv (Goldstein and Witz 1992).

Gasoline vapors cannot go undetected as easily as the other hazardous gases. Their presence is betrayed by their odor and irritant properties. Concentrations in the combustible range are physically intolerable.

OXYGEN DEFICIENCY

Oxygen deficiency is a condition of dangerously low amounts of oxygen in the local atmosphere. An oxygen-deficient atmosphere can develop when a relatively large amount of contaminant gas displaces and mixes with normal air. The contaminant gas may be otherwise physiologically harmless, such as methane. An oxygen-deficient atmosphere can also develop when oxygen is consumed in biochemical reactions mediated by aerobic bacteria, in geochemical reactions with iron, or in combustion reactions.

The effects of oxygen deficiency on the body are summarized in Table 1-6. The effects are slight until the oxygen concentration in the atmosphere declines to that of stationary air in the lungs, about 15%. Oxygen deficiency affects mental perception, a victim may be wholly unaware of the symptoms (Henderson and Haggard 1943, p. 146). Abrupt entry into a severely oxygen-deficient atmosphere can cause immediate loss of consciousness. At elevations above sea level, oxygen deficiency occurs at higher concentrations than shown in the table. At an elevation of 2500 m, symptoms of oxygen deficiency would begin to develop at an oxygen concentration of about 19.5% (Revoir and Bien 1997, p. 49). The minimum oxygen concentration permitted for underground construction in the United States is 19.5% (OSHA 1990, 29 CFR 1926.800.j.1.ii).

Table 1-6 Effects of Oxygen Deficiency at Sea Level

Concentration (%)	Effects
16–12	Increased breathing volume, accelerated heartbeat, impaired thinking and muscular coordination
12–10	Intermittent breathing, very faulty judgment, rapid fatigue
10–6	Nausea, vomiting, loss of strength, loss of consciousness
<6	Spasmodic breathing, convulsions, cardiac arrest

Source: Adapted from Revoir and Bien 1997, p. 48.

RADON

Radon is a radioactive gas common in rocks, soils, and groundwater. Health studies have conclusively linked radon to lung cancer among underground workers in uranium, iron, tin, lead, zinc, and fluorspar mines (Harley 1992). Radon has been found in some homes at levels comparable to those that have caused cancer among miners, a discovery that prompted numerous studies into the effects of environmental radon on human health. Radon is not among the hazardous gases addressed in detail in this text. Given the prevailing public attention on radon, an explanation for this exclusion seems appropriate.

The radon isotope of most interest to human health, radon-222 (or ^{222}Rn), is among 13 radioactive elements in the decay series of uranium-238 to the stable isotope lead-206. The uranium-238 decay series is shown in Figure 1-1. Elements in the series are formed from the decay of a radioactive parent via alpha decay—the spontaneous emission of two protons and two neutrons (an alpha particle), or beta decay—the conversion of a neutron to a proton and the emission of an electron (a beta particle). Alpha and beta particles ejected from the decaying atom radiate into the surrounding medium.

Uranium-238 is a widely distributed but minor constituent in the geologic environment. In igneous and sedimentary rocks, the average concentration of uranium-238 is about 0.0003%, though there is wide variation (Brookins 1990, Tbl. 2-2; Gundersen et al. 1992). In commercial-grade uranium ores, the concentration ranges from about 0.3% to 4% (Holaday 1974, p. 30; Wilkening 1990, p. 30). Uranium-238 has a half life of 4.5×10^9 years, so it provides an inexhaustible source of radon-222.

Radon-222 is potentially the most mobile element of the uranium-238 decay series. It is the only gas in the series, is soluble in water, is chemically inert, and has a moderately long half-life of 3.8 days. Radon-222 is formed from alpha decay of radium-226, its parent isotope. Alpha decay of radium on or near the surface of a rock or mineral can recoil newly formed radon out of the solid matrix and into adjacent fractures or pores. Free radon can diffuse through gas-filled

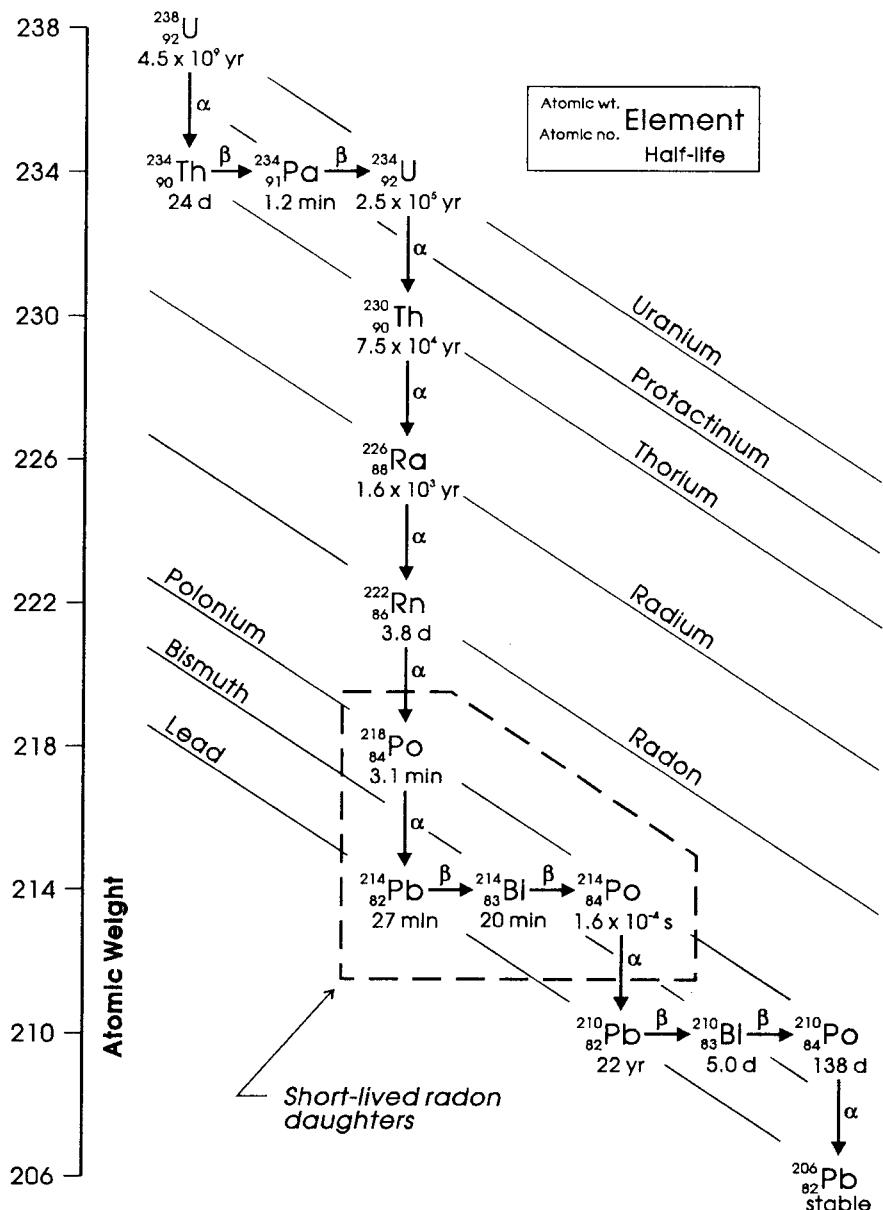


Figure 1-1. Uranium-238 radioactive decay series. α denotes alpha decay, β denotes beta decay.

void space or move in solution in groundwater. The atmosphere of an underground space can be contaminated by radon emanating from the surfaces of soil particles or broken rock, by diffusing from fractures or pores, or by coming out of solution from groundwater entering the space.

The health risk commonly attributed to airborne radon is actually derived from inhalation of its short-lived daughters. Decay of radon forms the first radon daughter, polonium-218, a solid charged particle (+2) with a half-life of 3.1 minutes. Because of its electrical charge, most airborne polonium-218 adheres to aerosols. In underground atmospheres, aerosols include water vapor, dust, diesel exhaust particulates, and oil mists. Decay of polonium-218 leads to the second, third, and fourth radon daughters: lead-214, bismuth-214, and polonium-214. These daughters for the most part remain on the carrier aerosol (Harley 1992).

Inhaled aerosols are captured on mucous layers in the lungs, concentrating radon daughters on lung tissues, particularly the upper bronchial passages. Alpha radiation from radon daughters trapped on lung tissues can lead to cancer. Decay of polonium-218 and polonium-214 bombards these tissues with alpha particles, rupturing DNA molecules and causing other cell damage (Brookins 1990, pp. 67–69). Tissues of the upper bronchial passages rapidly repair themselves when damaged, a characteristic that makes them comparatively more likely to develop cancer than other lung tissues because it facilitates regeneration of abnormal cells. Beta radiation from decay of lead-214 and bismuth-214 has little effect on cells because of the very small mass of the beta particle. Inhaled radon does not concentrate in the lung, consequently the dose of alpha radiation from radon decay is only about 1% of that from the radon daughters (Meyers, Stewart, and Johnson 1981).

The decay series following polonium-214 does not pose a health risk. Because of its long half-life, lead-210 tends to be swept from upper bronchial passages by normal clearing action of bronchial cilia—or it is absorbed into the body and cleared through other means.

The nature of the health risk due to exposure to radon is entirely different from the risk posed by exposure to methane, hydrogen sulfide, carbon dioxide, and gasoline vapors. With the latter gases, brief exposure to high concentrations can result in immediate injury or death. In contrast, underground workers who have contracted lung cancer attributed to radon have typically spent years in poorly ventilated mines in or near deposits containing high levels of uranium. Improvements in ventilation appear to have eliminated the excessive risk of lung cancer from radon in mines (Cohen 1981). Occasional brief lapses in good ventilation practice, lapses common in underground construction, appear tolerable with respect to radon. The same cannot be said of methane, hydrogen sulfide, carbon dioxide, and gasoline vapors.

Radiation limits for underground mining established by the U.S. Mine Safety and Health Administration are as follows (MSHA 1987, 30 CFR 57.5038–9):

- Maximum permissible activity concentration of 1 WL (working level)
- Maximum permissible annual exposure of 4 WLM (working level month)

WL is defined as the concentration of short-lived radon daughters in the underground atmosphere that will emit 1.3×10^5 meV of potential alpha energy per liter of air (Wilkening 1990, p. 126). WLM is defined as exposure to one WL for one working month, a period of 170 hours. To put this limit in perspective, in the United States the average annual environmental exposure from radon is about 0.22 WLM; the average annual exposure for full-time uranium miners in 1978 was about 1.45 WLM (Cohen 1982). Inoperable or deficient ventilation can allow activity concentrations to rise above allowable levels in the underground atmosphere.

A considerable amount of information is available on the occurrence of radon underground, its health implications, and means of control. In addition to the references cited, others are included in the bibliography for this chapter.

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2

Organic Matter in Sediments

INTRODUCTION

Living organisms produce organic matter, the material that gives form and function to life. Organic matter is rich in chemical energy and is a crucial source of energy and nutrients for many forms of living organisms. Only a small portion of the organic matter produced escapes consumption by organisms near the ground surface or in the water column to become incorporated into sediments.

Organic matter in sediments becomes a potential source of hazardous gas through processes of bacterial and thermal decomposition. The underground is inhabited by communities of bacteria to depths of hundreds of meters or more. Bacteria decompose organic matter into waste products that include methane, hydrogen sulfide, and carbon dioxide. Organic matter that escapes complete bacterial decomposition may be further decomposed in geochemical processes largely driven by heat associated with deep burial. Thermal decomposition of organic matter generates coal, petroleum, and associated thermogenic gases, notably methane.

An understanding of the origin, accumulation, and decomposition of organic matter in the ground and in bodies of water is important to identifying potential sources of hazardous gas.

CARBON

Living organisms construct elaborate chemical compounds to form and maintain their structure and to carry out chemical reactions that sustain life. All of these

compounds include carbon. The carbon cycle explains the eventuality of organic compounds in geologic environments, much as the hydrologic cycle explains the eventuality of groundwater.

Carbon Compounds

Carbon compounds occur in both organic and inorganic form. Living organisms generate all organic and most inorganic carbon compounds. Organic carbon compounds are rich in chemical energy, and are the source of bacterial and thermogenic gas. Organic carbon compounds are also called, more simply, *organic compounds* or *organic matter*. Inorganic carbon compounds contain little chemical energy. They can be decomposed to carbon dioxide in some geothermal systems.

Organic compounds perform specialized cellular functions, and some of these compounds are elaborately constructed. All are based on carbon. Carbon atoms form a molecular framework of straight chains, branched chains, rings, or combinations of these configurations. Attached around the carbon frame are groups of atoms, called *functional groups*, that impart specific chemical properties to the compound. Nearly all organic matter is composed of carbon bonded with oxygen, hydrogen, nitrogen, sulfur, and phosphorus. Elementary molecular building units called *monomers* are assembled into large molecules called *biopolymers*. Complex organic molecules are *biomacromolecules*. Organic compounds can comprise millions of atoms. Sediments containing organic carbon compounds, such as coal and organic shales, are characterized as *carbonaceous*.

Inorganic carbon compounds include oxides of carbon (CO_2), carbonates (CO_3^{2-}), and bicarbonates (HCO_3^-), among others. They may be generated by either biogenic or geochemical processes. Biogenic inorganic carbon compounds perform protective and supporting functions such as in shells, bones, and teeth. Calcium carbonate, for example, forms the supporting structures of plankton, frames of reef organisms, and shells. Geochemical processes generate abiogenic (not resulting from activity of living organisms) forms of inorganic carbon, such as the calcium carbonate ooliths that precipitate from seawater. Sediments consisting chiefly of inorganic carbon compounds, such as limestone, dolomite, and chalk, are called *carbonates*.

The Carbon Cycle

The earth's carbon may be apportioned between four conjoined reservoirs: the continental biological environment, the oceans, the atmosphere, and the lithosphere (the solid portion of the earth). Reservoir carbon may include living organisms or *biomass*, organic detritus (dead organic matter), and inorganic carbon compounds. The *carbon cycle* represents the unceasing exchange of carbon between these reservoirs. The carbon cycle can be divided into the biochemical subcycle, in which living organisms largely control carbon transfer between reser-

voirs; and the geochemical subcycle, in which geologic processes control carbon transfer between reservoirs.

Carbon Reservoirs

The continental reservoir includes land and freshwater environments to depths heavily populated by plant and animal life. Nearly all of the carbon held in the continental reservoir is organic, and nearly all of this originates from plants. About 25% of the total carbon held is living plants; most of the remainder is plant detritus (Killops and Killops 1993, Fig. 1.1).

The oceanic reservoir holds about 97% of its total carbon as dissolved inorganic carbon, and about 3% as organic carbon. Most organic carbon originates from phytoplankton, which acquire carbon from bicarbonates dissolved in seawater. Rivers contribute a small but important portion of organic carbon. Nearly all organic carbon in the ocean consists of dissolved and particulate detritus. Marine biomass makes up about 0.01% of total carbon. This biomass is evenly divided between phytoplankton and zooplankton (which graze on the phytoplankton).

The atmospheric reservoir holds nearly all its carbon in the form of carbon dioxide. The atmosphere provides a medium for rapid global transport of carbon.

The lithospheric reservoir is of greatest interest in this text, because it encompasses the near-surface underground. The lithospheric reservoir holds 2000 times the amount of carbon held in the other three reservoirs combined, and 99.95% of all the organic carbon in existence (Hunt 1972; Summons 1993; Tissot and Welte 1984, Tbl. I.1.1). Sedimentary rocks hold about 85% of the total lithospheric carbon. Sedimentary carbon is mostly carbonates but includes organic carbon in the form of coal, petroleum, and the organic fraction of shale. Igneous and metamorphic rocks hold the remaining 15% of total carbon, as elemental carbon and carbonates (Hunt 1972).

Biochemical and Geochemical Subcycles

The biochemical subcycle controls carbon transfer between the continental, the oceanic, and the atmospheric reservoirs (Bolin et al. 1983). The continental and oceanic reservoirs exchange carbon with the atmosphere, in the form of carbon dioxide. Photosynthesis is the main engine of the biochemical subcycle: it enables phototrophic organisms in continental and marine environments to convert inorganic carbon into new organic matter. Decomposer organisms eventually convert nearly all of this organic matter back into carbon dioxide. The biochemical subcycle turns rapidly; carbon residence time may be measured in weeks to years. Major carbon-conversion processes and the environments in which they occur are shown in Figure 2-1.

The geochemical subcycle controls carbon transfer through the lithospheric reservoir. Most carbon compounds enter the lithosphere through marine sedimen-

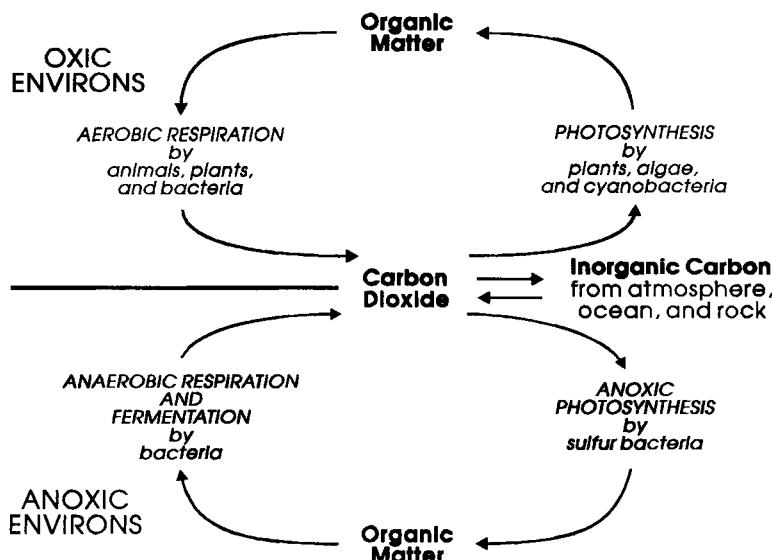


Figure 2-1. Biologic interactions between major participants of the carbon cycle. (Adapted from Summons 1993.)

tation. Some carbon enters through continental sedimentation, as evidenced by deposits of peat, coal, and some lacustrine shale. Carbon is released to the continental, oceanic, and atmospheric reservoirs via erosion and weathering, by volcanic activity, and at present by the burning of fossil fuels. Carbon residence time in the lithospheric reservoir is measured in millions of years.

Less than 0.1% of new organic matter generated in a given period of time escapes the biochemical subcycle to become incorporated into sediments. Though this rate of contribution of organic carbon to the sedimentary record is low, it has been maintained for a very long time, which explains why the overwhelming proportion of existing organic matter is held in the lithospheric reservoir.

CLASSIFICATION OF ORGANISMS

Living organisms are responsible for all of the generation and most of the destruction of organic compounds, and for the generation of bacterial gases. Organisms can be classified according to several schemes, among them the chemical processes they employ to survive, their evolutionary history, their similarity to other organisms, and the oxygen content of their normal environment. The terms introduced here are commonly applied in technical literature on the origin and fate

of organic matter underground, and some are used in subsequent portions of this text.

Metabolic Classification

Organisms have evolved diverse metabolic processes to exploit the wide range of physical environments found on earth. Metabolism refers to the sum of all the ongoing chemical processes of a cellular living organism. Organisms can be characterized by the processes they employ to acquire energy and carbon. Some organisms, particularly bacteria, use more than one metabolic process as a means of coping with temporal changes in their environment.

On the basis of energy acquisition, organisms can be characterized as *phototrophs* or *chemotrophs*. Phototrophs obtain energy from sunlight. Chemotrophs extract energy from chemical compounds found in their environment. Chemotrophs can be further differentiated into *chemoorganotrophs*, which obtain energy from existing organic compounds; and *chemolithotrophs*, which obtain energy from inorganic compounds (for example, H₂, H₂S, NH₃). The energy demands of an organism are generally far greater than the demand for molecular building material, making energy management a primary determinant in survival.

On the basis of carbon acquisition, organisms can be characterized as *autotrophs* or *heterotrophs*. Autotrophs synthesize “new” organic carbon compounds from inorganic source material, mainly CO₂ and mineral nutrients (for example, NH₃, Ca²⁺, H₂PO₄⁻, SO₄²⁻, K⁺). Heterotrophs acquire carbon and other resource elements from existing organic carbon compounds.

Genetic Classification

Genetic analyses show cellular organisms to have evolved along three lines originating from a common ancestor. These three phylogenetic groups are the *Bacteria* (Eubacteria in some texts), the *Archaea* (Archaeabacteria in some texts), and the *Eukarya*.

The Bacteria and Archaea are exclusively independent single-celled organisms, though some species form colonies of filaments or mats. The cells of both groups are simple in structure and lack centers of specialized function such as a nucleus, mitochondria, and chloroplasts. The Bacteria and Archaea are differentiated by their cell wall structure and means of synthesizing cell molecules. Both groups are metabolically diverse. The Archaea are noted for their adaptation to extreme environments distinguished by high temperature and high salinity. Bacteria and Archaea are collectively referred to as *prokaryotes*. Most prokaryotes are chemoorganotrophs.

The Eukarya, also known as *eukaryotes*, include unicellular and multicellular organisms. Eukaryote cells are much larger and more complex than those of prokaryotes and contain centers of specialized function.

Taxonomic Classification

Taxonomic groups are defined on the basis of form, structure, metabolism, environmental requirements, and cell chemistry, among other properties. Prokaryotes are referred to simply as “bacteria” (uncapitalized). Eukaryotes include algae, fungi, protozoa, plants, and animals.

Algae are phototrophic eukaryotes other than plants. Most are unicellular, and most inhabit aquatic habitats, both freshwater and marine. Abundant species of unicellular aquatic algae include the dinoflagellates, which are capable of movement via flagella; the coccolithophores, which incorporate an internal supporting structure of calcium carbonate; and the diatoms, characterized by a hard cell wall of silica (Brock et al. 1994; Killops and Killops 1993). In some texts, a highly productive group of aerobic photosynthetic Bacteria, the cyanobacteria, are included among the algae.

Fungi include molds, yeasts, and mushrooms. All fungi are chemoorganotrophs, as they lack chlorophyll. Most fungi are terrestrial, though there are freshwater and marine species.

Protozoa are unicellular, have a flexible cell membrane, are usually motile, and ingest particulate and dissolved organic matter into the cell. They are chemoorganotrophs. Protozoa inhabit freshwater, marine, and terrestrial habitats, often grazing on bacteria. The foraminifera, a productive group of protozoa, are marine organisms characterized by exterior shells of calcium carbonate (Brock et al. 1994).

Plants comprise bryophytes and vascular plants. All are phototrophs and all are terrestrial. Bryophytes include the mosses, notably the peat mosses. Vascular plants include seedless vascular plants, gymnosperms, and angiosperms (Raven, Evert, and Eichhorn 1992).

Animals comprise all forms of multicellular heterotrophs, including terrestrial and aquatic species.

Environmental Classification

Organisms can be classified by oxygen concentration in their normal environment. Aqueous environments are characterized by their dissolved oxygen concentration, as follows (Killops and Killops 1993, p. 6):

Oxic	$> 0.5 \text{ mL L}^{-1}$
Suboxic	0.1 to 0.5 ml L^{-1}
Anoxic	$< 0.1 \text{ ml L}^{-1}$

Aerobes rely on oxygen for survival; *anaerobes* use metabolic processes that don't require oxygen. *Obligate aerobes* require an oxic environment. *Obligate anaerobes* are killed in oxygenated environments because they lack defenses against toxic compounds generated from oxygen (H_2O_2 , O_2^- , and OH). *Facultative*

Table 2-1 Classification of Microorganisms by Their Relationship to Oxygen

Group	Relationship to oxygen
Aerobes	
Obligate	Required for growth
Facultative anaerobe	More active in presence of, but not required
Microaerophilic	Required at low levels
Anaerobes	
Obligate	Harmful or lethal
Aerotolerant	Not required, no reaction

Source: Brock et al. 1994, Tbl. 9.6.

anaerobes use alternative metabolic processes that function with or without oxygen. These and related terms are summarized in Table 2-1. Prokaryotes, or bacteria, include aerobes and anaerobes. Most eukaryotes are obligate aerobes.

PRODUCTION AND CONSUMPTION OF ORGANIC MATTER

An organism's source of carbon defines its relationship to other members of its biological community. Feeding relationships are described by a food web, as shown in Figure 2-2. The food web includes assimilatory and dissimilatory food chains. The assimilatory food chain is relevant to generation of a food source for bacteria. The dissimilatory food chain is relevant to bacterial generation of gases.

The overall trend in the assimilatory food chain is to generate and maintain organic compounds. The base of the assimilatory chain is formed by the *primary producers*, autotrophs that generate organic compounds from inorganic nutrients. Most primary producers are phototrophs. Primary and secondary feeders in the assimilatory chain are heterotrophs, incapable of forming organic compounds from inorganic nutrients. They feed on the primary producers or other feeders. In terrestrial environments, heterotrophs make small contribution to total biomass and can be ignored. In aquatic environments, primary feeders make up a major portion of total biomass, due to their thorough grazing on the primary producers; secondary feeders can be ignored.

The overall trend in the dissimilatory food chain is to break down complex organic compounds into inorganic matter, a process called *mineralization*. Depolymerizers occupy the head of the dissimilatory chain; they secrete enzymes that break down large carbon compounds into smaller components that the organism can absorb. Primary and secondary decomposers consume monomers released by depolymerizers or other decomposers (Ehrlich 1985). Some species

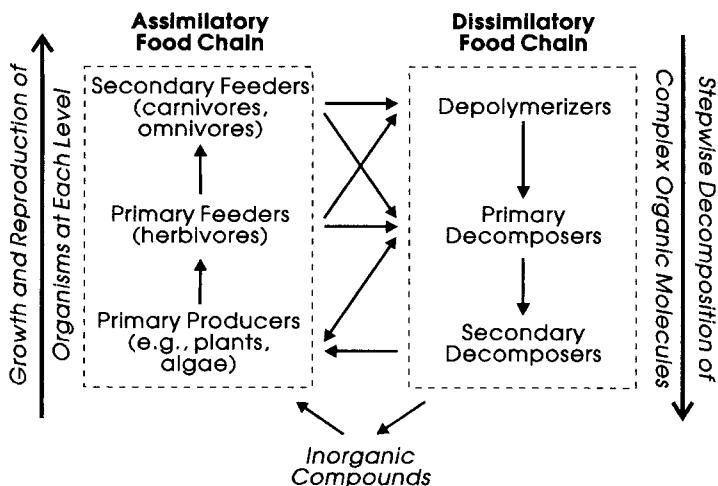


Figure 2-2. Generalized food web, depicting feeding relationships among organisms in a community. Main line relationships form a food chain. Dissimilatory chain is populated by bacteria and fungi. Arrows indicate flow of nutrients. (Adapted from Ehrlich 1985.)

of aerobic organisms are capable of completely mineralizing complex organic compounds. Anaerobic bacteria, the only active occupants of anoxic environments, lack the metabolic capability to mineralize all forms of organic compounds. In this text, members of the dissimilatory food chain will be collectively referred to as *decomposers*.

CHEMICAL COMPOSITION OF ORGANIC MATTER

There are more than 10 million known kinds of organic molecules. All fall within a small number of groups broadly characterized by molecular form or chemical characteristics. Molecular groups of geochemical interest include carbohydrates, proteins, lipids, and lignin. The first three groups are found in all living organisms. Lignin is unique to terrestrial plants. Elemental compositions of these groups are shown in Table 2-2. Elemental composition influences the susceptibility to bacterial decomposition and the makeup of thermal decomposition products. Organic compounds that perform structural or protective functions are resistant to bacterial decomposition and are more likely to be incorporated into sediments.

Carbohydrates are the most abundant molecular group. They include sugars, such as glucose, and their polymers. Cellulose, hemicellulose, and chitin are carbohydrates that perform structural and protective functions; they can be slowly degraded by a limited group of organisms. Starch is the principal form of energy

Table 2-2 Average Elemental Compositions of Geochemically Important Organic Molecular Groups

Molecular group	C	O	H	N	S
Carbohydrates	44	50	6		
Proteins	53	22	7	17	1
Lipids	76	12	12		
Lignin	63	32	5	0.3	0.1

Composition in weight percent.

Source: Adapted from Hunt 1996, Tbl. 4-1. © 1996 by W. H. Freeman.

storage in plants, algae, and some bacteria and is readily decomposed. Carbohydrates compose 30% to 50% of vascular plant tissue and up to 40% of diatoms and dinoflagellates (dry weight; Killops and Killops 1993, p. 61).

Proteins are made up of amino acid molecules linked together in long chains. Proteins catalyze biological reactions, contribute structural elements to cell walls, store nutrients, serve as bacterial toxins, and perform a variety of other functions. Proteins compose 5% of vascular plants and 25% to 50% of diatoms and dinoflagellates. Proteins are the most easily decomposed of the molecular groups.

Lipids are defined on the basis of solubility rather than molecular structure, encompassing a variety of compounds including fats, oils, and waxes. They are soluble in organic solvents, such as toluene. Lipids protect terrestrial plants from desiccation and microbial infection by forming the waxy coatings (cuticles) on leaves, stems and roots; they form insecticides, antibiotics, and resins; and they form the coverings of spores and pollen. In various organisms, lipids function in pigments important in photosynthesis, as energy reserves in the form of oils, and as structural components of cell walls. Lipids compose 5% to 25% of diatoms and dinoflagellates; their overall concentration in higher plants is relatively low. Lipids are resistant to bacterial decomposition. Algal lipids are a major precursor of petroleum, and plant lipids are a precursor of humic coal.

Lignin is formed from phenolic alcohols and is found only in vascular plants. It forms an integral part of the cell wall structure of woody tissue, performing both a structural and a protective function. Lignin composes 15% to 25% of vascular plants, most of the balance of wood that is not cellulose. Lignin is readily decomposed by fungi and by aerobic bacteria (Zeikus 1981). It is almost completely resistant to anaerobic bacteria. Lignin is a major precursor of humic coal.

INCORPORATION OF ORGANIC MATTER INTO SEDIMENTS

Organic matter incorporated into sediments becomes a potential source of bacterial and thermogenic gas. On a global scale, environmental conditions strongly disfavor survival of organic matter beyond about the first meter of the sediment surface. Nearly all is mineralized at the soil surface, in the water column, and in upper aquatic sediments. Aerobic organisms can completely mineralize organic matter; it can be incorporated into sediments only if it reaches an anoxic environment.

Aerobic organisms generate anoxic conditions in sediment pore space and quiescent waters where their biochemical oxygen demand exceeds the oxygen supply. Oxygen can be resupplied by bulk flow of air or oxic water into the environment or by diffusion. But diffusion is a very slow process, especially through water. Organic-rich sediments or bottom waters isolated from circulating water turn anoxic quickly.

Incorporation of organic matter into sediments depends on a number of factors. Prominent among these are rate of primary production, rate of sedimentation, and point of onset of anoxic conditions in the sedimentation zone (Arthur and Sageman 1994; Canfield 1994). These factors are inextricably related. A high rate of primary production creates a high biochemical oxygen demand, promoting anoxic conditions. Sedimentation isolates organic matter from air or oxygenated water. A high sedimentation rate reduces residence time at the sediment surface and exposure to aerobic decomposition. Primary production can contribute to rate of sedimentation, as in peat-forming environments where organic matter is the principal sedimentous material.

Organic Matter in Terrestrial Sediments

Terrestrial environments are very unfavorable to incorporation of organic matter into sediments. Air and moisture promote rapid mineralization. Organic-rich terrestrial sediments are generally characterized by high water table and rapid burial; they include fluvial sediments, mires, organics incorporated into glacial drift, and landfills. The primary producers of organic matter are plants. The most important decomposers are aerobic and anaerobic bacteria, and fungi. Organic compounds most likely to be incorporated into terrestrial sediments are carbohydrates, lipids, and lignin (Barnes, Barnes, and Bustin 1990).

Climate plays a role in preservation of organic matter because of its influence on the metabolic activity of decomposers. Primary production in temperate climates is lower than in tropical climates, but because bacterial activity is seasonally limited in temperate climates the amount of organic matter preserved in sediments is greater.

Organic Matter in Aquatic Sediments

Freshwater and marine aquatic environments are far more favorable for incorporation of organic matter into sediments than terrestrial environments, due to a comparatively more rapid onset of anoxic conditions in the sedimentation zone (Tissot and Welte 1984, p. 21). Most of the biomass in aquatic environments is made up of phytoplankton and zooplankton, small organisms that live in surface waters and drift with the current. Phytoplankton include unicellular algae and cyanobacteria. Zooplankton include protozoa and small aquatic animals. The most important decomposers are aerobic and anaerobic bacteria.

Unicellular algae are the primary producers of organic matter in oxic waters; anaerobic phototrophic bacteria are primary producers in shallow anoxic waters. Phototrophic activity takes place within the surface layer of water penetrated by light, the limnetic zone in lakes and the euphotic zone in the oceans. Benthic algae can be important primary producers in water depths of less than 50 meters (Tissot and Welte 1984, p. 22). Benthic algae are multicellular algae attached to bottom sediments. Zooplankton and other herbivores consume 40% to 95% of primary production in aquatic environments (Hobbie and Fletcher 1988) and compose up to 50% of the biomass in marine environments (Killops and Killops 1993, Fig. 1.1). Consequently, they contribute a large proportion of detrital organic matter to sediments. Aquatic organisms are most likely to contribute carbohydrates, proteins, and lipids to sediments (Barnes, Barnes, and Bustin 1990).

Rivers contribute partially decomposed plant matter to lakes, deltas, estuaries, and coastal marine sediments (Chester 1990, p. 469). Structural and protective compounds in plant matter make it more resistant to decomposition than aquatic organic matter. The importance of this terrestrial contribution depends on its relation to aquatic primary production and proximity to the river mouth. Terrestrial organic matter may be preponderant in some aquatic sediments.

Incorporation of organic matter in aquatic sediments is favored by high primary production, quiescent water, concurrent deposition of a limited amount of clay and silt, and anoxic conditions in the water column and at the sediment surface. Quiescent water promotes anoxic conditions and allows particulate organic matter to settle. Concurrent deposition of clay and silt particles seals sediment pores from the water above, promoting anoxic conditions. Organic matter adsorbs to mineral surfaces, especially clay, which provides some protection from bacteria.

Benthic feeders populate aquatic sediments overlain by oxic bottom waters. They cannot survive anoxic conditions. Benthic feeders consume particulate organic matter that reaches the sediment surface. They also disturb the sediment surface by burrowing and moving about, oxygenating the sediments and aiding

mineralization of organic matter by aerobic bacteria. Bioturbation by benthic feeders tends to destroy laminar structure in sediments. Anoxic bottom waters preclude benthic activity, favoring preservation of organic matter.

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3

Bacterial Gases

THE NATURE OF BACTERIAL GASES

The near-surface underground is a diverse habitat for many species of bacteria. Among the mass of rock, soil, and water underground, bacteria may seem immaterial, but over time they can alter their environment in ways that affect underground construction. Bacteria underground have no direct access to the energy of the sun; most acquire chemical energy by decomposing organic compounds incorporated in sediments. Among the waste products of bacterial decomposition are potentially hazardous amounts of methane, hydrogen sulfide, and carbon dioxide.

Individual species of bacteria are distinguished in part by their biochemical means of energy acquisition. Metabolic diversity among species enables bacteria as a group to exploit organic compounds within a wide variety of geologic environments. Geochemical characteristics of an environment determine what processes of energy acquisition can be employed, the species of bacteria that the environment can support, the extent to which organic matter can be utilized as an energy source, and what gases can be generated. Groundwater flow provides nutrients that bacteria cannot obtain from sediments. Thus, there is a relationship between groundwater flow systems and the character and distribution of bacterial communities.

Bacterial gases are generally associated with organic-rich Holocene sedi-

ments, and man-made environments such as landfills and sewers. But these gases can also occur in much older sediments. Anaerobic bacterial communities can persist in organic-rich sediments for thousands of years. Some sediments millions of years old retain bacterial methane generated early in the sediment's history. Aerobic bacteria can decompose organic matter hundreds of millions of years old that has been recently exposed to oxygenated groundwater. Their waste products provide substrates for anaerobic bacteria that become active after the aerobes have depleted available oxygen. This chapter describes geochemical constraints on bacterial decomposition of organic matter, and gas generation. Geologic factors affecting bacterial gas generation are described in more detail in Chapter 8.

ENERGY AND LIVING ORGANISMS

All living organisms, including bacteria, are highly ordered, complex molecular systems, far out of chemical equilibrium with their physical environment. They maintain this chemically unstable state through their metabolic processes. Cellular metabolism demands an almost continuous supply of energy, either light energy from the sun or chemical energy from the environment. Bacteria employ oxidation-reduction reactions as a means of acquiring energy. An introduction to biological processes of energy acquisition helps explain how bacterial gases are generated and why they occur where they do.

Energy Transfer via Oxidation–Reduction Reactions

In an oxidation-reduction reaction between chemical elements or compounds, covalent bonds are reconfigured and new products are formed. Transfer of bonding electrons among reactants involves an energy exchange. An *endergonic reaction* requires energy to force an overall electron shift toward higher-energy orbits. An *exergonic reaction* releases energy in an overall electron shift toward lower-energy orbits. Bacteria acquire energy by mediating exergonic reactions. The energy exchange is more important to the organism than the reaction products.

Elements of a covalently bonded compound share bonding electrons to establish a stable configuration of electrons in their outer orbitals. But unlike elements do not share bonding electrons equally. *Electronegativity* is a measure of the tendency of an element to acquire bonding electrons. The more electronegative element acquires dominant control of the shared electrons, considered an electron “gain.” Electron gain is called *reduction*; the electron acceptor is *reduced*. The less electronegative element suffers an electron “loss.” Electron loss is called *oxidation*; the electron donor is *oxidized*. A balance between electron gain and loss is maintained among reactants. In exergonic reactions the electron donor is considered the energy source, and the amount of energy released is proportional to the oxidizing power of the electron acceptor.

Table 3-1 Electronegativities of Organic Constituents

Element	Electronegativity
Oxygen	3.44
Nitrogen	3.04
Sulfur	2.58
Carbon	2.55
Hydrogen	2.20
Phosphorus	2.19

Source: Lide 1996.

The measure of electronegativity can range on a scale from 0 to 4. Electronegativities of the major constituent elements of organic matter are shown in Table 3-1. Oxygen has the highest electronegativity (3.44) and is by far the most common electron acceptor in biologic oxidation-reduction reactions. Oxygen has two unpaired electrons in its outer orbitals and tends to fill these orbitals by acquiring two bonding electrons. Carbon has an intermediate electronegativity (2.55). Elemental carbon has four unpaired electrons in its outer orbitals, which hold a stable configuration of eight paired electrons. Carbon can form four covalent bonds, by acquiring electrons from less electronegative elements or by losing electrons to more electronegative elements.

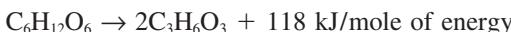
Bacteria mediate exergonic oxidation-reduction reactions by providing electron carrier molecules to serve as reaction intermediaries. These carriers accept electrons from the primary electron donor, then transfer them to the terminal electron acceptor (Brock et al. 1994, p. 97). Bacteria conserve energy released in the exchange, in the form of high-energy chemical bonds in intracellular organic compounds. If not biologically mediated, exergonic reactions would occur much more slowly, some would not go forward, and energy released would be lost as heat.

Forms of Oxidation-Reduction Reactions

Bacteria as a group acquire energy from a wide variety of geologic environments via several oxidation–reduction reaction pathways. Many species of bacteria employ more than one pathway to adapt to environmental variables. Oxidation–reduction reactions employed by bacteria underground, which have no access to sunlight, are described below. Biologically mediated oxidation–reduction reactions involve numerous steps and intermediate reaction products. Only summary reactions are shown in the following descriptions.

Fermentation

Fermentations are oxidation–reduction reactions in which a single organic compound serves as the electron donor and provides the electron acceptor. Carbon in the reactant is partially oxidized to form an intermediate product, which is then partially reduced to form a final product. Fermentation is mediated by a small minority of anaerobic bacteria and yields a small amount of energy. An example is the reduction of glucose to lactic acid, mediated by lactic acid bacteria (Brock et al. 1994, p. 99–100):



A second example is the reduction of methanol to methane, a decomposition process mediated by the methanogens group of bacteria (Brock et al. 1994, p. 826):



In this reaction, methanol carbons are reduced to form methane, and oxidized to form carbon dioxide.

Aerobic Respiration

Respiration reactions are a form of oxidation-reduction in which separate compounds serve as electron donor and electron acceptor. Electron donors (the energy source) are most often organic but may be inorganic. Electron acceptors may be organic or inorganic.

Aerobic respiration is defined as the use of molecular oxygen (O_2) as the terminal electron acceptor. Aerobic respiration is employed by aerobic and facultative anaerobic bacteria, and it yields the greatest amount of energy of biologically mediated oxidation–reduction reactions. It is the only biologic means of completely converting complex organic compounds to carbon dioxide, water, and minerals. An example is the oxidation of glucose (Brock et al. 1994, p. 109):



In this reaction, glucose carbon is oxidized to carbon dioxide, and oxygen is reduced to water. Note the difference in energy yield between this reaction and fermentation of glucose.

Anaerobic Respiration

Anaerobic respiration is defined as the use of oxidized inorganic or organic compounds as the terminal electron acceptor. Anaerobic respiration is employed by facultative and obligate anaerobes; it yields less energy than aerobic respiration but more than fermentation. An example of anaerobic respiration is the formation

of methane from carbon dioxide and hydrogen, a reaction mediated by the methanogens (Brock et al. 1994, p. 832):



Hydrogen, the energy source in this reaction, is oxidized to water. Carbon, the electron acceptor, is reduced to methane.

CHARACTERISTICS OF BACTERIA

Prokaryotes, or bacteria, feature a rigid cell wall surrounding a cytoplasmic membrane. The cell wall may be shaped as a sphere or ovoid, cylinder (or rod), curved rod, or coiled rod. The cell wall is porous, which allows transfer of dissolved nutrients to, and waste products from, the cytoplasmic membrane. The cytoplasmic membrane is the site of electron transport in exergonic oxidation–reduction reactions. All bacteria require liquid water for metabolism and reproduction, and so may be considered aquatic organisms.

Bacteria have inhabited the earth for 3.5 billion years, and over this time have adapted well to life underground. Their shape and small size gives them a large surface-area to volume ratio, which enables them to interact efficiently with their geochemical environment (Nealson and Stahl 1997). They lack the complex cell functions of eukaryotes, which enables bacteria to survive periods of environmental instability and to inhabit extreme environments. Most species of bacteria are metabolically diverse, utilizing numerous substrates or multiple oxidation–reduction pathways. Some species of bacteria exude extracellular enzymes to break down organic macromolecules into smaller units that can penetrate cell wall pores. Many species of bacteria are motile, employing flagella attached to the cell wall.

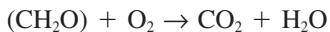
BACTERIAL DECOMPOSITION OF ORGANIC MATTER

Organic matter is the main source of energy for the vast majority bacteria inhabiting the underground. Diverse communities of bacteria break down organic compounds in a stepwise progression. Large organic molecules are broken into progressively smaller and simpler organic compounds and mineral matter. Compounds that are least resistant to bacteria, or labile, are most readily consumed. Decomposition rate declines as the elimination of labile compounds renders organic matter increasingly resistant, or refractory, to resident bacteria. While a small portion of the organic matter consumed is incorporated into bacterial cell structure, most is used as an energy source.

Decomposition Process

In mediating energy-gathering oxidation-reduction reactions, bacteria employ available electron acceptors in the environment. Electron acceptors are generally not used concurrently but in decreasing order of their oxidizing power. Species of bacteria that can use the most powerful electron acceptors available have a competitive advantage, and they effectively suppress other species that rely on less powerful electron acceptors. Important acceptors, in order of oxidizing power, are $O_2 > NO_3^- > Mn^{4+} > Fe^{3+} > SO_4^{2-} > CO_2$ (Capone and Kiene 1988). As an electron acceptor is depleted, the prevailing metabolic pathway shifts to the next most powerful acceptor available. The terminal niche in the decomposition process in a particular environment is occupied by species that can utilize the most powerful electron acceptor available. An oxidation-reduction sequence in a confined aquifer containing organic matter is shown in Figure 3-1. Each reaction zone in the succession may span distances from millimeters to kilometers, a function of the availability and rate of depletion of electron acceptors (Kieft and Phelps 1997). Electron acceptors determine what terminal decomposition products will be generated, among them carbon dioxide, hydrogen sulfide, and methane.

Most detrital organic matter is subjected to aerobic respiration, at least in the early stages of decomposition. Aerobic respiration is represented by the generalized reaction:



where (CH_2O) represents an organic substrate. Aerobes can completely mineral-

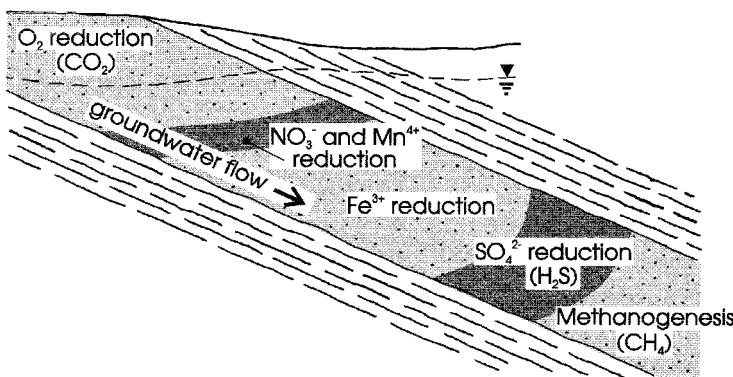
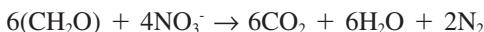


Figure 3-1. Conceptual distribution of terminal oxidation-reduction reactions in a confined aquifer. Potentially hazardous gases are shown in parentheses. (Adapted from Lovley and Chapelle 1995.)

ize complex organic compounds, utilizing the high oxidizing power of oxygen. Carbon is oxidized to carbon dioxide (CO_2), nitrogen to nitrate (NO_3^-), sulfur to sulfate (SO_4^{2-}), and phosphorus to phosphate (PO_4^{3-}) (Mechalas 1974).

Aerobes may consume all available oxygen, causing the environment to become anoxic. Anaerobic bacteria continue the decomposition process, utilizing less powerful electron acceptors. Anaerobes are limited in the substrates they are capable of breaking down and in the extent to which they can mineralize them. Various species develop communal relationships that promote efficient utilization of substrate resources, with residues of one group providing a resource for another group. Anaerobic decomposition products, such as methane, hydrogen sulfide, and refractory organic compounds, retain some of the energy originally conserved in organic matter (Widdel 1988).

Anaerobic respiration begins with the use of nitrates as an electron acceptor, as in the generalized reaction (Foth 1990, p. 196):

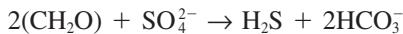


The process generally occurs along the oxic/anoxic interface. It is called *denitrification* because the gaseous nitrogen products generated in topsoil tend to escape to the atmosphere. The reaction is mediated by denitrifier bacteria, typically facultative anaerobes. Human and animal waste and nitrogen fertilizers are principal sources of nitrates; aerobic decomposition of organic matter is a lesser source (Chapelle 1993, p. 247–251). Nitrates are very limited in most pristine continental environments, making denitrification a relatively minor factor in the near-surface underground. The process has not been shown to generate hazardous amounts of gas.

Denitrification is followed by the anaerobic respiration processes of *manganese reduction* and *iron reduction*. Manganese reduction (Mn^{4+} to Mn^{2+}) is a minor factor in organic matter decomposition because manganese is a minor constituent of crustal rocks, and the manganese ion Mn^{4+} is relatively insoluble in water. The reduction of ferric iron to ferrous iron (Fe^{3+} to Fe^{2+}) can be significant in organic matter decomposition. Iron is a common but minor constituent of most soils and rocks, except in relatively pure biogenic carbonate and silicate rocks, which contain very little iron. Iron reduction is limited by the low solubility of ferric iron. Neither process has been shown to generate hazardous amounts of gas.

Fermentation plays an important role in subsequent anaerobic decomposition processes. Fermentative bacteria break down biopolymers into acetate, hydrogen, and short-chain fatty acids, providing substrates for other anaerobes that would otherwise have no access to the energy retained in biopolymers. Lignin and hydrocarbons are almost completely refractory to fermentative bacteria, so for the most part they remain unavailable to other anaerobes (Brock et al. 1994, p. 610).

Iron reduction is followed by *sulfate reduction*, mediated by the sulfate-reducing bacteria. Sulfate reduction is represented by the generalized reaction (Berner 1985):



Sulfate is readily available in marine waters and upper marine sediments. It is very limited in some, but not all, continental environments.

Sulfate reduction is followed by *methanogenesis*, mediated by the methanogens group of bacteria. Methanogens utilize both fermentation and anaerobic respiration pathways. Methanogenesis is the predominant terminal decomposition process in most anoxic continental environments, where sulfate concentrations are low (Capone and Kiene 1988).

Bacterial Gas Generation

Carbon dioxide, hydrogen sulfide, and methane are terminal products of organic matter decomposition. In natural environments these gases often occur together in gaseous phase or solution phase mixtures, though the mixtures are usually dominated by one gas.

Carbon Dioxide Generation

Carbon dioxide is generated by a wide variety of bacteria. It is a principal terminal decomposition product of aerobic respiration and a secondary product of fermentation and anaerobic respiration. Up to 50% of carbon dioxide present in the root zone (approximately the top meter of terrestrial sediments) may be generated by root respiration (Amundson and Davidson 1990), but that source is ignored here.

Carbon dioxide is the major hazardous bacterial gas found in unsaturated oxic environments. In anoxic environments it is a common constituent of gas mixtures dominated by hydrogen sulfide or methane. Carbon dioxide generation in oxic and anoxic aqueous environments from a laboratory incubation of sediment is shown in Figure 3-2. Ground conditions are described in the figure. In this example, the rate and cumulative production of carbon dioxide under oxic conditions is three times that for anoxic conditions.

Aerobic bacteria in the unsaturated zone are sustained by oxygenated infiltrating water. Carbon dioxide generation by aerobic respiration is concomitantly related to oxygen deficiency in gas-filled pore space. The ratio of moles of oxygen consumed to moles of carbon dioxide generated depends on the chemistry of the organic carbon substrate. Data from a field study near a lignite mine, shown in Figure 3-3, indicate a ratio of about 1 mol O₂ to 1 mol CO₂. At a site contaminated with spilled gasoline, this ratio was about 8 mol O₂ to 5 mol CO₂ (McLinn and Rehm 1997). Gaseous carbon dioxide concentrations in unsaturated sediments may rise to as high as about 19% (vol), at which point oxygen depletion causes

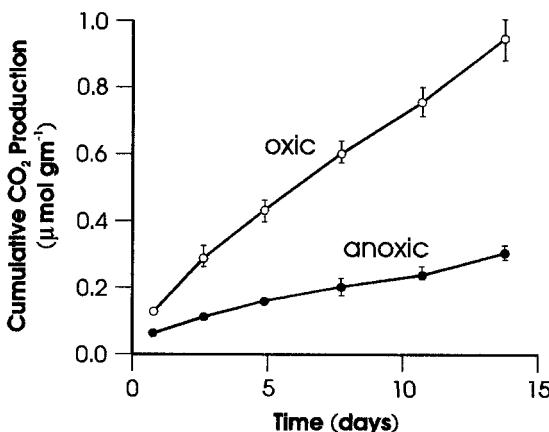


Figure 3-2. Bacterial CO₂ production from samples of sediment incubated in laboratory under oxic and anoxic conditions. Site description: Parris Island, South Carolina, Atlantic Coastal Plain, U.S.; 16 m below ground surface; semi-confined aquifer; water table near ground surface. Sample description: Miocene; sandy silt containing 0.1–1.0 dry wt % organic matter. Site groundwater conditions: dissolved O₂ content 0–5 mg L⁻¹; 20°C; pH 6.70. Predominant bacterial population: facultative anaerobes. Laboratory incubation does not represent production rates in place. Laboratory CH₄ production zero to two orders of magnitude less than CO₂ production. (From Chapelle et al. 1988. © 1977 Geological Society of America, Boulder, Colorado.)

the environment to become anoxic and aerobic respiration to cease (Chapelle 1993, p. 181; Drake 1980). Atmospheric nitrogen generally makes up most of the balance of gas mixtures in the unsaturated zone.

Carbon dioxide concentrations of up to 95% (vol) have been reported in the unsaturated zone in landfills (Matsufuji et al. 1993). Following a period of oxic conditions lasting days or months, much carbon dioxide is generated during the initial period of anoxic decomposition (Farquhar and Rovers 1973), but this is quickly superseded by methanogenesis.

The amount of carbon dioxide that aerobes can generate in saturated oxic environments is limited by the solubility of oxygen. Aerobes consume dissolved oxygen and turn the environment anoxic before they can generate carbon dioxide much in excess of potentially hazardous concentrations. (Potentially hazardous concentrations of gas in gaseous phase and in solution phase are defined in Chapter 7.) In addition, carbon dioxide solubility in water is about 30 times greater than oxygen solubility. Bacterial carbon dioxide generated in oxic waters cannot reach saturation concentration; that is, it cannot reach concentrations high enough to form bubbles of CO₂.

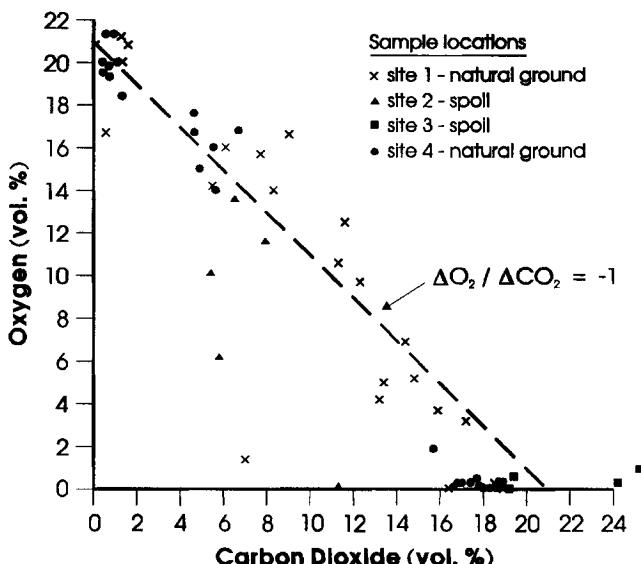


Figure 3-3. Gas in pore space in unsaturated ground above and in a stratum of lignite, and in lignite-rich spoil. All sites near a lignite mine in North Dakota, western Great Plains, U.S. Multiple sampling depths at each site, from 3 to 14 m. Line represents a 1:1 mole ratio of oxygen consumed to bacterial carbon dioxide generated (not a best linear fit). (Data from Haas et al. 1983 and Thorstenson et al. 1983.)

Hydrogen Sulfide Generation

Hydrogen sulfide is generated by sulfate-reducing bacteria, a group that uses sulfate (SO_4^{2-}) as an electron acceptor. Most sulfate reducers are members of the Bacteria, though the group includes hyperthermophiles (temperature optima above 80°C), which are members of the Archaea (Brock et al. 1994, p. 749–751, 839). They are obligate anaerobes, though they may tolerate oxygen for a matter of hours or days (Widdel 1988). Sulfate reducers are widely distributed in anoxic terrestrial, freshwater, and marine environments. They prefer neutral or slightly alkaline pH conditions, but as a group they tolerate a wide range of conditions from highly acidic to highly alkaline.

Sulfate reducers are the terminal decomposers in anoxic sulfate-rich environments. As a group they oxidize a variety of organic substrates including organic acids, fatty acids, alcohols, and hydrogen. Sulfate reduction using acetate (a fatty acid) as a substrate is represented by the summary equation:



Sulfate is abundant in seawater, and sulfate reduction is the principal terminal anaerobic decomposition process in upper marine sediments. The molar concentration of sulfate in seawater is considerably higher than that of oxygen, enabling sulfate to diffuse much deeper into the sediment than oxygen (Jørgensen 1983). Progressing down through the sediment column, sulfate reduction begins where oxygen is depleted from pore water and ends where sulfates are depleted. The depth of sulfate depletion depends on the rate of decomposition relative to sulfate flux from the water column; it may extend to a few centimeters in organic-rich coastal sediments, to 200 meters below the sediment surface beneath less productive areas of the ocean (Claypool and Kvenvolden 1983; Jørgensen 1983). In stagnant marine waters in basins and fiords, the top of the sulfate reduction zone may extend into the water column (Widdel 1988). Sulfate ion concentrations in seawater are about 2700 mg L^{-1} . Sulfate concentrations in excess of 290 mg L^{-1} are generally considered to be nonlimiting to sulfate reduction in marine environments (Capone and Kiene 1988).

Sulfate reduction in continental environments is limited by sulfate concentration, which in most fresh waters is about 10 to 20 mg L^{-1} (Capone and Kiene 1988). In a model study of a freshwater lake containing a sulfate ion concentration of 10 mg L^{-1} and a relatively small amount of organic matter, sulfate reduction ceased when the sulfate concentration declined to about 3 mg L^{-1} ; this occurred within a centimeter or two of the sediment surface (Lovley and Klug 1986). Similar levels of sulfate depletion have been observed in groundwaters in continental environments (Hem 1985, p. 116).

In a few continental environments, sulfates are not limiting. Relatively high sulfate concentrations can occur in groundwaters flowing through soils or rocks containing gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4). The sulfate saturation concentration in water in gypsiferous rocks is about 1400 mg L^{-1} , at 10°C . Higher sulfate concentrations can occur in sodium and magnesium sulfate waters (Matthes 1982; p. 254). High sulfate concentrations are also generated by weathering of pyrite and reduced forms of organic sulfur (Van Stempvoort et al. 1994).

Sulfate reduction occurs in some oil field waters, particularly where the oil field has been flooded with seawater to increase petroleum production. Water injection introduces bacteria to the reservoir (Cord-Ruwisch, Kleinitz, and Widdel 1987). Sulfate reducers in oil fields appear to survive mainly on substrates made available by aerobic bacteria, though sulfate reduction directly on crude oil has been demonstrated (Rueter et al., 1994). Hydrogen sulfide concentrations of up to 680 mg L^{-1} were reported in a water-flooded oil field in Kazakhstan (Nazina et al. 1995). In fields that have not been water-flooded but are in contact with oxygenated groundwaters, sulfate reducers appear most active along the oxic/anoxic boundary.

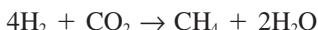
Sulfate reducers cannot generate hydrogen sulfide in concentrations high enough to form bubbles of H_2S in saturated sediments. Where sulfate reduction

is not limited by the availability of organic matter or sulfate, it is constrained by hydrogen sulfide toxicity on the bacterial community. Sulfate reducers cannot tolerate hydrogen sulfide concentrations in excess of about 700 to 1700 mg L⁻¹ (Jørgensen 1983). The saturation concentration of hydrogen sulfide in water is about 3900 mg L⁻¹ at 20°C and 1 atm. In natural waters, hydrogen sulfide concentrations of 100 to 400 mg L⁻¹ are considered high (Hem 1985, p. 117). (A concentration of 4 mg L⁻¹ in water can equilibrate to a fatally toxic concentration [1000 ppmv] in air, as described in Chapter 7.)

Methane Generation

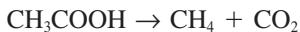
Methane is generated by a diverse group of Archaea known collectively as the methanogens. All are obligate anaerobes. They can survive brief exposure (a span of hours) to oxic conditions but are less tolerant of oxygen than the sulfate reducers (Zinder 1993). Most methanogens prefer moderate-temperature environments, though extremely thermophilic species have been described (Whitman, Bowen, and Boone 1992). Methanogenesis is limited below temperatures of 15°C, though it can occur at temperatures near 4°C. Most methanogens prefer pH conditions between about 6 and 8, though they have been found in bogs where the pH is near 4, and in soda lakes where the pH is about 9 (Whitman 1985; Zinder 1993).

Methanogenesis is the principal terminal anaerobic decomposition process in continental environments. It is also important in marine sediments below the sulfate reduction zone. Methanogens cannot separate carbon-carbon bonds. They are limited to a few simple substrates including hydrogen, acetate, and some C₁ compounds. Two major methanogenic pathways are acetate fermentation and carbon dioxide reduction (Whiticar, Faber, and Schoell 1986). Nearly all methanogens are capable of the carbon dioxide reduction pathway:



Carbon dioxide reduction is important in decomposition of older organic matter, as may be incorporated into glacial deposits (Coleman, Liu, and Riley 1988), and in marine sediments depleted of sulfates (Capone and Kiene 1988).

Acetate fermentation is represented by the summary equation:



Acetate fermentation tends to predominate in the decomposition of younger, labile organic matter. It accounts for about 70% of the methane generated in terrestrial and freshwater environments and in anaerobic sewage digestion (Mah et al. 1977).

Methanogens can generate methane in excess of the solubility of the gas in water, at which point bubbles of nearly 100% CH₄ form. Sediments containing more than 0.2% total organic carbon (TOC) can generate a gaseous phase (Clay-

ton 1992). Most methane generated near the sediment surface is lost to the atmosphere by ebullition.

Methanogens are at least partly responsible for generation of small amounts of higher hydrocarbon gases, such as ethane (Oremland et al. 1988; Kim and Douglas 1972). Higher hydrocarbons constitute on the order of 10 ppm or less of total bacterial hydrocarbon production.

BACTERIAL COMMUNITIES UNDERGROUND

Distribution of Bacteria

Microorganisms inhabiting underground environments comprise bacteria almost exclusively. Eukaryotes, such as protozoa, compose a small minority but are generally excluded by their large size, limited metabolic capabilities, and oxygen requirement (Nealson and Stahl 1997). Viable bacteria have been recovered from depths of 2.7 kilometers below ground surface (Boone et al. 1995). How they come to inhabit deep regions is not clear. Bacteria inhabiting pore spaces in sedimentary soil and rock may be survivors or descendants of original surface colonies, or they may have been carried underground by groundwater, or introduced through the construction of wells (Riser-Roberts 1992, p. 51).

Bacterial counts do not decrease uniformly with depth, as a general rule. In terrestrial soils they may decrease from the surface to the C horizon by several orders of magnitude, but below the C horizon, bacterial counts vary with ground conditions (Madsen and Ghiorse 1993). Porosity and permeability are factors in bacterial distribution. The size of bacterial cells is on the order of 1 micrometer (μm), and their survival forms in soils are somewhat smaller (Ghiorse and Wilson 1988; Roszak and Colwell 1987). All particulate soils and some porous rocks can accommodate bacteria. Counts in soils show an inverse relationship to clay content (Konopka and Turco 1991; Suflita et al. 1990).

Most species of bacteria require organic matter to survive but are not limited to organic-rich sediments. The underground is generally an *oligotrophic* (low-nutrient) environment, exhibiting dissolved organic carbon (DOC) concentrations less than 2 mg L^{-1} (Thurman 1985, p. 14). *Oligotrophs* are bacteria that can grow and multiply under low-nutrient conditions. Other forms of bacteria survive oligotrophic periods by entering a dormant state that, evidence suggests, they can maintain for millions of years (Roszak and Colwell 1987; Amy 1997). Groundwaters associated with organic-rich sediment such as peat, coal, and organic shale, and oil-field waters, may exhibit DOC concentrations from ten to hundreds of milligrams per liter or more. Organic carbon concentration is not necessarily a factor in bacterial population density, as some organic matter is refractory to anaerobes (Sinclair et al. 1990).

Bacteria tend to attach to clay particles or dissolved or particulate organic

matter, to form communities of a few to hundreds of cells. In oligotrophic sediments the majority of bacteria are attached to sediments. In sediments rich in labile organic matter, there may be little difference in population density between the attached fraction and an unattached fraction in groundwater (Hazen et al. 1991). Communities of attached bacteria appear to be more diverse than those of unattached bacteria (Chapelle 1993, p. 158).

The metabolic activities of a bacterial community may alter its immediate environment (microenvironment) from its surroundings (macroenvironment). For example, facultative anaerobes in a community may consume all available oxygen, making the microenvironment anoxic. This creates suitable local conditions for obligate anaerobes, in a macroenvironment that may remain oxic. Microenvironments provide for stable, diverse populations of bacteria.

Bacterial Environments and Groundwater Flow

Microbial communities in the near-surface underground have access to oxygen and organic matter via infiltrating meteoric water. Nutrients not available from sediments can only be provided by flowing groundwater. There is a close relationship between groundwater geochemistry and bacterial metabolism. Because of this relationship, the concept of groundwater flow systems can be used to explain the distribution of bacterial macroenvironments (Chapelle 1993, pp. 174–207).

Groundwater flow occurs through both unsaturated and saturated ground. Flow in the saturated zone can be broadly divided into local, intermediate, and regional flow systems, as shown in Figure 3-4. The example depicts a homogeneous unconfined aquifer where flow is controlled by topography, but the concept can be applied to confined aquifers where flow is controlled by permeability. Connection to the surface is progressively more attenuated in each of the four flow zones (unsaturated > local > intermediate > regional). Each is characterized by a particular set of environmental conditions that affect the bacterial population the zone is likely to support, as summarized in Table 3-2.

The Unsaturated Zone

The unsaturated zone of terrestrial environments is closely connected to organic matter and oxygen at the ground surface. Meteoric water enters the unsaturated zone following moderate to heavy precipitation or snowmelt. Gases are freely exchanged between infiltrating water and open pore space. Gases also diffuse directly between the pore space and the atmosphere, but this means of exchange is of lesser importance. Conditions are generally oxic, due to gas exchange with oxygenated water periodically infiltrating from the surface.

The unsaturated zone tends to be the most biologically active of the four flow zones. Aerobic bacteria consume oxygen and generate carbon dioxide, caus-

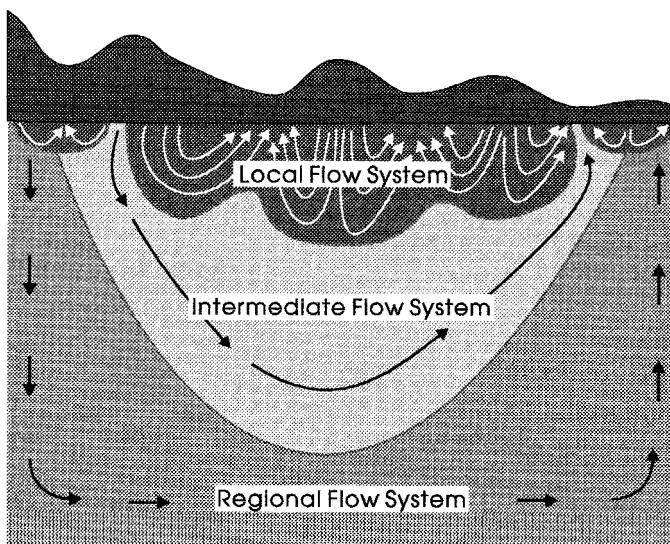


Figure 3-4. Groundwater flow systems in the saturated zone of an unconfined homogeneous drainage basin. (Adapted from Toth 1988.)

ing carbon dioxide concentrations to rise with depth. The level of bacterial activity strongly depends on the availability of water and organic matter. A study of unsaturated sediments in a high desert showed that bacterial activity was limited by a lack of organics; oxygen concentrations near atmospheric were found to a depth of 70 m (Colwell 1989).

Local Flow Systems

Groundwater flow within a local system is constrained within a recharge area on a topographic high and a discharge area in an adjacent topographic low. Local flow may penetrate hundreds of meters in an area of high relief, or a few tens of meters in an area of low relief. The depth of local flow may also be influenced by permeability. Local flow systems often correspond to shallow water table aquifers.

Local flow systems are closely connected to the surface and are strongly affected by precipitation. Groundwater charged with nutrients may be quickly transported into local flow systems, either directly from the surface or indirectly through the unsaturated zone. Bacterial activity may be aerobic or anaerobic. Oxic conditions may prevail in areas of frequent recharge and limited organic matter.

Table 3-2 Environmental Attributes of Groundwater Flow Zones

Zone	Connection to surface recharge	Groundwater flow rates	Oxygen status	Examples
Unsaturated Local flow system	Very close Close	50–500 m yr ⁻¹ 1–100 m yr ⁻¹	Generally oxic Oxic or anoxic	— Water table aquifer
Intermediate flow system	Limited	0.1–1 m yr ⁻¹	Generally anoxic	Confined aquifer
Regional flow system	Virtually non-existent	Almost stagnant	Anoxic	Deep basin, petroleum reservoir

Source: Adapted from Chapelle 1993, Tbl. 7.1, and Lovley and Chapelle 1995.

Intermediate Flow Systems

The recharge and discharge areas of an intermediate flow system are separated by one or more topographic highs. These systems often correspond to confined aquifers of moderate depth, generally less than 300 m.

Intermediate flow systems are considerably less connected to the surface than unsaturated and local flow systems. Recharge rates are generally much lower than for local flow systems. Intermediate flow systems are generally anoxic, and inorganic nutrients are often limiting. Bacterial communities rely primarily on organic matter that has been incorporated into sediments. The level of bacterial metabolism tends to be low, because organic matter buried with sediments tends to be refractory due to prior decomposition. Oxic conditions may prevail in systems that lack organic matter.

Regional Flow Systems

In a regional flow system, the recharge area occupies the water divide and the discharge area is located in the bottom of the regional basin. Flow paths are long, and flow rates are very low. Because of long residence times, the water may be highly mineralized. The depth of these systems is often greater than 300 m. Regional flow systems develop in sedimentary basins.

Regional flow systems are for practical purposes isolated from the surface, and anoxic. Where temperatures are below 100°C and organic matter is available, they may be inhabited by sulfate reducers and methanogens.

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4

Thermogenic Gases

THE NATURE OF THERMOGENIC GASES

Thermogenic gases are generated by abiogenic decomposition of organic matter in sediments, largely driven by geothermal heat associated with deep burial. Complex organic compounds are reconfigured into simpler gaseous and liquid products and solid residue. Products of abiogenic decomposition include coal, crude oil, methane and higher hydrocarbon gases, and carbon dioxide. Gaseous and liquid products may be expelled from organic-rich sediments into surrounding strata.

Though they may be generated at depths of a kilometer or more, thermogenic gases can reach the near-surface underground. Gases formed with coal or petroleum can migrate long distances, in gaseous phase or in solution in groundwater, to accumulate in near-surface deposits. Migrating crude oil carries gas in solution, which exsolves as oil approaches the surface. Coal or petroleum source rocks brought to the surface by erosion of overlying strata may retain gas. Small accumulations of thermogenic gas, of no commercial value, can be hazardous to construction in the near-surface underground.

This chapter describes the processes that form thermogenic gases. Expulsion of gases from source beds, and their subsequent migration, retention, and alteration underground are described in Chapter 6.

DIAGENESIS, CATAGENESIS, AND METAGENESIS

Organic matter held in subsiding sediments may be subjected to three stages of decomposition. These stages are known as *diagenesis*, *catagenesis*, and *metagenesis* (Tissot and Welte 1984, p. 69–73). (This sedimentology definition of diagenesis should not be confused with the mineralogy definition, which refers to changes in mineral matter.) These geochemical processes reduce complex organic compounds to simpler gases and liquids, and a more homogeneous and ordered solid residue. Each decomposition process is complex, but each has a dominant propensity. Diagenesis is a bacterially mediated elimination of energy-rich molecular bonds. Catagenesis is an abiogenic, heat-driven elimination of noncarbon and loosely held carbon elements. Metagenesis is a pressure-driven reconfiguration of remaining carbon. These processes are without distinct boundaries.

Diagenesis

Virtually all organic matter is subjected to the decomposition process of diagenesis. It occurs in the water column and within the upper few hundred meters of sediment, under low pressures and at temperatures generally less than 50°C. Aerobic bacteria are active in early diagenesis, and anaerobes become important when available oxygen in the sedimentary environment has been consumed. Bacteria decompose organic matter to acquire energy. They separate high-energy molecular bonds, then re-form the molecular pieces into simpler products held together by lower-energy bonds.

Bacteria eliminate practically all biomacromolecules in the upper few meters of sediment (Tissot and Welte 1984, p. 74). The first compounds to disappear are the most easily degraded. Carbohydrates, abundant in higher plants, are easily degraded, as are proteins. Compounds that perform a protective function, such as in plant resins, waxes, and spore casings, are resistant to microbial attack. Lipids are prominent among these resistant compounds. Lignin, an important component of terrestrial plants, is refractory to anaerobes, so is largely preserved where plant matter is quickly deposited in an anoxic environment. As diagenesis progresses, compounds resistant to bacterial decomposition, which may have entered the sedimentary record as minor constituents, comprise an increasingly important portion of remaining organic matter. Bacterial waste products include carbon dioxide in oxic environments, and methane and hydrogen sulfide in anoxic environments.

Commensurate with the biochemical phase of diagenesis is a geochemical phase characterized by abiogenic chemical reactions. These spontaneous reactions reformulate the organic debris of bacterial decomposition into *geomacromolecules*, of high molar mass. The geochemical phase of diagenesis begins in the oxic environment and continues in the anoxic environment, gradually gaining significance as microbial activity declines.

By the end of diagenesis, organic matter remaining in the sediment consists mainly of a mass of biomacromolecules and geomacromolecules. It may include some biomolecules selectively preserved from bacterial decomposition, such as by association with clay minerals. All of this organic matter can be characterized as insoluble in water, and refractory to bacteria.

Catagenesis

Catagenesis is an organic matter decomposition process largely driven by heat; it occurs at temperatures ranging from about 50° to 150°C (Tissot and Welte 1984, p. 71). Heat sources include normal geothermal gradients associated with deep burial, contemporaneous igneous intrusions, and geothermal groundwater flow. Burial depths necessary for catagenesis vary with geothermal gradient. Typical geothermal gradients measured in geologically stable areas range from 15 to 30°C per kilometer (Duff 1993, p. 168).

The dominant reaction product at a particular energy level of catagenesis is related to bond energy. Oxygen-bearing functional groups tend to separate at low temperatures, followed by carbon–carbon bonds, then carbon–hydrogen bonds at high temperatures (Levine 1993). The respective dominant reaction products are water, carbon dioxide, liquid hydrocarbons, and methane. Several kinds of geochemical reactions are usually occurring at any one time, generating multiple reaction products.

Catagenic reactions compel dramatic changes in composition and structure of residual organic matter. Its carbon concentration rises and bulk declines as oxygen- and hydrogen-rich reaction products are expelled. Molecular structure becomes increasingly aromatic, that is, more of the remaining carbon is reconfigured into very stable benzene-type rings, and the ring structures condense into polycyclic formation. Molecular condensation is most intense in late catagenesis. This progressive change in residual organic matter during catagenesis and metagenesis is called *muration*.

Metagenesis

Metagenesis is mainly a process of molecular condensation of the carbonaceous residue of catagenesis. Limited amounts of methane are generated, mainly by thermal cracking of higher hydrocarbons previously generated but not yet expelled. By late metagenesis, residual organic matter in the sediment resembles graphite.

Thermogenic Gases

The principal thermogenic gases associated with coal formation and petroleum generation are methane and carbon dioxide. The higher hydrocarbon gases ethane

(C₂H₆), propane (C₃H₈), and *n*-butane (C₄H₁₀) are common but subordinate constituents.

Thermogenic gas is sometimes characterized as “wet” or “dry,” a reference to the presence of higher hydrocarbon gases and condensates (light liquid hydrocarbons). “Wet gas” has C₁/(C₁ → C₅) ratios of 0.94 or below; it is a product of catagenesis. “Dry gas” has C₁/(C₁ → C₅) ratios of 0.94 to 1.0; it is commonly a product of metagenesis.

Thermogenic gases may in some cases be distinguished from bacterial gases by the ratio C₁/(C₂ + C₃). The ratio for thermogenic gas is often less than 50, and for bacterial gas is commonly greater than 1000 (Bernard, Brooks, and Sackett 1977). Ratios between 100 and 1000 may indicate a mixture of thermogenic and bacterial gases. Exceptions to this rule are common. Thermogenic gases may exhibit a ratio well over 100 in cases of gases generated in the very early stage of catagenesis, or gases stripped of ethane and propane during migration through low-permeability strata or through coal. A more reliable indicator of source of gas is its isotopic composition, as noted in Chapter 10.

COAL AND COAL GASES

Coals are formed from concentrated deposits of organic matter, most commonly terrestrial plant matter, that have been rapidly submerged into an anoxic environment and then buried by clastic sediment. In the course of deep burial in a sedimentary basin, the organic-rich deposits are compressed, heated, and thermally decomposed. The natural conversion of organic matter into coal is called *coalification*. The process generates gases, principally thermogenic carbon dioxide and methane. A considerable amount of gas is adsorbed to organic surfaces in the coal and may be released later when physical conditions that affect adsorption, such as temperature and pressure, change. In later stages of coalification, thermogenic methane is generated far in excess of the capacity of the coal to retain gas and is expelled into surrounding strata. Coal, then, can act as both a source and a reservoir of gas.

Coal Grade and Type

Coal grade refers to the relative amounts of organic matter and mineral matter in the coal or coaly deposit. Coal grades based on percent of ash, on a dry weight basis, include commercial coal—less than 25%; impure coal—25% to 50%; and coaly shale or coal-laminated shale—more than 50% (ASTM D 2796). A consistent nomenclature for organic-rich rocks has not been established, and other terms and definitions are in common use.

Coal type depends on the nature of the original organic matter and the

manner of its preservation. *Humic coals* are derived mainly from celluloses, hemicelluloses, and lignins of terrestrial plants that have been preserved in peat-forming environments. They make up over 80% of the world's coal (Hunt 1996, p. 400). Contributing plant varieties can range from mosses to trees; consequently, humic coals exhibit a diverse composition. *Sapropelic coals* are derived from lipid-rich particulate organic matter that has been generated in or washed into shallow lakes, ponds, and coastal lagoons and preserved in anoxic muds. Boghead coal is a sapropelic coal type derived mainly from algae. Cannel coal is a sapropelic type derived mainly from terrestrial plant spores and cuticles. Sapropelic coals may occur with humic coals or separately (Thomas 1992, p. 8).

Rank

Coalification processes act on organic matter and on water loosely bound to organic surfaces. Coal properties related to these non-mineral constituents can be used to establish the stage to which the deposit has been coalified. Coalification stage is identified by *rank*, a scale specific to coal type. Main stages of humic coal formation are, in order of increasing rank: peat → lignite → subbituminous coal → bituminous coal → anthracite. Peat is a precursor of humic coal, not a coal rank. Boundaries between ranks are transitional. Lignite and subbituminous coals are considered low-rank coals, bituminous coals and anthracites are considered high-rank coals.

Numerous definitions of rank boundaries and means of defining them are in common use. The most useful rank parameters are coal properties that are affected in a strong and consistent way by maturation. Commonly used rank parameters include the following:

Fixed carbon content (FC). Weight percent of solid residue other than ash obtained by burning; $FC\% = 100 - (H_2O\% + Ash\% + VM\%)$. Water, ash, and volatile matter contents are determined from “proximate analysis” (ASTM D 3172 to 3175).

Volatile matter content (VM). Weight percent of products, except water, given off by burning; $VM\% = 100 - FC\%$, where 100 represents the total carbon content. Nearly all volatile matter is formed by thermal decomposition of the organic fraction of coal.

Gross calorific value. Amount of heat produced per unit mass of coal when combusted under standard conditions.

Vitrinite reflectance. Percentage of directly incident light reflected from vitrinite macerals in coal, under specified conditions.

Water content.

No single rank parameter is useful over the full range of coalification. Gross calorific value and water content are useful for low-rank coals. Fixed carbon

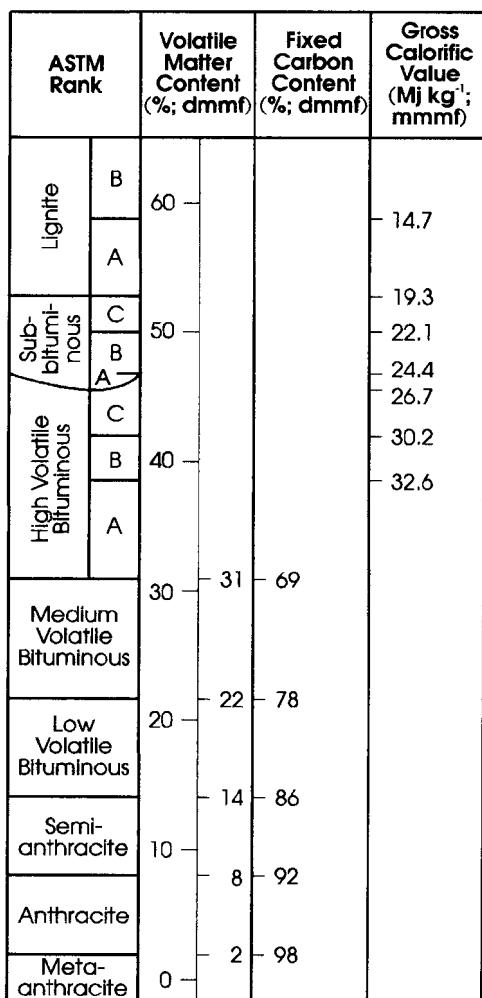


Figure 4-1. ASTM rank stages of coal, and rank parameters. (From ASTM D 388.)

content, volatile matter content, and vitrinite reflectance are useful for high-rank coals. Rank stages of coal as defined by the American Society for Testing and Materials (ASTM) are shown in Figure 4-1.

Vitrinite reflectance is the most commonly used parameter for measuring thermal maturity of organic-rich rocks, including coals and petroleum source rocks. Vitrinite reflectance is directly related to the aromaticity of the vitrinite

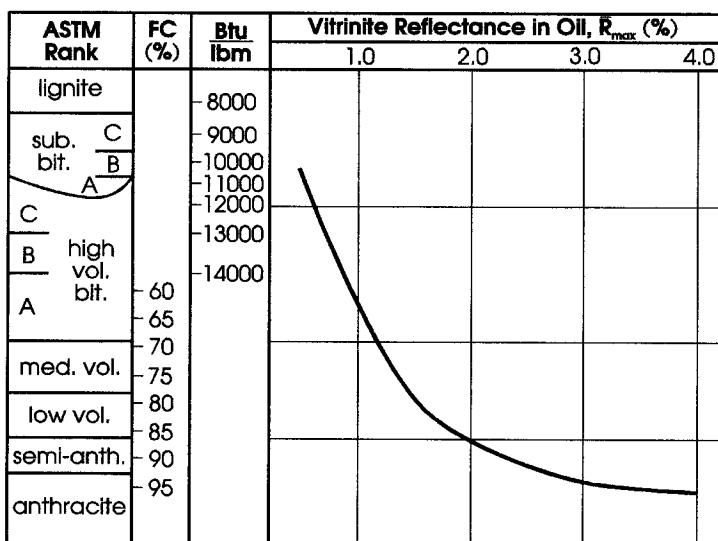


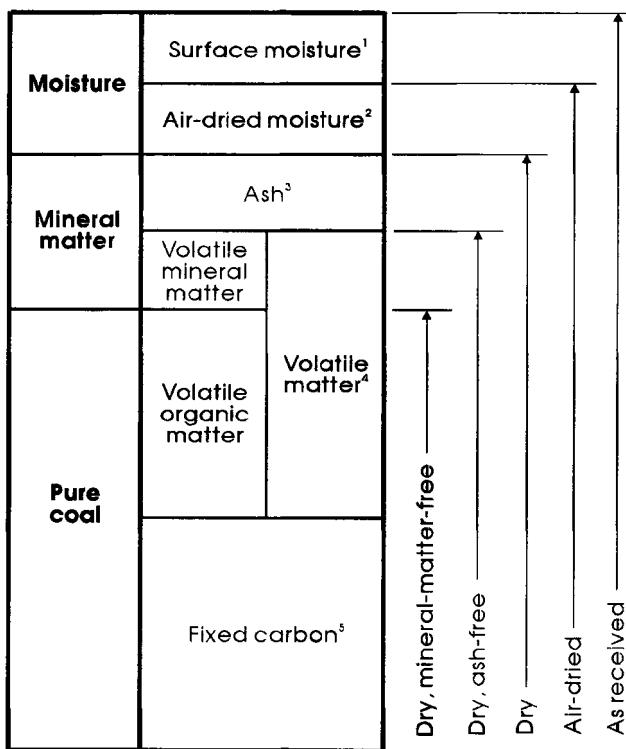
Figure 4-2. Vitritine reflectance and ASTM rank. FC is fixed carbon content; Btu is gross calorific value, in British thermal units. (Adapted from Castaño and Sparks 1974. © 1974 Geological Society of America, Boulder, Colorado.)

maceral, which increases with maturation. (Macerals are described below.) The following nomenclature is used in reporting vitrinite reflectance data: R_m or R_o is the statistical mean of the representative population; R_{\max} and R_{\min} are maximum and minimum reflectivities, respectively; R_o refers to measurements made with the microscope objective immersed in oil; and R_a refers to measurements made in air (Hunt 1996, p. 366). The relationship between vitrinite reflectance and ASTM coal rank is shown in Figure 4-2.

Reporting Coal Properties

Coal properties are typically reported on the basis of weight of one or more of the main constituents of organic matter, mineral matter, and water. Common reporting bases are defined in Figure 4-3. In low-ash coals, mineral-matter-free and ash-free bases of measurement are approximately equal.

Moisture contents for coal are typically calculated on the basis of wet weight, whereas for soil and rock they are routinely calculated on the basis of oven dry weight. The term “moisture content” is not easily defined for coal. Water in coal includes *adherent*, *bulk*, or *free moisture*—retained in a free state on the surface, in cracks, or in cavities; *inherent* or *bed moisture*—physically adsorbed in micropores and capillaries of the coal structure; *chemically bound*

**NOTES:**

¹ Surface moisture is incidental water, held as a film on the surface of a coal sample. It can be removed by air-drying at about 40°C.

² Air-dried moisture is that remaining after air-drying, which can be removed by oven drying at approximately 110°C in a nitrogen atmosphere or slight vacuum.

³ Ash is inorganic residue remaining after combustion, and represents most of the mineral matter.

⁴ Volatile matter includes constituents, excluding moisture, that are liberated at high temperatures in the absence of air.

-Volatile mineral matter includes inorganic compounds which can be detached from mineral surfaces, such as CO₂ from carbonates, SO₂ from sulphides, and H₂O from clays.

-Volatile organic matter is derived from the organic fraction of coal.

⁵ Fixed carbon is organic residue remaining after volatiles have been driven off. In addition to carbon, it includes bound N, S, H, and possibly O.

Figure 4-3. Analytical fractions and bases for reporting coal data. (From Ward 1984.)

moisture—associated with the organic molecular structure of coal; and **water of hydration**—associated with inorganic constituents, such as clay minerals (Mukhopadhyay and Hatcher 1993). The usual procedure in reporting coal moisture content is to quote the analytical procedure used to measure it (for example, ASTM D 1412, D 3173, or D 3302), and not to define the nature of the water

included in the determination (Allardice and Evans 1978). “As received” and “air-dried” contents, defined in Figure 4–3, are the most commonly used definitions for reporting analytical results.

Macerals

Coalified organic matter is composed of macerals, microscopic-sized analogues to the mineral constituents of rocks. Like the mineral composition of a rock, the maceral composition of a coal reflects the composition and diversity of the source material and to some extent its depositional history. Macerals preserve traces of cellular structure or retain other visible evidence of their origin that can be discerned under a microscope. Three main maceral groups are the huminite/vitrinite group, the liptinite (or exinite) group, and the inertinite group.

Huminite/vitrinite group macerals originate from wood, bark, leaves, roots, and similar plant tissues. Lignin is a prominent contributor. Precursor compounds are characterized by low atomic hydrogen/carbon ratios. Huminite macerals change to vitrinite in the transition from lignite to bituminous coal, a process called vitrification. Vitrinite is dark brown to lustrous black in appearance. Vitrinite macerals generally make up the largest proportion of humic coals.

Liptinite group macerals, also known as exinite, originate from spores, pollen grains, leaf cuticular waxes, resins, and single-cell algae. These constituents are rich in lipids. Liptinite precursor compounds are characterized by high atomic hydrogen/carbon ratios. Their high hydrogen content gives liptinite group macerals the capacity to generate more hydrocarbons than vitrinite, at low to medium ranks. Liptinite macerals generally make up a small proportion of humic coals, rarely in excess of 20%. They occur in higher concentrations in sapropelic coals (Diessel 1992, p. 70, 113).

Inertinite group macerals originate from terrestrial plant tissues that have been strongly oxidized prior to burial, by aerobic bacterial decomposition or by fire. Inertinites consist of 90% to 100% aromatic carbon (Tissot and Welte 1984, p. 238). The group name is derived from the fact that they are relatively inert through coalification, generating only small volumes of hydrocarbons. The proportion of inertinite macerals in humic coals rarely exceeds 20% (vol.).

Coalification

Diagenesis

Diagenesis is the first stage of coalification and carries the process through subbituminous rank. Diagenesis involves bacterial decomposition, abiogenic chemical reactions, and physical compaction of organic matter. The conversion of terrestrial plant matter to peat is largely mediated by bacteria. Low-temperature abiogenic chemical reactions become important in the formation of lignite and subbi-

tuminous coal. The greatest *physical* changes that occur during coalification are in the transition from peat to subbituminous coal, where increasing burial pressure causes porosity and moisture content to decrease, and density to increase.

Catagenesis

Catagenesis is the intermediate stage of coalification and carries the process through the bituminous ranks. It involves the generation, entrapment, and subsequent partial destruction of volatile hydrocarbons. Catagenesis of high volatile bituminous coals generates liquid-range hydrocarbons too large to easily escape the organic matrix. In most coals these volatiles remain trapped, until they are thermally cracked to methane in later stages of coalification. Catagenesis of medium to low volatile bituminous coals generates large quantities of methane.

As gases and water are expelled from coal, the elemental composition of macerals changes along predictable paths, called coalification paths. Coalification paths followed by maceral groups are shown in Figure 4-4. The starting composition on each path varies by nature of the source organic matter. The atomic oxygen/carbon ratio (O/C) progressively declines early in the coalification process as oxygen is expelled in the form of carbon dioxide and water. The hydrogen/carbon ratio (H/C) declines as hydrogen is subsequently expelled in the form of hydrocarbons, principally methane, and water. Most of the oxygen is eliminated in diagenesis and early catagenesis, and most of the hydrogen is eliminated in late catagenesis and metagenesis. Maturation brings all coalification paths to convergence.

The approximate boundaries of influence of diagenesis, catagenesis, and metagenesis in the maturation of coal are delimited on Figure 4-4 by isolines of vitrinite reflectance. Diagenesis is represented by the field to the right of vitrinite reflectance 0.5%. Catagenesis is represented by the field of vitrinite reflectance from 0.5% to 2%. Metagenesis is represented by vitrinite reflectance greater than 2%.

Metagenesis

Metagenesis is the final stage of coalification and carries the process through the anthracite ranks. The elemental composition of the coal changes little, except for a small decrease in hydrogen content resulting from expulsion of methane. Changes that occur during metagenesis are primarily structural. Polycyclic ring structures in the organic matrix become larger and increasingly oriented parallel to the bedding plane with maturation, further development of a trend established during catagenesis.

Coalification Temperatures

Heat is the principal driving mechanism for abiogenic processes of coalification. Temperatures required for coal formation are, very approximately, 10° to 40°C for low-rank coal, 40° to 100°C for bituminous coal, and 100° to 150°C for anthracite

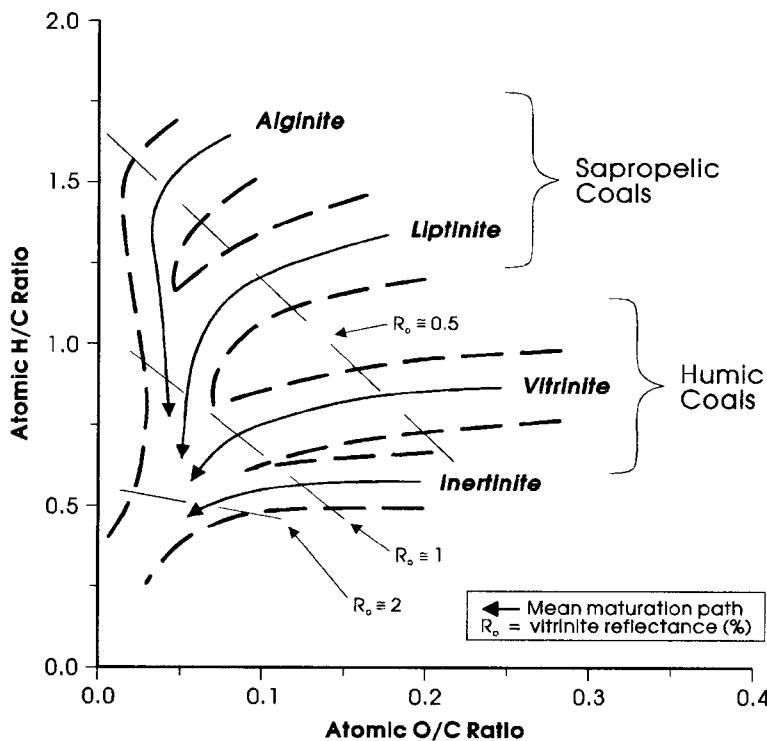


Figure 4-4 Coalification paths of main maceral groups. Humic coals are predominantly vitrinite but contain variable amounts of liptinite and inertinite. Alginite is a member of the liptinite group of macerals; it is derived from algae, the source of boghead coal. (Adapted from Meissner 1984.)

(Killops and Killops 1993, p. 102–103). Coalification to bituminous rank, driven by heat associated with normal geothermal gradients, requires burial depths of at least 1.5 km, more frequently 2.5 to 4 km (Stach et al. 1975). Time is also a factor in coalification, as shown in the general relationship in Figure 4-5. Coal will not reach full maturation without adequate heat, even with prolonged burial time. Folding and thrusting pressures associated with orogenic processes have little influence on coalification (Hacquebard and Donaldson 1974; Damberger 1991).

Coal Gases

Bacterial Coal Gases

Bacterial gas generation during coalification is most intense in peat and gradually declines as coal advances into lignite and subbituminous ranks. The fate of this

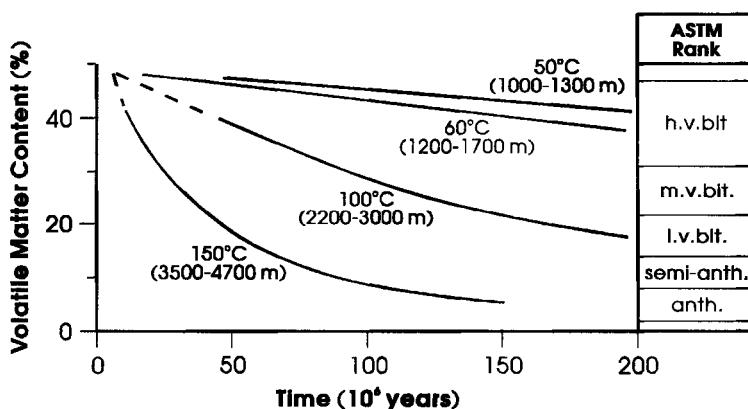


Figure 4-5. Coal maturation with time. Burial depth shown in parentheses. (Adapted from Teichmüller and Teichmüller 1965.)

gas is controversial. Some researchers are of the opinion that essentially all of it escapes to the atmosphere through limited soil cover, or is lost in solution in pore waters expelled from the compacting coal (Scott, Kaiser, and Ayers 1994). Others believe that bacterial methane generated in lignite and subbituminous coal subjected to rapid burial can be retained in potentially hazardous concentrations (Law, Rice, and Flores 1991). All ranks of coal can contain late-stage bacterial gas generated subsequent to coalification, as described in Chapter 8.

Thermogenic Coal Gases

Gases found in coal exhibiting vitrinite reflectance above 0.5% are mainly of thermogenic origin (Scott 1994). Thermogenic coal gases generally comprise 80% to 99% methane, 0.1% to 10% carbon dioxide, 0.01% to 8% ethane, 0% to 4% propane, 1% to 8% nitrogen, and possible trace amounts of other gases (Kim and Kissell 1988; Creedy 1988). Thermogenic coal gases include little or no hydrogen sulfide.

The composition of thermogenic gas generated in coal changes with maturation. Oxygen-rich gases (mainly carbon dioxide) predominate in early catagenesis, and hydrogen-rich gases (mainly methane) predominate in late catagenesis and metagenesis, as shown in Figure 4-6. Most carbon dioxide generated in early catagenesis appears to be carried out of the coal in solution in groundwater expelled by compaction. Small amounts of thermogenic methane may be generated at vitrinite reflectance slightly less than 0.5%. More significant amounts of methane, and most higher hydrocarbon gases, are generated at vitrinite reflectance between 0.5% and 0.8% (Scott 1994). Methane generation increases rapidly

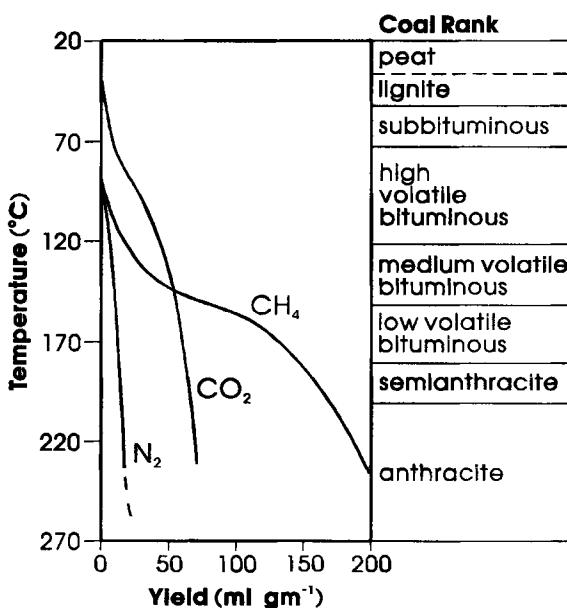


Figure 4-6. Estimated cumulative gas yield from humic coals. (From Hunt 1996, Fig. 7-14 A. © 1996 by W. H. Freeman.)

above vitrinite reflectance of 0.8%, and peaks between 1.2% and 2%. Small amounts of methane are generated during metagenesis.

Degree of rank maturation is the most influential parameter affecting generation of thermogenic gas, but coal composition is also a factor. The capacity of maceral groups to generate methane and carbon dioxide is shown in Figure 4-7. Liptinite macerals have a high hydrogen concentration, and a proportional capacity to generate methane and higher hydrocarbon gases at an early stage of thermal maturation. All maceral groups have similar gas generating potential at high degrees of maturation, where coalification paths converge.

Late-stage coalification may be responsible for natural gases containing 50% to 100% nitrogen, as reported in some regions (Krooss et al. 1995). Nitrogen becomes the major gas component at temperatures above 300°C, in the anthracite and meta-anthracite stages of coalification. Nitrogen expelled from coal may flush previously generated methane from overlying reservoirs that lack the capacity to hold all of the gases generated.

PETROLEUM AND PETROLEUM GASES

Petroleum is generated by abiogenic, predominantly thermal decomposition of organic matter in petroleum source rocks. Most petroleum is generated from ma-

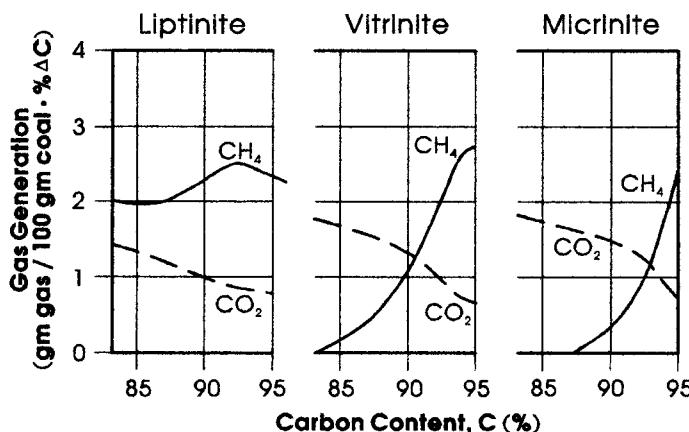


Figure 4-7. Gas generation from various macerals, per 1% change in carbon content, at various degrees of coalification. Micrinite is a member of the inertinite group of macerals. Curves derived mathematically, from mass balance analysis. (Adapted from Jüntgen and Karwell 1966.)

rine and lacustrine sedimentary rocks containing finely disseminated organic matter. Crude oil and gas generated from petroleum source rocks may migrate considerable distances through surrounding strata, before escaping to the surface or becoming trapped in a reservoir. Gases are the most mobile products of petroleum generation, and the most volatile, which makes them the greatest concern to underground construction.

Composition and Nature of Petroleum

The term *petroleum* has various definitions among branches of petroleum science. In this text, petroleum refers to naturally occurring gaseous, liquid, or solid products of petroleum generating reactions, products that are soluble in organic solvents. The term *crude oil* refers to liquid reaction products that are capable of migrating through soils and rocks. The terms *native asphalt* or *bitumen* are applied to semisolid to solid reaction products that are immobile under normal subsurface conditions, due to their high viscosity. These high viscosity reaction products include *heavy oil* and *extra heavy oil*, both of which are heavier than water. Bituminous rocks in the near-surface underground are also known as tar sands, oil sands, and rock asphalt (Speight 1999, p. 15).

Petroleum consists predominantly of hydrocarbon compounds, which, by definition, consist only of hydrogen and carbon. Crude oil and native asphalt normally include a lesser fraction of non-hydrocarbon compounds, composed of carbon chains and rings with functional groups containing nitrogen, sulfur, and

oxygen. These non-hydrocarbons, also known as *NSO compounds*, comprise much of the heaviest fraction of petroleum. Products of petroleum generation form complex solutions; crude oils may contain, in addition to hundreds of liquid compounds, gaseous hydrocarbons and asphalt compounds.

All hydrocarbon compounds are combustible, but only the lightest are capable of mixing with air in an underground excavation to generate an explosion hazard. All hydrocarbon gases (C_1 to C_4 compounds) contribute to the explosion hazard. Of the liquid constituents, only the gasoline fraction (C_5 to C_{10}) is capable of volatilizing in air at normal temperatures. Crude oil that has migrated to the near-surface underground is subjected to weathering processes that tend to strip it of light constituents; these processes are described in Chapter 6. Asphalt contains few light hydrocarbons. Crude oil or asphalt exposed in an excavation may not contribute significantly to the explosion hazard, though they may constitute a fire hazard.

Kerogen

Kerogen is operationally defined as organic matter disseminated in marine and lacustrine sedimentary rocks that is insoluble in organic solvents, such as carbon bisulfide (Selley 1998, p. 202; Tissot and Welte 1984, p. 131–132; Durand 1980). Kerogen constitutes most of the organic matter in these rocks that survives diagenesis, and is the principal source of petroleum compounds. Kerogen originates from phytoplankton, zooplankton, bacteria, and other indigenous aquatic organisms, and from plant detritus washed in from land areas. Organic detritus in oxic aquatic environments may be long exposed to attack by zooplankton and bacteria in the water column, and by benthic organisms at the sediment surface. Organic detritus in an anoxic water column is exposed to attack by anaerobic bacteria, including sulfate-reducing bacteria in marine environments, and methanogens in lacustrine environments. Most kerogen is so altered by biological decomposition that it is visibly unrecognizable, or amorphous. Petroleum source rocks typically contain lesser amounts of structured kerogen, in the form of macerals, which retain evidence of their original cellular structure and can be identified under a microscope.

Kerogen that has not been severely thermally decomposed can be classified on the basis of bulk elemental composition, more specifically on atomic hydrogen/carbon and oxygen/carbon ratios (H/C and O/C). Bulk elemental composition is a strong indicator of the nature of the source material and depositional environment. Composition influences the potential for the sedimentary rock to generate oil and gas, hence the interest in classifying kerogen. Both amorphous kerogen and structured kerogen contribute to bulk elemental composition. Four kerogen types have been defined for classification purposes, namely Type I, Type II, Type III, and Type IV.

Type I kerogen is formed from the remains of algae and bacteria preserved in anoxic muds of quiet, shallow lacustrine environments and some marine environments. The source organic matter is characteristically rich in lipids. Thermally immature Type I kerogens have a high H/C (greater than 1.25), and low O/C (less than approximately 0.15; Whelan and Thompson-Rizer 1993). Type I kerogen is a prolific producer of crude oil and gas because of its high hydrogen concentration. It is related to boghead coal, and like sapropelic coals is relatively rare.

Type II kerogen most often forms from the remains of phytoplankton, zooplankton, and bacteria preserved in marine sediments. Terrestrial plant matter washed into the environment may make a contribution. Thermally immature Type II kerogens have a relatively high H/C (less than approximately 1.3), and low O/C (from approximately 0.03 to 0.18). The hydrocarbon yield from Type II kerogen is less than from Type I, but the frequent occurrence of this type makes it a major source of crude oil and gas.

Type III kerogen forms from mainly terrestrial organic matter preserved by rapid burial in oxic coastal marine and deltaic sediments. It contains much structured kerogen, dominated by vitrinite macerals. Thermally immature Type III kerogens have a relatively low H/C (usually less than 1.0), and a high O/C (from approximately 0.03 to 0.3). Type III kerogen has a low potential for generating crude oil because of its low initial hydrogen concentration. It can generate gas if subjected to catagenesis.

Type IV kerogen originates from organic matter that has been strongly oxidized by aerobic bacterial decomposition or fire. It is usually of terrestrial origin. It is equivalent to the maceral inertinite. Type IV kerogen that has not undergone high temperature catagenesis is characterized by a very low H/C (less than 0.5), and a high O/C (for example 0.25 to 0.30; Tissot and Welte 1984, p. 155). It has no potential to generate crude oil, and little potential to generate gas.

Elementary compositions of kerogens from three type-deposits of petroleum source rocks and one coal, at the diagenesis stage of decomposition, are shown in Table 4-1.

Petroleum Source Rocks

Petroleum source rocks are commonly shales and carbonates derived from organic-rich sediment deposited in low-energy marine and lacustrine environments. (The term *shale* as used in petroleum geology is synonymous with *mudrock* and does not imply fissility). Source rocks are defined as any rock capable of generating and expelling enough petroleum to form an accumulation of crude oil or gas (Hunt 1996, p. 323). *Effective source rocks* have actually generated and expelled petroleum. *Potential source rocks* could expel hydrocarbons upon heating but are thermally immature and have not done so. Source rocks that have generated

Table 4-1 Elementary Compositions of Some Typical Kerogens at Diagenesis Stage of Maturation

Kerogen Type	Weight %					Atomic %				
	C	H	O	N	S	C	H	O	N	S
I ^a	75.9	9.1	8.4	3.9	2.6	38.7	55.9	3.2	1.7	0.5
II ^b	72.6	7.9	12.4	2.1	4.9	40.3	52.5	5.2	1.0	1.0
III ^c	72.7	6.0	19.0	2.3	0.0	45.2	44.8	8.8	1.2	0.0
Lignite ^d	68.6	5.1	21.2	2.6	2.5	46.0	41.2	10.7	1.5	0.6

^a Uinta Basin, ^b Paris Basin, ^c Douala Basin, ^d Yugoslavia.

Source: Data from Tissot and Welte 1984, Table 11.4.1.

only gas, due to low hydrogen concentration (Type III kerogen), may be referred to as *gas shales*. Potential source rocks that contain enough Type I or Type II kerogen to generate commercially viable amounts of crude oil upon artificial heating are commonly referred to as *oil shales*. The term has little petrographic significance for it is applied to mudrocks as well as to some organic-rich carbonates. Oil shales grade into sapropelic coals with increasing organic matter content (Solley 1998, p. 429–430).

Source rocks of low thermal maturity generally contain a minimum of about 0.5% TOC (total organic carbon; Tissot and Welte 1984, p. 496–497). Source rock TOC content usually does not exceed 5% but can be considerably higher. The TOC content accounts for most but not all organic matter in sediments, because organic matter also contains noncarbon elements. Total organic matter (TOM) content can be estimated from TOC content using the multiplication factors in Table 4-2.

Organic matter content and thermal maturity affect the color of source rocks. Thermally mature organic-rich shales may range from dark gray (TOC 0.5% to 1.5%), to grayish black (TOC 1.5% to 3.0%), to black (TOC >3%)

Table 4-2. Multiplication Factors for Estimating Total Organic Matter Content from Total Organic Carbon Content

Maturation stage	Kerogen type			Coal
	I	II	III	
Diagenesis	1.25	1.34	1.48	1.57
End of catogenesis	1.20	1.19	1.18	1.12

Source: Tissot and Welte 1984, Table V.1.1. Copyright Springer-Verlag.

(Potter, Maynard, and Pryor 1980, Fig. 1.25). Thermally immature organic-rich shales tend to be more brown than black (Arthur and Sageman 1994).

Petroleum Formation

Petroleum is generated by abiogenic decomposition of organic matter in sediments, in geochemical reactions driven mainly by heat associated with deep burial. Time is also a factor in petroleum generation because low-temperature thermal reactions over prolonged periods can advance maturation somewhat. The process is not thoroughly understood, in part because of the difficulty of duplicating, in a laboratory, geochemical reactions that occur over geologic time periods (Speight 1999, p. 85). Petroleum source rocks usually exhibit a degree of thermal maturation reached during their maximum depth of burial, not necessarily their present-day depth (Hunt 1996, p. 136).

Crude oil and gas are generated and expelled from petroleum source rocks during catagenesis, which generally occurs at temperatures ranging from about 50° to 200°C (Hunt 1996, p. 127). The principal period of oil formation occurs during early to mid catagenesis, at temperatures ranging from about 60° to 160°C (Hunt 1996, p. 128). The principal period of gas formation occurs during mid to late catagenesis. The most important factor in petroleum generation is the hydrogen content of organic matter in the source rock (Hunt 1996, p. 329). Type I and Type II kerogen generate and expel crude oil and gas. Type III kerogen expels only gas and gasoline range hydrocarbons. Because of its low hydrogen content it generates few heavy hydrocarbons, and these tend to be retained in the organic matrix until they are thermally cracked to gas at higher temperatures.

Metagenesis occurs at temperatures ranging from about 200 to 250°C (Hunt 1996, p. 137). By the metagenesis stage, most non-carbon elements have been eliminated from the organic matrix. Oil generation ceases, and gas generation declines. The most significant change that occurs during metagenesis is a physical reordering of the molecular structure of residual kerogen.

An approximate distribution of hydrocarbons generated in a hypothetical deep profile of organic-rich sediments is shown in Figure 4-8. The actual distribution depends on kerogen type, rapidity of burial, thermal conditions in the deposit, and ability of petroleum products to migrate from the source rock.

As crude oil and gas are generated with source rock maturation, residual kerogen is gradually depleted of oxygen and hydrogen. The decline in oxygen and hydrogen concentrations define a maturation pathway. Maturation pathways for type kerogens are shown in Figure 4-9. Petroleum source rocks typically contain a mixture of kerogens, often dominated by one type. Their maturation pathways follow the trends for type kerogens, but may fall anywhere within the boundaries shown.

Vitrinite reflectance can be used as a maturation parameter in petroleum

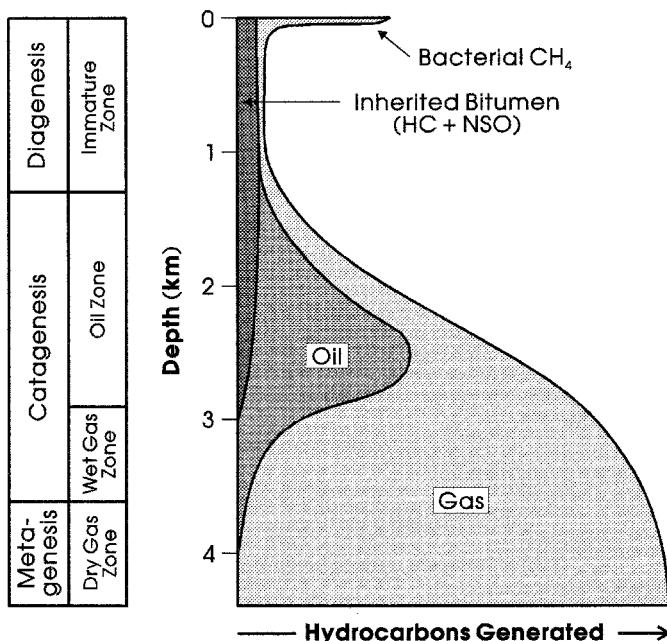


Figure 4-8. Relative amount and nature of hydrocarbons generated from sedimentary organic matter with depth of burial. Depth scale indicative of conditions in Mesozoic and Paleozoic source rocks. Inherited bitumen comprised of relatively unaltered biomolecules derived from living organisms. (Adapted from Tissot and Welte 1984, Fig. 11.7.1. Copyright Springer-Verlag.)

source rocks, as in coal (Castaño and Sparks 1974). The approximate boundaries of influence of diagenesis, catagenesis, and metagenesis in the maturation of kerogen are delimited on Figure 4-9 by isolines of vitrinite reflectance. As an approximation, diagenesis is represented by the field to the right of vitrinite reflectance 0.5%. Catagenesis is represented by the field of vitrinite reflectance from 0.5% to 2%. Metagenesis is represented by vitrinite reflectance greater than 2%. Actual boundaries vary somewhat with kerogen type, as shown in Figure 4-10.

Petroleum Gases

Petroleum gases are generated by abiogenic reactions during late diagenesis, catagenesis, and metagenesis. Bacterial gases are generated in the diagenesis stage of petroleum formation, but are not retained to become trapped in petroleum reservoirs. Petroleum gases generally consist of more than 70% methane and less than 10% carbon dioxide. Ethane concentrations are commonly less than 10%

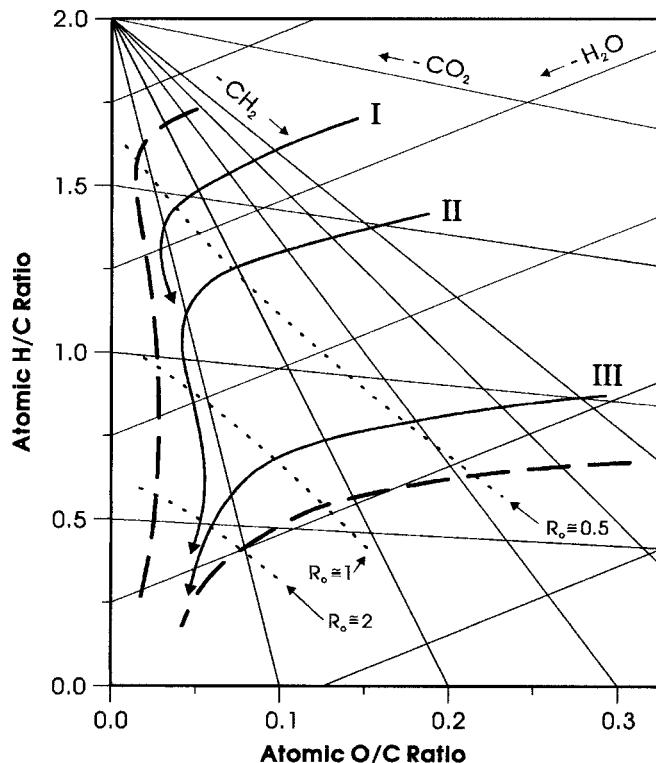


Figure 4-9. Evolution paths of type kerogens. R_o is vitrinite reflectance (%). The effects of formation of water, carbon dioxide, and hydrocarbons (CH_4) on maturation of kerogen are shown. (Adapted from Tissot and Welte 1984, Fig. II.5.1. Copyright Springer-Verlag.)

and rarely exceed 20%. In most cases, propane concentrations are less than 5%, and *n*-butane concentrations are less than 2%. (From analysis of data from Bureau of Mines 1992.)

Gas generation in relation to temperature, and by association, with depth of burial, is represented in Figure 4-11. The most active period of thermogenic gas generation is during catagenesis. Gases generated in greatest abundance are methane, carbon dioxide, and higher hydrocarbon gases. The high proportion of hydrocarbon gases (CH_4 and C_2H_6+) generated from Type I and Type II kerogens is related to the high H/C ratio of the source kerogen; similarly, the high proportion of carbon dioxide generated from Type III kerogen is related to the high O/C ratio of the source kerogen. Methane is generated during late catagenesis by cracking of carbon-carbon bonds in kerogen and in previously generated petro-

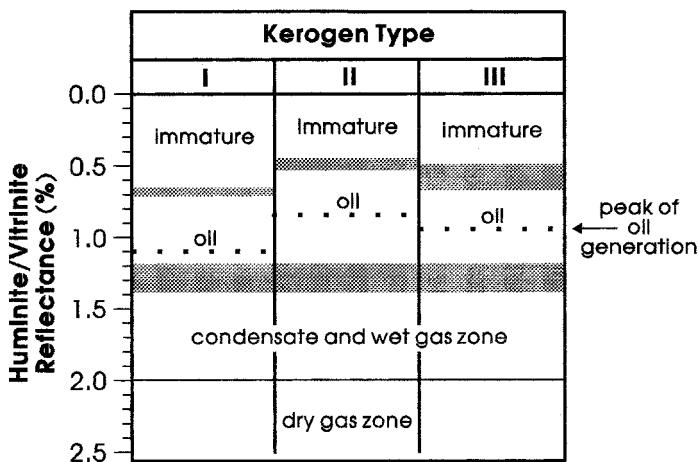


Fig. 4-10. Approximate boundaries of oil and gas zones. Boundaries may vary slightly with time-temperature relationship and with organic matter composition. (From Tissot and Welte. 1984, Fig. V.1.16. Copyright Springer-Verlag.)

leum that has not yet escaped the source rock. During metagenesis, methane is generated from the small amount of hydrogen remaining in the kerogen matrix, and from cracking of previously generated hydrocarbons.

Petroleum source rocks that have matured to a level between late-stage diagenesis and early catagenesis may have generated enough methane to constitute a hazard to underground construction. Organic-rich Devonian shales on the distal margins of the Appalachian Basin, a large sedimentary basin in the eastern United States, have generated sufficient gas to form gaseous phase accumulations in fractures and porous layers of sediment. These accumulations commonly discharge into boreholes, and in some areas migrate to the surface. This gas poses a hazard to tunnel construction in cities located on the basin margin, including Rochester, New York; Cleveland, Ohio; and Columbus, Ohio; as shown in Figure 8-14. These shales contain Type II kerogen. On the basin margin, vitrinite reflectance ranges from about 0.37% to 0.50% (McLaughlin, McLaughlin, and Kneller 1987); total organic carbon content generally ranges from about 0.2% to 15%, and averages about 3% to 4% (Knapp and Stith 1982).

Thermogenic hydrogen sulfide may be generated with petroleum by two mechanisms: thermal decomposition of organic sulfur compounds, and thermochemical sulfate reduction. The first mechanism can account for hydrogen sulfide concentrations of 3% or less in thermogenic gases. It occurs in late catagenesis

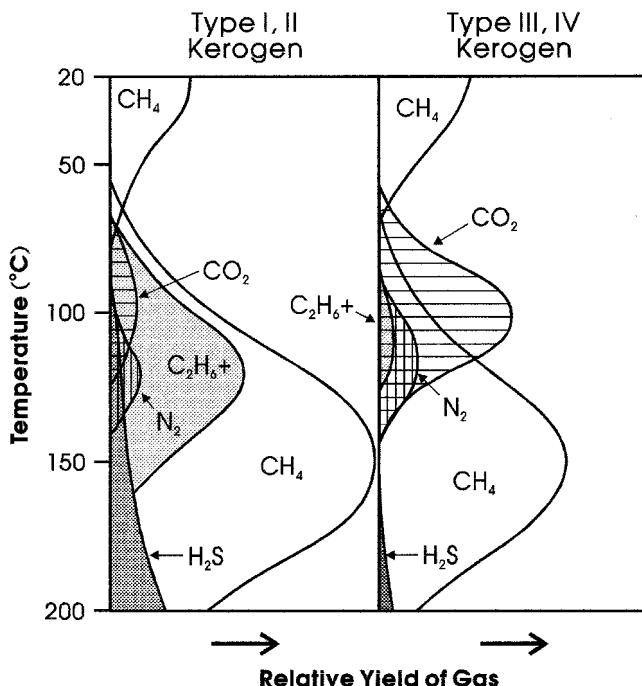


Figure 4-11. Gas generation from organic matter disseminated in aquatic sediments. Bacterial CO₂ and H₂S not shown. Gaseous higher hydrocarbons represented by C₂H₆+.
(From Hunt 1996, Fig. 7-1. © 1996 by W. H. Freeman.)

and in metagenesis, when carbon-sulfur bonds in kerogen and petroleum compounds are cracked. The amount of organic sulfur available limits the amount of hydrogen sulfide that can be generated. Kerogen in marine sedimentary rock may be rich in sulfur and more likely to generate hydrogen sulfide. The second mechanism, thermochemical sulfate reduction, is responsible for high concentrations of hydrogen sulfide, greater than 10%, found in a few deep, high-temperature reservoirs (Orr 1977). Thermochemical sulfate reduction requires sulfate minerals, and is inhibited in iron-rich rocks. It tends to occur in carbonate/evaporite sequences. This reaction occurs at temperatures above about 140°C (Worden, Smalley, and Oxtoby 1995). Thermogenic hydrogen sulfide does not appear to survive natural migration from deep petroleum source rocks to the near-surface underground. It is consumed in reactions with iron-bearing minerals, or is dispersed in solution in groundwater, as described in Chapter 6.

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5

Geothermal Gases

THE NATURE OF GEOTHERMAL GASES

Geothermal gases occur in areas of anomalously hot rock and in areas of normal geothermal gradients where groundwater circulates through excessively deep fractures. These areas are usually associated with young volcanism or tectonism. Geothermal gases originate mainly from magma degassing, and from thermal metamorphism of rocks conveying hot waters. Gases consist predominantly of carbon dioxide but may include hydrogen sulfide and methane. Dynamic geothermal systems feature groundwater convection cells that convey gases to shallow depths. This chapter describes the basic elements of geothermal systems capable of placing hazardous concentrations of gas in the near-surface underground. The geology of geothermal areas is described in more detail in Chapter 8.

DYNAMIC GEOTHERMAL SYSTEMS

A geothermal system is an area anomalously warmer than surrounding rock of the same depth, from which heat can be extracted via natural or artificial circulation of water or steam. Geothermal systems exhibit a number of forms. This chapter is focused on dynamic, liquid-dominated, high- and low-temperature geothermal systems. In this type of system, heat transfer occurs on a large scale, mostly via natural, continuous groundwater convection. Groundwater migrates

as much as several kilometers deep, is heated, and ascends to the surface. High-temperature systems exhibit fluid temperatures greater than 150°C. Low-temperature systems exhibit fluid temperatures less than 150°C, but at least 10°C above surrounding rock (Sorey, Nathenson, and Smith 1983). Vapor-dominated systems, in which most of the heat transfer is via steam convection, are not considered here as they are relatively rare. The short-lived (in geologic time) dynamic systems established on the flanks of active volcanoes are also not considered.

Dynamic geothermal systems are usually associated with Quaternary volcanism, Cenozoic tectonism, or both (McNitt 1970). These geologic processes elevate hot rocks in the crust and generate large-scale fractures that provide permeable pathways for deep groundwater migration. Quaternary volcanism occurs mainly along lithospheric plate subduction zones, spreading centers, and within stable continental (cratonic) areas over mantle convection plumes (Heiken 1982). Liquid-dominated systems tend to occupy basins and valleys within these regions (Healy 1975). Magma intrusions serve as the heat source. Volcanogenic systems are invariably high-temperature systems (Nicholson 1993, p. 3). Cenozoic tectonism tends to occur along young orogenic belts, in continental areas undergoing extension, and along transform plate margins. High geothermal gradients in these areas may or may not be associated with volcanism. Tectonism can generate both high- and low-temperature systems. The majority of geothermal systems are located along plate subduction zones and spreading centers, where active volcanism, mountain building, and rifting are concentrated.

MODEL OF A DYNAMIC GEOTHERMAL SYSTEM

The basic elements of a dynamic, liquid-dominated geothermal system include a heat source, permeable rock, and water. These elements are depicted in Figure 5-1. Heat from the heat source is transferred through impermeable rock by conduction. This heat warms groundwater in overlying permeable rock. Warmed water rises toward the surface through the path of least resistance, to be replaced by cooler, denser water descending through surrounding permeable rocks, establishing a groundwater convection cell. Chemical reactions occur between system fluids and between fluids and minerals in the rocks. Gases may originate directly from the magmatic heat source, from thermal metamorphism of host rocks, from reactions between acid waters and host rocks, and from atmospheric gases dissolved in meteoric waters recharging the system.

Heat Source

The heat source lies at the base of the geothermal system and provides the energy that circulates the fluids. Heat is transferred from the source to geothermal fluids by conduction, across a temperature gradient through solid rock. Volcanogenic

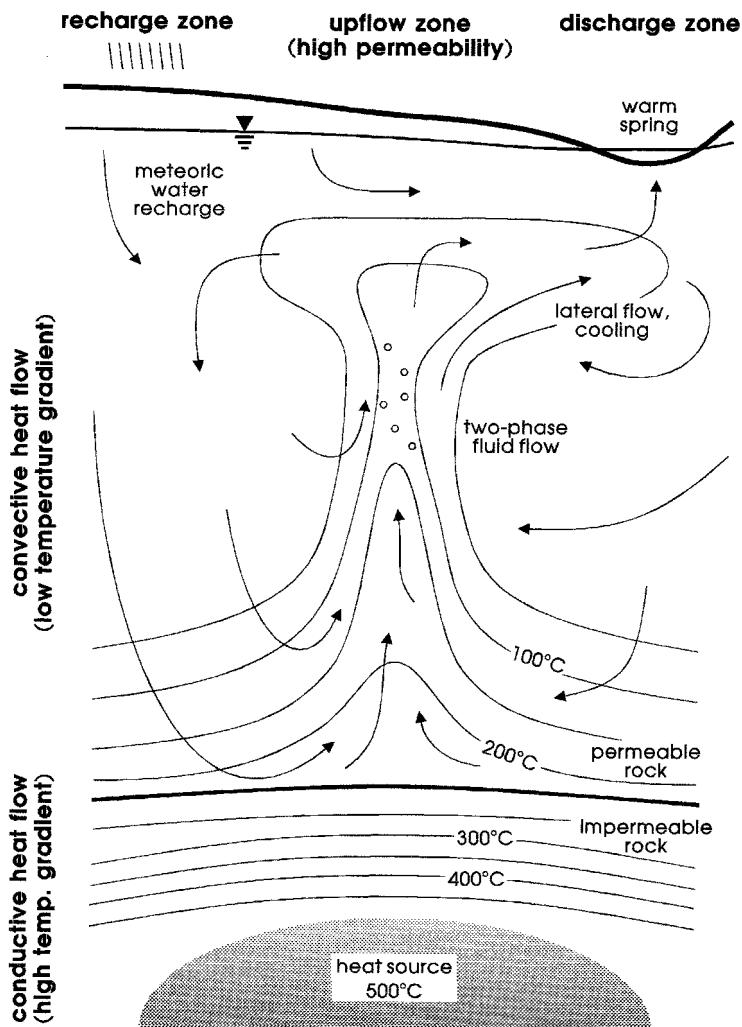


Figure 5-1. Conceptual model of a dynamic, liquid-dominated, high-temperature geothermal system. Depth of fluid circulation up to 7 km. Actual fluid flow distribution controlled by available recharge, permeability, and heat. Isotherm temperatures are for illustration only. (Developed from Nicholson 1993 and Elder 1965.)

geothermal systems are driven by heat from magma intrusions. These are the most active heat sources. Magma intrusions may lie at depths from 3 to 10 km, and their temperatures may range from 300° to 1100°C (Wright 1988). In systems associated solely with tectonism, the heat source may consist of uplifted basement rocks that have not yet cooled; or water may be heated by circulating through unusually deep fractures in areas of near-normal gradients (Nicholson 1993, p. 3). The life of a geothermal system is limited by the duration of cooling of the heat source. Cooling of a magma intrusion may take from 10⁵ to 10⁶ years (Henley and Ellis 1983). Geothermal systems driven by high regional heat flow not associated with volcanism may last from 10³ to 10⁵ years (Rybäck 1981).

Permeable Rock

Groundwater convection cells in dynamic geothermal systems are somewhat open flow systems, in which cool groundwaters moving into the system replenish geothermal waters that flow out of the system. The system requires a continuous permeable network extending from the surface to the proximity of the heat source. Permeable rock containing hot fluids is commonly referred to as the reservoir. The reservoir in a dynamic system more closely resembles an aquifer because it is charged with moving water.

Permeability in deep rock is most commonly attributed to regional fractures. They capture groundwater seepage from a broad area and channel it to the heat source. These deep fractures form around the rim of collapse calderas, over domes capping magma intrusions, around fault blocks developed during mountain building, and along rifts. Regional fractures may allow water to penetrate 5 to 7 km deep (Nicholson 1993, p. 7). Fracture permeability tends to decrease with depth, as rock discontinuities are closed by mineral precipitation and pressure. Mineral precipitation and ductile closure of discontinuities are particularly efficient at temperatures above 350° to 400°C (Fournier 1989). Regional fractures become increasingly important to deep circulation as smaller discontinuities are progressively closed over time. Occasional tectonic activity helps to keep fractures open (Curewitz and Karson 1997).

Permeability nearer the surface may derive from pore space in clastic sediments and pyroclastic rock, and local fracture networks. Matrix permeability in laterally extensive strata near the surface may allow considerable lateral movement of geothermal waters, compared to relatively confined and predominantly vertical flow in underlying regional and local fracture networks. Mineral precipitation from geothermal waters may reduce near-surface rock permeability to some degree.

Hydrogeology of the System

Fluid flow through a geothermal region might be described as a coupling of a normal groundwater flow system with a convection cell. Groundwater flow

through the normal system is driven by topography. Most commonly, the normal system is recharged in highland areas by precipitation and snowmelt and is discharged by flow to streams, lakes, rivers, and the sea. The normal groundwater system contributes cold water to and receives hot water from the convection cell.

Heating of cold water that reaches the base of the system establishes a groundwater convection cell. Cold water from the normal groundwater system descends through permeable rock, usually along peripheral features. The area of down-flow is generally believed to be considerably larger than the heat source (Garg and Kassoy 1981). As water approaching the heat source is warmed, it becomes less dense and less viscous (Norton 1984). Buoyant pressure from surrounding cooler water forces the warm water to ascend through the least restricted route to the surface, often a fault intersection. Almost all waters entering the geothermal system are meteoric, with a possible contribution of up to 5% magmatic water entering from the base of the system.

Steam forming in the rising fluid may stimulate convection. Fluid pressures in a liquid-dominated system are close to hydrostatic. If the fluid pressure in the rising water column declines to the saturation vapor pressure, vapor bubbles form and two-phase flow is established. Saturation vapor pressure is a function of temperature. A vigorous convection cell can develop in highly permeable rock. The relationship between depth of boiling and fluid temperature is shown in Figure 5-2. The presence of gas in solution facilitates boiling by depressing the boiling point curve.

Fluid temperatures at the base of the convection cell usually do not exceed 250°C (White, Muffler, and Truesdell 1971). The base of some systems is occupied by brine rather than water, and brine temperatures may exceed 400°C (Nicholson 1993, p. 7). Brine may be expelled from magma, or it may form from salts leached from wall rocks. Brine is heavier than water, so it tends to accumulate at the base of the system and does not mix easily with meteoric water in the convection cell. Convecting water is heated as it passes over the brine.

Temperatures of geothermal waters vary widely with depth and proximity to the warm plume. Water ascending through the lower parts of the system maintains an approximately uniform temperature, close to the base temperature. Most of the heat transfer in the up-flow zone is via convection rather than conduction. In the upper parts of the system, hot water is cooled by boiling, by mixing with cool water, and by conducting heat into cooler rocks. Hot and cool waters mix on the margins of the system, in networks of intersecting discontinuities and in the pores of clastic sediments.

The character of geothermal flow near the ground surface depends on permeability, topography, and depth to groundwater table. Warm water ascending through a deep fracture network may, upon encountering porous strata, flow laterally. Warm water has been observed flowing in normal groundwater flow systems as much as 15 km from the heat source (Healy 1975). If the water table intersects the ground surface, geothermal waters may form a hot spring.

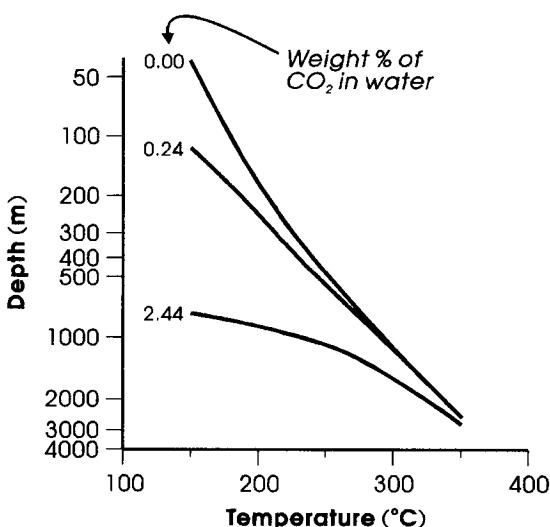


Figure 5-2. Depth at which water at a given temperature will begin to boil, for CO₂ concentrations shown. Assumes hydrostatic pressure conditions on the water column. Conditions at top of water column are 100°C and 1 bar pressure. Curves must be depressed for systems where boiling point conditions do not occur at ground surface. (Adapted from Mahon, McDowell, and Finlayson 1980.)

Geochemistry of the System

Geothermal water contains more than the usual amount of dissolved minerals. Most solutes come from reactions of hot water with wall rocks. Some originate from meteoric water and from volatiles expelled from magma. Solutes in geothermal water can be divided approximately into the common rock-forming constituents of limited solubility—including silica, aluminum, sodium, potassium, calcium, magnesium, iron, and manganese—and the more soluble elements, such as chloride, bromide, boron, arsenic, and cesium (Ellis and Mahon 1977, p. 81). Solution concentrations depend on temperature, rock type, fluid composition, and availability of rock surfaces to flowing water. Mineral concentrations can be extremely varied.

Minerals are usually dissolved in the hotter parts of the geothermal system, and precipitated in the cooler parts. The most abundant mineral precipitates found in geothermal systems are silica in various forms, and calcium carbonate in the forms of calcite and aragonite. Silica as quartz is most likely to be deposited where temperatures decrease abruptly, such as on the margins of fields (Grindley and Browne 1975). Calcite is deposited where carbon dioxide concentrations decline (Ellis 1963; Arnórsson 1989). Calcite deposition is greatest from geothermal waters highly charged with carbon dioxide (Ellis and Mahon 1977).

Geothermal Gases

Gases are normally present in active geothermal systems and are widely discharged at the surface. Common gases include carbon dioxide, hydrogen sulfide, methane, nitrogen, hydrogen, and ammonia. In 70% to 80% of explored areas, more than 90% of the total gas volume is carbon dioxide (Mahon 1975). Of the remaining gases, none are consistently secondary.

Carbon Dioxide

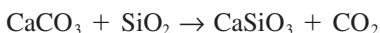
Geothermal carbon dioxide comes from two principal sources: magma degassing and thermal metamorphism of marine carbonate sedimentary rocks. A lesser source is acid water reaction with carbonate rocks. All sources may be active in a single geothermal system.

Carbon dioxide exsolves from magma as it rises from the mantle, from depths of 50 km or more, to the surface. Carbon dioxide and water are by far the major volatiles present in magma (Gerlach 1999).

Carbon dioxide is generated by metamorphism of marine carbonate rocks (limestone and dolomite) that convey hot water through fractures and solution features. Geothermal systems associated with marine sedimentary rocks commonly generate much greater amounts of carbon dioxide than systems associated primarily with volcanic rocks (Mahon, McDowell, and Finlayson 1980; Farmer 1965). Examples of metamorphic reactions include the decarbonation of siliceous carbonates (Panichi and Tongiorgi 1975):



and



These reactions typically occur at temperatures above 200°C.

Carbon dioxide is also generated by dissolution reactions between acid water and carbonate rock, represented by:



Geothermal waters are acidified by disproportionation reactions between SO₂ and H₂O, and disassociation of HCl and HF.

At low temperatures, carbon dioxide solubility decreases with increasing temperature. This trend changes at high temperatures. At temperatures above about 175°C, solubility *increases* with increasing temperature, as shown in Figure 5-3.

Other Gases

Methane is a common and usually minor constituent gas in geothermal systems. It originates from thermal decomposition of organic matter. Methane can be a

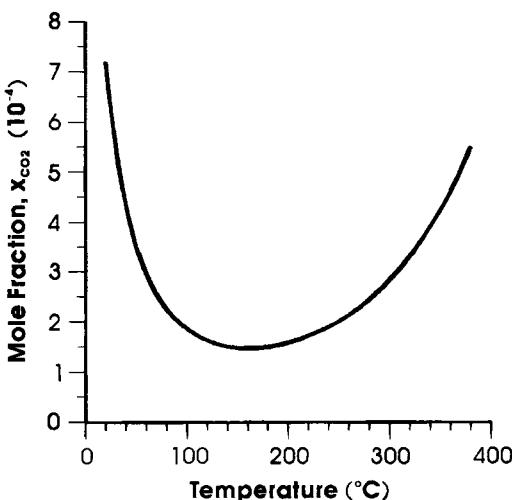


Figure 5-3. Mole fraction solubility of carbon dioxide in water, at a partial pressure of 1 standard atmosphere. (Based on Naumov equation, in Ross 1977.)

principal constituent gas in low-temperature geothermal systems hosted in organic-rich sedimentary rocks (Nicholson 1993, p. 106).

Hydrogen sulfide is also a minor constituent of geothermal gas mixtures, but its high toxicity may render this minor fraction hazardous. Hydrogen sulfide may originate from magma degassing, or from thermal metamorphism of reservoir rocks. It is relatively chemically reactive among geothermal gases and tends to be removed by reactions with wall rocks to form iron sulfides.

Most nitrogen found in geothermal systems originates from the atmosphere and enters the system dissolved in meteoric water. Nitrogen may be a major constituent gas in low-temperature systems (Nicholson 1993, p. 106).

Hydrogen and ammonia may originate from thermal decomposition of organic matter. Hydrogen may also originate from reactions between hot water and ferrous iron in host rocks.

Discharge of Gases

Gases in solution in deep geothermal waters may not remain in solution as warm waters rise to the surface. Boiling causes gases to leave the liquid phase in strong preference for the vapor phase. The rapid loss of gases with boiling is shown in Figure 5-4. Gases may also escape solution in systems where boiling conditions are not reached. Gas bubbles ebullate from waters saturated with gas, as waters rise and hydrostatic pressure declines. Boiling and ebullition can have a major

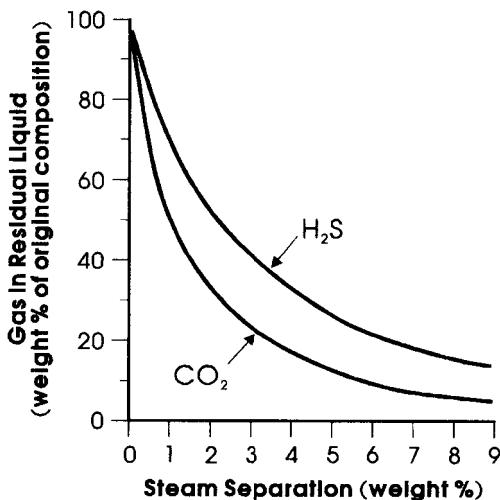


Figure 5-4. Decrease in gas concentration in liquid, following steam separation. Vapor phase in contact with liquid phase; liquid temperature 260°C. The less soluble gas, CO_2 , enters the vapor phase more readily. (Adapted from Nicholson 1993, Fig. 3.3. Copyright Springer-Verlag.)

effect on how gases are discharged from the system. Once separated from water, a gaseous phase may migrate through the system independently. A gaseous phase below the water table tends to be driven up by buoyancy, whereas a solution phase in water in shallower parts of the system tends to travel laterally along hydraulic head gradients.

Gas discharge from the system is also affected by cooling. Cooling promotes retention of gases in solution by inhibiting steam and gas bubble formation. Warm waters on the periphery of the system may exhibit higher gas concentrations than hotter waters in the center because of the more vigorous degassing that occurs in the central part of the system (Arnórsson and Benjamínsson 1980).

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6

Migration and Retention of Gases in Geologic Media

INTRODUCTION

Gas is encountered underground in such a variety of geologic environments that few could be categorically declared gas-free. The presence of gas is easiest to explain when the environment in question is actively generating gas. But generation is only one aspect of gas distribution. Gas can become separated in space or in time from its origin, so explaining its presence in a particular geologic setting becomes more complicated. This chapter describes forces that control movement, retention, and temporal existence of natural gases in soils, rocks, and groundwater.

The first few sections in this chapter address topics relevant to all gases underground regardless of origin. These topics include:

- Permeability and porosity—characteristics of void space in soils and rocks that influence gas migration and retention
- Gas flow—hydraulic energy, density, and chemical gradients that cause gas to move
- Gas retention—the manner in which gas is held in soils, rocks, and groundwater
- Gas consumption—biochemical and geochemical reactions that change a particular gas into other molecular species

These general discussions are followed by descriptions of flow and retention mechanisms important for bacterial, coal, and petroleum gases. This chapter does

not address thermal groundwater convection, the principal transport mechanism for geothermal gases, as this is addressed in Chapter 5. The general descriptions here are relevant to geothermal gases that have escaped the thermal convection cell.

POROSITY AND PERMEABILITY

Porosity and permeability are familiar concepts in underground construction, routinely applied to problems of groundwater flow. But they can also be applied to flow of a gaseous phase. This section introduces porosity and permeability terms used in this text. The origin and character of porosity and permeability in soils and rocks is described in engineering and geology literature and will not be addressed here (for example, Selley 1988, Chap. 3; and Selley 1998, Chap. 6).

Porosity

Porosity is a storage property defined as that proportion of the bulk volume of soil or rock occupied by interstices:

$$\phi = \frac{\text{volume of pore space}}{\text{volume of bulk solid}} \quad (6-1)$$

where ϕ is *total porosity*. Typical porosities of soils and rocks are shown in Table 6-1. Total porosity comprises matrix porosity and fracture porosity. Matrix porosity includes intergranular space, vugs, and solution features.

Only those pores that are interconnected and part of a continuous network contribute to the capacity of soil or rock to transmit fluids. This volume of inter-

Table 6-1 Typical Porosities of Soils and Rocks

Soils	ϕ	Rocks	ϕ
Gravel, coarse	0.24–0.36	Sandstone	0.05–0.30
Gravel, fine	0.25–0.38	Siltstone	0.21–0.41
Sand, coarse	0.31–0.46	Limestone, dolomite	0.00–0.20
Sand, fine	0.26–0.53	Karst limestone	0.05–0.50
Silt	0.34–0.61	Shale	0.00–0.10
Clay	0.34–0.60	Fractured crystalline rocks	0.00–0.10
		Dense crystalline rocks	0.00–0.05
		Basalt	0.03–0.35
		Weathered granite	0.34–0.57
		Weathered gabbro	0.42–0.45

Source: Domenico and Schwartz 1990, p. 26. © 1990 John Wiley.

connected pores can be less than the total pore volume. The proportion of interconnected pores open to fluid flow is *effective porosity*:

$$\phi_e = \frac{\text{volume of interconnected pores}}{\text{volume of bulk solid}} \quad (6-2)$$

Continuous pore space can be closed to a gaseous phase by capillary water. Effective porosity to the gaseous phase then becomes a function of pore water saturation:

$$\phi_e = \phi \left(1 - \frac{S}{100} \right) \quad (6-3)$$

Finally, for fractured rock, it may be useful to distinguish fracture porosity from matrix porosity. Fracture porosity is (Nelson 1985, Equation 1-11):

$$\phi_f = \frac{e}{D + e} \quad (6-4)$$

where e is average effective width of fractures, and D is average spacing between parallel fractures. Fracture porosity depends on scale. Fracture porosity of undisturbed rock is typically low, on the order of 10^{-5} to 10^{-4} . In highly fractured zones or proximate to excavations it may be considerably higher, on the order of 0.1 (Lee and Farmer 1993, p. 32, 99–101).

Permeability and Single-Phase Flow

Steady laminar flow of a single incompressible fluid through a saturated, homogeneous porous medium is described by Darcy's law, which in its original form is:

$$q = K A \frac{\Delta h}{\Delta x} \quad (6-5)$$

where q is volumetric flow rate ($\text{cm}^3 \text{ s}^{-1}$), K is hydraulic conductivity (cm s^{-1}), A is cross-sectional area of the flow channel (cm^2), Δh is the difference in hydraulic head between the ends of the flow channel (cm), and Δx is the length of the flow channel (cm).

Hydraulic head h is the sum of pressure head and elevation head. The difference in hydraulic head is:

$$\Delta h = \frac{\Delta p}{\rho G} + \Delta z \quad (6-6)$$

where p is pressure ($\text{kg m}^{-1} \text{ s}^{-2}$), ρ is mass density of the fluid (kg m^{-3}), and G is the gravitational constant (m s^{-2}).

Hydraulic conductivity K is a function of the properties of both the porous medium and the fluid. The effects of pore and fluid properties can be isolated using the relationship:

$$K = \frac{k \rho G}{\mu} \quad (6-7)$$

where k is *permeability* (cm^2), a property of the porous medium; ρ is mass density of the fluid (g cm^{-3}); G is gravitational acceleration (cm s^{-2}); and μ is absolute viscosity of the fluid ($\text{g cm}^{-1} \text{s}^{-1}$).

Substituting Equations 6-6 and 6-7 into Equation 6-5:

$$q = \frac{k \rho G}{\mu} A \frac{\left(\frac{\Delta p}{\rho G} + \Delta z \right)}{\Delta x} \quad (6-8)$$

This form of the Darcy equation can be used to analyze flow of a fluid or a gaseous phase through a particular porous medium. A gaseous phase has a relatively low fluid density, so the effect of gravity can be ignored. For gaseous phase flow, Equation 6-8 simplifies to:

$$q_g = \frac{k A \Delta p}{\mu \Delta x} \quad (6-9)$$

Absolute viscosity of gas is independent of pressure, and it increases only slightly with temperature. Viscosities of several gases are shown in Table 6-2.

Permeability k can be expressed in units of cm^2 , as noted, or in *darcys*. The darcy is defined as the permeability of a porous medium that allows a fluid, of viscosity 1 centipoise (cP ; $10^{-2} \text{ g cm}^{-1} \text{s}^{-1}$), under a hydraulic gradient of 1 atm cm^{-1} , to flow through an area of 1 cm^2 at a rate of $1 \text{ cm}^3 \text{s}^{-1}$ (absolute viscosity of water at $20^\circ\text{C} = 1 \text{ cP}$). Thus:

$$1 \text{ darcy} = \frac{(1 \text{ cp})}{(1 \text{ cm}^2)} \left(\frac{\text{cm}}{1 \text{ atm}} \right) \left(\frac{1 \text{ cm}^3}{\text{s}} \right) = 0.987 \text{ } \mu\text{m}^2 \approx 1 \times 10^{-8} \text{ cm}^2$$

Table 6-2 Absolute Viscosities of Gases

Gas	Viscosity (μP)
Air	182
Methane	109
Carbon dioxide	147

Viscosities at 20°C .

Source: Lide 1996.

The permeability (k) of a porous medium is related to its hydraulic conductivity (K) to water by:

$$\begin{aligned}1 \text{ darcy} &\approx 1 \times 10^{-3} \text{ cm s}^{-1} \\1 \text{ cm}^2 &\approx 1 \times 10^5 \text{ cm s}^{-1}\end{aligned}$$

Relative Permeability and Two-Phase Flow

Water and a gaseous phase are immiscible fluids, meaning they do not mix. In a porous medium partially saturated with water, pore space occupied by water is not readily available to the gaseous phase, and vice versa. Each fluid reduces the permeability of the medium to the other. *Effective permeability* is the permeability, to one fluid, of a porous medium partially saturated with another immiscible fluid. *Relative permeability* is the ratio of effective permeability to absolute permeability. Relative permeability depends on the proportions of fluids in the pore space. A general relationship for water and a gaseous phase in sand is shown in Figure 6-1. The sum of the relative permeabilities of a partially saturated porous medium to two immiscible fluids is always less than 1.0.

In porous soils or rocks containing water and a gaseous phase, water has a greater tendency to spread over solid surfaces than gas. Water is the *wetting*

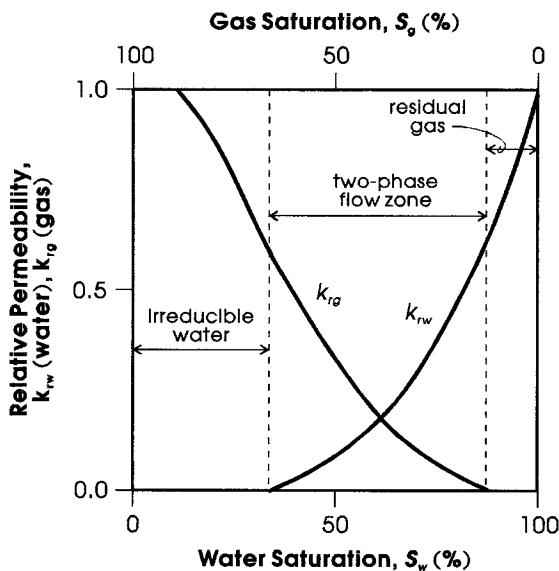


Figure 6-1. General relative permeability of gas and water in unconsolidated sand. (Adapted from Wyckoff and Botset 1936.)

fluid, gas the *nonwetting fluid*. Water tends to occupy the smaller interstices, gas the larger ones. Water must reach 20% to 40% saturation in order to flow; gas must reach at least 5% to 10% saturation (Levorsen 1967, p. 111–112). Wettability is responsible for the lack of symmetry between the relative permeability curves of Figure 6-1. The relative permeability relationship is influenced by pore structure, mineral surface chemistry, and whether or not the medium is imbibing or draining water. The relationship for a particular medium can be accurately determined only by experiment (Dullien 1992, p. 339–341).

Simultaneous flow of water and a gaseous phase through a porous medium is *two-phase* flow. Each fluid moves through separate flow channels independent of the other. The Darcy equation can be applied thus:

$$q_i = \frac{k_i \rho_i G}{\mu_i} A \frac{\Delta h_i}{\Delta x} \quad (i = 1, 2) \quad (6-10)$$

where k_i is the effective permeability of the medium to fluid i . Two-phase flow of water and a gaseous phase is possible within a limited range of saturations, the two-phase flow zone, as shown in Figure 6-1.

GAS MIGRATION

Gas underground in gaseous phase or in solution phase in groundwater is subject to physical and chemical forces that can cause it to migrate through geologic media. These forces are directed along energy gradients. Gas migrates along hydraulic energy gradients by *bulk flow*, along density gradients by *buoyant flow*, and along chemical gradients by *diffusion*.

Bulk Flow

The term *bulk flow* is used in this text to refer to fluid migration through porous media along hydraulic energy gradients. Gas can migrate by bulk flow in gaseous phase, or in solution phase in groundwater. Bulk flow of gas or water is described by the general form of the Darcy equation, Equation 6-8.

Gaseous Phase Bulk Flow

Gas in gaseous phase in the unsaturated zone moves by bulk flow through highly porous and permeable materials such as gravels, uniformly graded sands, and fractured rock. Hydraulic energy gradients in pore gases are induced by changes in atmospheric pressure that accompany changes in weather. The depth of atmospheric influence depends on thickness, permeability, and moisture content of unsaturated zone materials, and on the permeability of surface cover such as an organic soil layer.

Atmospheric pressure variations may be an insignificant factor in the exchange of gases between the unsaturated zone and the atmosphere, below a depth

of a few meters (Rose, Hawkes, and Webb 1979, p. 504–505). Pore gases can also be forced through permeable unsaturated ground along pressure gradients induced by large fluctuations in the water table. This may occur in alluvial deposits along rising or falling rivers, in areas undergoing dewatering, or in areas where dewatering has ceased and the water table is recovering.

Solution Phase Bulk Flow

Circulating groundwater is the principal distributor of gas in the saturated zone. All gases can be carried in solution. Gas may enter solution in groundwater directly from source strata or from a gaseous phase migrating through or trapped within the aquifer. Bulk flow of gas in solution is generally confined to permeable pathways. Groundwater flow is adequately described in hydrogeology texts and is not addressed here.

Buoyant Flow

Buoyant flow is the upward movement of a gaseous phase through saturated permeable ground or a body of water; it is driven by the difference in densities between the gas body and water. Pressure throughout the gas phase is essentially equal to water pressure at the base of the gas body. So at every point on the gas–water interface above the base of the gas body, gas pressure is slightly greater than water pressure. This pressure difference tends to propel the gas body through the water. The driving pressure at any point on the gas–water interface is:

$$p_b = G h (\rho_w - \rho_g) \quad (6-11)$$

where p_b is *buoyant pressure*, G is gravitational acceleration, h is height above the base of the gas body, ρ_w is the mass density of water, and ρ_g is the mass density of gas (Berg 1975). Buoyant pressure is greatest at the top of the gas body, so flow is preferentially upward.

Buoyant flow in porous media is opposed by *capillary pressure*, which acts across pore openings along the gas–water interface. Buoyant pressure must overcome capillary pressure for the gas–water interface to advance past the pore opening. Capillary pressure is the result of surface tension of water. It acts across a pore opening as shown in Figure 6-2. The magnitude of this pressure is:

$$p_c = p'' - p' = \frac{2 \gamma \cos \theta}{r} \quad (6-12)$$

where p_c is capillary pressure, γ is surface tension of water, θ is *wettability*, and r is pore radius. This equation is valid for very small openings where gravity has a negligible effect on pressure distribution across the pore. The surface tension of water at normal temperatures and pressures in the near-surface underground is about 70 dyn cm^{-1} (Schowalter 1979). Water is considered a perfect wetting fluid on previously wetted mineral surfaces, so the wettability term $\theta = 0^\circ$ and $\cos \theta = 1$.

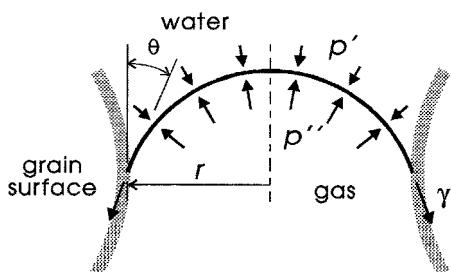


Figure 6-2. Forces acting on a meniscus spanning a pore. Surface tension γ causes a pressure difference between p' and p'' . The angle θ , between the solid and fluid-fluid interface, is measured through the denser fluid.

A body of gas tends to rise through interconnected pore space as a continuous filament, as shown in Figure 6-3. The filament penetrates the largest interconnected pores because they offer the least resistance. Flow is obstructed if the gas body encounters smaller pores, and cannot resume until the height of the gas body increases enough to overcome the obstruction. This can be accomplished with the accretion of other gas bodies moving up from below; consequently, buoyant flow is often intermittent. There are no physical limits to the distance gas can migrate by buoyant flow: it will continue as long as any part of the gas body can move upward (Schowalter 1979).

Diffusion

Diffusion is the net flow of molecules down a chemical concentration gradient, in flow driven by constant random molecular motion. A gas may diffuse through a gaseous mixture or through water. The process is described in Figure 6-4. Net flow rate is determined by the freedom of movement that diffusing molecules have in the medium. Diffusing molecules meet resistance by colliding with molecules moving in opposing directions. Diffusion of a solute is always accompanied by counter-current diffusion of the solvent to maintain a mass balance.

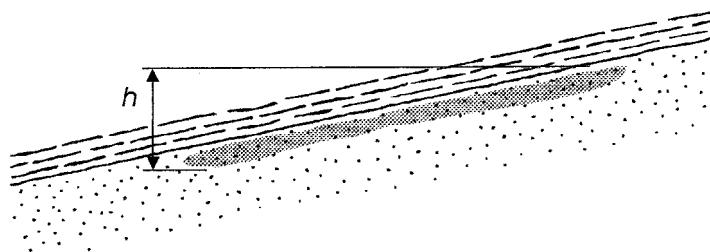


Figure 6-3. Gaseous phase filament moving up-dip in a sandstone stratum capped by a shale seal. Driving force at leading edge of filament is proportional to height h .

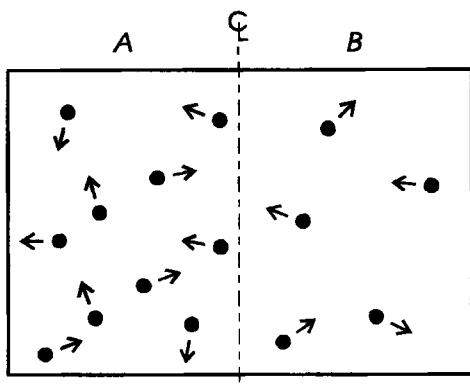


Figure 6-4. Molecular diffusion of a solute in a fluid medium. Solute molecules only are shown. Molecules in random motion. During some time period, on average, a fraction of molecules in region A will move to the right, and the same fraction in region B will move to the left. Because there is a greater concentration of molecules in region A, net flow is to the right.

Diffusion is a mechanism of dispersal. In an open system the diffusing substance will become so widely distributed that it is effectively eliminated. In a closed system, net flow continues until the concentration gradient is leveled. Diffusion flow of a gaseous phase into water will continue until the solubility limit of the gas has been reached.

Diffusion flow of gas is orders of magnitude slower than bulk flow or buoyant flow. It can be significant over geologic time periods (millions of years), or over very short distances (microscale). It is a factor in gas flow in the unsaturated zone, and in gas migration from petroleum source rocks and coal into surrounding strata.

This *molecular diffusion* should not be confused with *eddy diffusion*, which refers to dispersal in an observably turbulent medium. Eddy diffusion is an important mode of dispersion of hazardous gas in an underground atmosphere. Molecular diffusion is hereafter referred to simply as diffusion.

Diffusion in Water and Gas

Net flow by steady-state diffusion is described by Fick's first law:

$$J = -D \frac{\Delta c}{\Delta x} \quad (6-13)$$

where J is particle flux in one dimension ($\text{mol cm}^{-2} \text{ s}^{-1}$), D is the *diffusion coefficient* ($\text{cm}^2 \text{ s}^{-1}$), Δc is change in amount concentration along the concentration gradient (mol cm^{-3}), and Δx is length of the concentration gradient (cm). The

Table 6-3 Diffusion Coefficients for Gases in Air at 1 Atmosphere Total Pressure

Gas	Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)			
	5°C	15°C	25°C	36°C
Methane	0.194	0.207	0.220	0.233
Hydrogen sulfide	0.146	0.155	0.166	0.176
Carbon dioxide	0.137	0.146	0.155	0.164
Nitrogen	0.180	0.191	0.204	0.215
Oxygen	0.182	0.193	0.205	0.217
Water vapor	0.186	0.200	0.214	0.228

Reported values may vary by a factor of 2.

Source: Lerman 1988, p. 105.

minus sign indicates that net flow is from high to low concentration. Alternatively, flux can be calculated in $\text{g cm}^{-2} \text{ s}^{-1}$, using mass concentration.

The diffusion coefficient expresses the ease with which diffusing molecules move through the medium. It is a function of the size of the diffusing molecules, the nature of the medium, and temperature. Diffusion coefficients for several gases in air and in water are shown in Tables 6-3 and 6-4, respectively. Note from these tables that gas diffusion in water is about four orders of magnitude slower than in air.

The rate of change in concentration of the diffusing substance at a particular point is described by Fick's second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (6-14)$$

Solving this equation requires specifying one boundary condition for time and two for space. The solution for diffusion from semi-infinite space 'A' into semi-

Table 6-4 Diffusion Coefficients for Gases in Water

Gas	Diffusion coefficient ($10^{-4} \text{ cm}^2 \text{ s}^{-1}$)			
	5°C	15°C	25°C	35°C
Methane	0.095	0.131	0.173	0.222
Hydrogen sulfide	0.110	0.151	0.200	0.256
Carbon dioxide	0.106	0.146	0.193	0.247
Nitrogen	0.111	0.153	0.202	0.258
Oxygen	0.126	0.174	0.230	0.294

Reported values may vary by a factor of 2 to 3.

Source: Lerman 1988, p. 96.

infinite space ‘B’, where the concentration of the diffusing substance in source ‘A’ remains constant, is (Thibodeaux 1979, p. 76):

$$\frac{c - c_s}{c_i - c_s} = \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \quad (6-15)$$

In this equation, c is the amount concentration of diffusing substance within space ‘B’ at distance x from the contact, at time t ; c_s is the constant concentration of diffusing substance at the contact; c_i is the initial concentration of diffusing substance in space ‘B’; and D is the diffusion coefficient for diffusing substance in space ‘B’. The term “erf” is the error function, a mathematical probability function. The error function is tabulated in Table B-8, in Appendix B.

Diffusion in Porous Media

Molecular diffusion in porous media is restricted to tortuous paths along interconnected pores. The net flow rate is considerably slower than it would be in pore fluids absent the solid matrix. Diffusional flux through porous media is described by:

$$J = -D_{\text{eff}} \frac{\Delta c_{\text{fluid}}}{\Delta x} \quad (6-16)$$

where J is particle flux per unit total area, D_{eff} is the *effective diffusion coefficient*, and Δc_{fluid} is the change in amount concentration of diffusing substance in the pore fluid over distance Δx along the concentration gradient. This equation assumes that pore spaces are large compared to the mean free path length of diffusing molecules, so that interference by collisions with pore walls can be neglected. This assumption is valid for diffusion in permeable soils and rocks.

The effective diffusion coefficient can be derived from the coefficient for diffusion in the bulk pore fluid by:

$$D_{\text{eff}} \approx \frac{\phi}{\tau} D \quad (6-17)$$

where porosity ϕ accounts for the fraction of the bulk volume available to diffusing molecules, and τ represents the tortuosity of the pore space (Koorevaar, Menelik, and Dirksen 1983, p. 186). Tortuosity is the ratio of the length of the migration path between two points along the concentration gradient, to the straight line distance between them. For approximate work, $\tau = 2$. Numerous other relationships have been developed for estimating an effective diffusion coefficient for saturated and for dry soils and rocks (Nelson and Simmons 1995; Lerman 1988, p. 90–92, 102–104). It is apparent from Equation 6-17 that diffusion through porous media may be about four to ten times slower than through pore fluids alone.

The effective diffusion coefficient for partially saturated porous media can be approximated using the Millington equation:

$$D_{\text{eff}} = D \frac{(\phi - \omega_v)^{10/3}}{\phi^2} \quad (6-18)$$

where D is the coefficient for diffusion in air, and ω_v is volumetric water content (Stephens 1996, p. 42). Numerous other relationships have been developed for partially saturated porous media (Collin and Rasmussen 1988).

In petroleum reservoir engineering work, a slightly different approach is sometimes taken. The flux equation is (Krooss and Leythaeuser 1996):

$$J = -D'_{\text{eff}} \frac{\Delta c_{\text{bulk}}}{\Delta x} \quad (6-19)$$

where $D'_{\text{eff}} = D/\tau$, and $c_{\text{bulk}} = \phi c_{\text{fluid}}$. Comparison with Equations 6-16 and 6-17 shows that the end result is the same. This form is more easily applied to some published solutions for diffusion through homogeneous media of various geometries and boundary conditions (as in Equation 6-15, and in Crank 1975, and Cussler 1984).

Effective diffusion coefficients (D'_{eff}) for light hydrocarbons in saturated sedimentary rocks, ascertained from experiment, range from 8×10^{-2} to about $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (Krooss and Leythaeuser 1988). Gas migration by diffusion is a very slow process. Diffusion through sedimentary rocks (sandstone, siltstone, and claystone), as calculated from Equation 6-15, is shown in Figure 6-5.

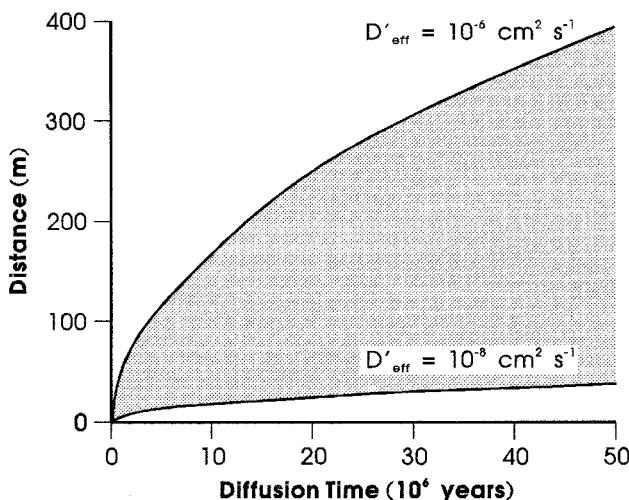


Figure 6-5. Diffusion distances over geologic time. Assumes diffusion into an infinite half-space, with constant bulk concentration c_s at the boundary and zero concentration c_i throughout the medium at the beginning of diffusion. Curves define a $c_s/2$ concentration front, and represent minimum and maximum diffusion distances to be expected, based on most probable range of effective diffusion coefficients for light hydrocarbons in saturated sedimentary rocks. (Adapted from Krooss 1987.)

GAS RETENTION

For a natural gas to reach hazardous concentrations, there must be a medium in place, either at the source or along a migration route, that will receive the gas and slow its dissipation into the surrounding environment. A receiving medium allows gas to accumulate. A gaseous phase can accumulate in pores and fractures in the unsaturated zone, and in reservoirs below the water table. A solution phase can accumulate in groundwater. An adsorbed phase can accumulate in organic strata. Gas in an accumulation is not necessarily static: gas may continually enter and leave the accumulation. The accumulation itself may be mobile, as in the case of gas in solution in migrating groundwater. This section describes the general nature of gas retention in the unsaturated zone, in groundwater aquifers, in conventional gas reservoirs, and in unconventional (tight) gas reservoirs.

Retention in the Unsaturated Zone

In the unsaturated zone, gas is held in gaseous phase in pores and fractures. Pore gas may be derived from atmospheric gas, possibly altered by bacterial decomposition of organic matter; or it may originate from below, consisting of bacterial, thermogenic, or geothermal gas that has migrated from deeper sediments.

A gaseous phase in a deep unsaturated zone is subject to weak dissipating forces. Barometric pressure fluctuations drive gaseous phase bulk flow into the atmosphere only in the upper few meters of sediment. Diffusion between the unsaturated zone and the atmosphere is a slow process and may not keep pace with the rate of entry of hazardous gas into the zone. Meteoric water infiltrating the unsaturated zone exchanges atmospheric solution gas with the gaseous phase in open pores; the effectiveness of this exchange depends on the local rate of groundwater recharge.

The significance of the unsaturated zone as a reservoir for hazardous gas depends on its porosity, thickness, and the concentration of hazardous gas it contains. Highly porous soils and porous or highly fractured rock above a deep water table can pose a risk to underground construction.

Retention in Groundwater Aquifers

Groundwater aquifers are the most common reservoirs of hazardous gas in the near-surface underground. They hold gas in solution, potentially in large amounts and in a mobile state. Groundwater may acquire bacterial, thermogenic, or geothermal gases anywhere along its seepage path. Acquisition is a function of a number of factors, including the charge rate of gas into solution from source strata or gaseous bodies, gas solubility, and groundwater flow rate. The amount of gas held in solution in an aquifer depends on its depth, temperature, porosity,

and physical dimensions. Gas escapes the groundwater reservoir by exsolution following a decrease in hydrostatic pressure, and by diffusion.

Conventional Gas Reservoirs

Conventional gas reservoirs are rare in the near-surface underground, but they have the potential to discharge gas at high volumetric flow rates into an excavation below the water table. A conventional gas reservoir consists of a porous medium, of moderate to high permeability, that contains a gaseous phase pore fluid. The gas is trapped in the reservoir by an overlying layer of impermeable material, or seal. The seal is configured along a migration route so as to arrest gaseous phase buoyant flow. Conventional reservoirs and the mechanics of how they capture and hold a gaseous phase have been studied extensively by workers in the petroleum industry. Reservoirs likely to be encountered in the near-surface underground operate on a much smaller scale than those sought by petroleum explorationists, but their mechanics are the same. Conventional gas reservoirs in the near-surface underground may contain bacterial, thermogenic, or geothermal gases.

Reservoir Soils and Rocks

Reservoir soils and rocks are porous and permeable enough to allow a gaseous phase to enter and accumulate. Storage capacity comes from matrix porosity, fracture porosity, or both. Reservoirs are almost always formed of sediments, which may be broadly classified into clastics and chemical precipitates. Clastics include erosion products such as aeolian, lacustrine, and marine sands; fluvial and colluvial sands and gravels; and the sedimentary rocks formed from them. Chemical precipitates include mineral matter formed at the site of deposition, such as crystalline limestones and dolomites, and occasionally chalks. Less common reservoir rocks include fractured igneous and metamorphic rocks, and porous volcanic rocks (Levorsen 1967).

The amount of gas retained in a conventional reservoir in the near-surface underground is:

$$V_g = A b \phi \left(1 - \frac{S}{100} \right) \left(\frac{p_r}{p_a} \right) \quad (6-20)$$

where V_g is volume of gas in the reservoir, at ground temperature and atmospheric pressure; A is reservoir area; b is reservoir thickness; ϕ is reservoir porosity; S is water saturation; p_r is total pressure on gas in the reservoir (hydrostatic plus atmospheric), and p_a is atmospheric pressure. Water saturation in conventional reservoirs typically ranges from 10% to over 50%; it is inversely related to reservoir permeability (Levorsen 1967, p. 153).

Seals

A seal is a continuous layer of saturated soil or rock capable of blocking buoyant flow of a gaseous phase. A seal may cap a carrier bed, as shown in Figure 6-3, or a reservoir. Seals are typically composed of fine-grained sediments such as clays, silts, mudstones, shales, and evaporites. Permafrost can form seals in perennially cold regions.

Seal capacity is the minimum buoyant pressure necessary for a gaseous phase to displace capillary water in the seal. It is a function of pore size. The relationship between capillary pressure and pore size was shown in Equation 6-12. Where pore size of the seal is very small compared to pore size of the reservoir, the maximum height of a gas column that the seal can hold is (Allen and Allen 1990, p. 353):

$$h_c = \frac{2 \gamma}{r_s G (\rho_w - \rho_g)} \quad (6-21)$$

where h_c is *critical height*, γ is surface tension of water, and r_s is a representative pore radius of the seal. Pore radius can be estimated from (Marle 1981, p. 23):

$$r_s = \sqrt{\frac{k}{\phi}} \quad (6-22)$$

where k is permeability and ϕ is porosity. Equations 6-21 and 6-22 are appropriate for order-of-magnitude estimates. Silty and clayey soils and rocks can develop enormous seal capacities. Water saturation is an essential condition of the seal. Without it, the gaseous phase would move through seal pores by bulk flow. A seal is not necessarily impervious to water, which can flow through the seal at a rate depending on hydraulic gradient and permeability.

Seal capacity is determined by the weakest point of the seal, the widest continuous opening through the sealing surface. Though capacity is not a function of thickness, thicker seals have a lower probability of defects, so tend to be more effective. A gaseous phase can leak by bulk flow through a small fracture in the sealing surface, at a rapid rate on a geologic time scale. An ideal seal is continuous over a wide area, and ductile. All rocks in the near-surface underground exhibit brittle behavior, which limits their ability to trap large accumulations. Gas will diffuse through seal pore water. Loss by diffusion can be significant over geologic time periods (Downey 1984).

Traps

A trap is composed of a reservoir, top and lateral seals, and possibly a bottom seal. It is the entire arrangement of soil or rock that can block buoyant flow of a gaseous phase. There are three general forms of traps: structural traps are formed by deformation of strata, stratigraphic traps are formed by variations in

lithology, and combination traps include elements of both. A few basic trap configurations are shown in Figure 6-6.

To accumulate a gaseous phase, a trap must lie on a migration path and must have formed prior to migration. Common charging mechanisms are short-range lateral migration (with a vertical component) along permeable carrier beds, and vertical migration through faults and fractures (Demaison and Huizinga 1994).

Groundwater in a reservoir containing a gaseous phase is typically undersaturated with gas, except close to the margins of the gaseous accumulation. Gas diffuses from the accumulation into the groundwater at a very slow rate, typical

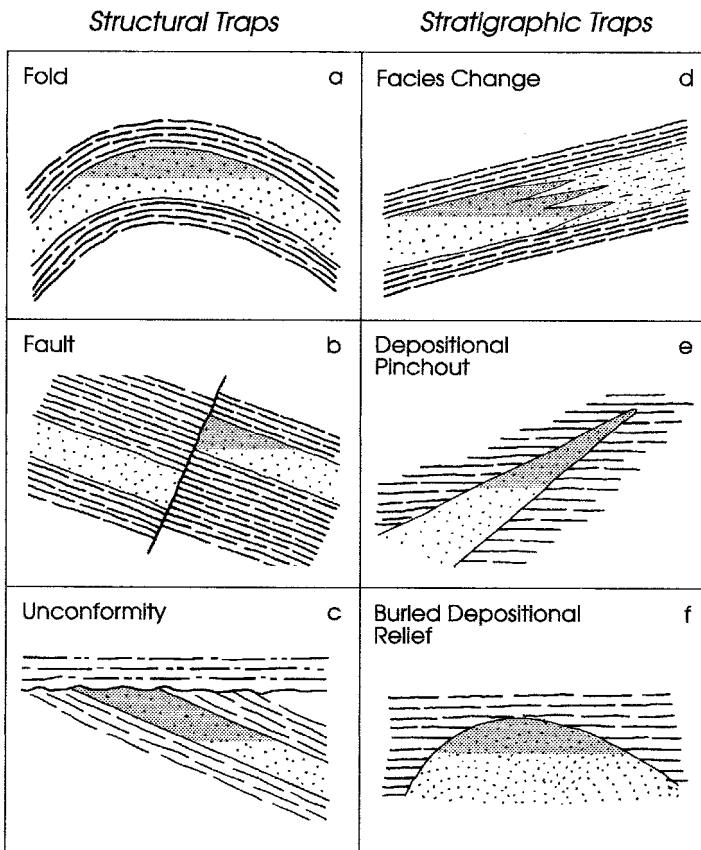


Figure 6-6. Basic forms of traps associated with conventional gas reservoirs. (Adapted from Biddle and Wielchowsky 1994.)

of diffusion flow. Groundwater flow rate through the reservoir is usually high enough to carry off solution gas before it can reach saturation levels (Dickey and Hunt 1972).

Traps in the near-surface underground that could hold potentially hazardous volumes of gas may be more subtle than Figure 6-6 suggests. A gaseous phase a few centimeters in height and a few meters in lateral dimension could, if released into an excavation, quickly generate a hazardous atmosphere. Traps this small may be impossible to locate in an exploration program but could be inferred from study of the site geology, local gas generating mechanisms, and potential migration routes.

Faults

Faults can be a factor in trap formation, in their charging with gas, and in leakage of their contents. An example of faulting in trap formation is shown in Figure 6-6b, where faulting has placed a reservoir material adjacent to a seal material. Faults may or may not offer open pathways for gas migration. Fault planes in regional tensional stress fields in the near-surface underground are generally transmissive; even very narrow openings are highly permeable. In active compressional settings, the fault plane is seldom an open fracture (Downey 1990).

Unconventional Gas Reservoirs

Unconventional gas reservoirs consist of low-permeability sedimentary rocks that contain bacterial or thermogenic gas generated within the reservoir, or thermogenic gas forced in under pressure from conterminous source rocks. They include rock or rock sequences of very fine grained sandstone, siltstone, organic shale, chalk, and coal (Rice and Shurr 1980; de Witt 1987). They retain gas in pores and fractures in solution phase, in gaseous phase, or in adsorbed phase on organic matter. Coal is unique among unconventional gas reservoirs because of its ability to retain adsorbed phase gas; its behavior is described in more detail in a following section. Unconventional reservoirs do not exhibit a consistent relationship between porosity and permeability, as conventional reservoirs generally do (Spencer 1985). Their permeability to gas is generally less than 0.1 md, exclusive of fracture permeability (corresponds to hydraulic conductivity of $1 \times 10^{-7} \text{ cm s}^{-1}$). Porosity may range from 5% in sandstones and shales to 25% in chalcs (Law and Spencer 1993).

The low permeability of unconventional reservoirs impedes gaseous phase migration necessary to form large accumulations, as occur in conventional reservoirs. They generally retain a gaseous phase in discrete, widely distributed stratigraphic traps. Reservoir permeability is derived primarily from the fracture network. Local permeability networks allow short-distance migration. Structural

traps may form in moderately porous unconventional reservoirs, such as chalks and some sandstones, that have been heavily faulted and folded (Spencer 1985; Rice 1981). The gas migrates from disseminated stratigraphic traps, along the fracture network, to the structural trap.

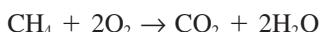
They are called unconventional reservoirs in the petroleum industry because they usually cannot be produced at economical rates from conventional wells without enhancing the hydraulic connection between the well and the fracture network, such as by hydrofracturing or use of explosives. Gas flow rate from the reservoir, in response to pressure reduction around a well or excavation, is mainly a function of fracture permeability.

BIOCHEMICAL AND GEOCHEMICAL CONSUMPTION OF GASES

Methane and hydrogen sulfide retain a significant amount of chemical energy and can serve as electron donors in biochemical and geochemical oxidation-reduction reactions. Oxygen is rapidly consumed in some geochemical reactions. Exposure to environments that support these reactions is a deciding factor in the preservation of these gases underground.

Methane Consumption

Methane that escapes anoxic environments may be consumed by the *methanotrophs*, a diverse group of aerobic bacteria that use methane as a source of energy and cellular building material. They are members of a larger group called the *methylotrophs*, bacteria that consume reduced carbon compounds containing no carbon-carbon bonds. Methanotrophs mediate the oxidation of methane in a series of reactions summarized by:



Methanotrophs are found in virtually every terrestrial and aquatic environment pervaded by both methane and oxygen (Hanson and Hanson 1996; Mancinelli 1995). Studies of stratified lakes show methanotrophs concentrated in a narrow depth interval along the top of the hypolimnion (bottom layer of water), where methane diffusing up from anoxic waters meets oxygen diffusing down from the epilimnion (top layer of water). Methanotrophs in sediments are similarly distributed along the interface of oxic and anoxic environments.

Methane is oxidized in anoxic environments on diffusing into a sulfate reduction zone. This process is not yet understood; it may occur through a consor-

tium of geochemical and biochemical reactions (Kiene 1991; Hoehler et al. 1994). Little of the methane that enters a sulfate reduction zone escapes oxidation.

Hydrogen Sulfide Consumption

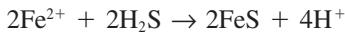
Geochemical Consumption

Hydrogen sulfide reacts with soluble iron and colloidal iron associated with clays to form iron sulfides in oxic and anoxic environments. Most terrigenous sediments contain enough iron to consume all bacterial hydrogen sulfide generated within them. Most marine carbonates and silicates are very limited in iron, which may allow hydrogen sulfide to accumulate. Reactive forms of iron include ferric iron (Fe^{3+}), and ferrous iron (Fe^{2+}). Ferric iron is the most stable form in oxic environments, and its compounds tend to be relatively insoluble. Ferrous iron is the most stable form in anoxic environments, and its compounds tend to be relatively soluble.

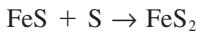
In the presence of hydrogen sulfide, ferric iron is reduced to ferrous iron (Widdel 1988):



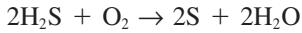
Ferrous iron reacts almost immediately with hydrogen sulfide to form ferrous sulfide, an insoluble black precipitate:



Ferrous sulfide combines with elemental sulfur to form pyrite, a reaction that may take years to complete (Berner 1970):



Hydrogen sulfide is also oxidized spontaneously by oxygen to form elemental sulfur:

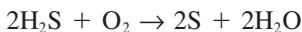


Sulfur produced in this reaction contributes to the formation of pyrite. Hydrogen sulfide in oxic waters has a half-life ranging from about 20 minutes to a week, depending on $\text{O}_2/\text{H}_2\text{S}$ ratio and pH (Morse et al. 1987). Reaction rates increase with increasing oxygen, and vary in a nonuniform manner with pH.

Biochemical Consumption

Hydrogen sulfide that escapes anoxic environments is used as a source of energy and cellular building material by the *colorless sulfur bacteria*. They are a diverse group of aerobic bacteria found in freshwater and marine environments, where they frequently inhabit the oxic-anoxic interface. The colorless sulfur bacteria

mediate the oxidation of hydrogen sulfide, in a series of reactions summarized by (Robertson and Kuenen 1992):



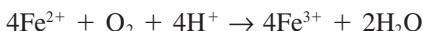
These bacteria compete with geochemical oxidation noted above.

Hydrogen sulfide is also consumed in shallow anoxic fresh and marine waters by the *phototrophic sulfur bacteria*, also known as the purple and green bacteria (Jørgensen 1983). The reaction is photosynthetic, with hydrogen sulfide acting as an electron donor.

Oxygen Consumption

Oxygen consumption is of interest in compressed air work in permeable ground. Air lost into the formation can be rapidly depleted of oxygen, in biochemical and geochemical reactions. This lost air, deficient in oxygen, can become a hazard if it flows back into the excavation following a reduction in working pressure, or if it migrates into a nearby excavation or underground structure. Oxygen consumption in biochemical reactions has been described in Chapter 3.

Oxygen is consumed in geochemical reactions with reduced minerals, mainly ferrous iron. Oxidation of ferrous iron to ferric iron is represented by the reaction (Domenico and Schwartz 1990, p. 451):



Ferrous iron is soluble and the most common form of iron in groundwater (Hem 1985, p. 77). Ferrous iron concentrations in groundwater can reach 50 mg L^{-1} in anoxic groundwaters in iron-rich sediments (Driscoll 1986, p. 98). Groundwaters high in iron may initially appear clear; upon exposure to air they become slightly cloudy and eventually precipitate a rust-colored deposit. The reaction of ferrous iron with oxygen is rapid: oxygen concentration in air within an anoxic, iron-rich deposit may decline significantly in a matter of minutes to a few hours (Kohyama and Hayashi 1972).

BACTERIAL GAS FLOW AND RETENTION

Bacterial gases consist mainly of carbon dioxide, hydrogen sulfide, and methane, and for the most part are generated at burial depths less than 1000 m (Rice and Claypool 1981). Bacterial gases are exposed to destructive and disseminating forces at these shallow depths, which makes them less likely to survive long distance migration than thermogenic and geothermal gases. Bacterial gas reservoirs tend to be located close to the source. Gases are usually associated with

ongoing or recent bacterial activity, though some environments can retain bacterial methane for millions of years.

Bacterial Gases in the Unsaturated Zone

The unsaturated zone is relatively closely connected to the atmosphere. Infiltrating meteoric waters periodically recharge this zone with oxygen and dissolved organic matter, supporting aerobes that generate carbon dioxide. Aerobes acting on high concentrations of labile organic matter in the unsaturated zone may create a biological oxygen demand sufficient to turn pore space anoxic, and methane becomes the predominant gas generated.

Infiltration of meteoric water causes frequent and rapid environmental changes in the unsaturated zone, due in part to rapid exchange of gases between meteoric waters and the pore space. This can cause pore gas concentrations to fluctuate, though the effects decrease with depth. Two studies on the Central Great Plains of the United States show that carbon dioxide concentrations remain relatively constant throughout the year, below depths of about 6 m (Haas et al. 1983; Wood and Petraitis 1984).

Bacterial Gases in the Saturated Zone

Bacterial methane may be present in solution in groundwater or may be trapped in gaseous phase in conventional and unconventional reservoirs. Hydrogen sulfide may be present in solution. Bacteria cannot generate hydrogen sulfide in concentrations that approach its solubility in water, so it does not occur in the saturated zone in gaseous phase. Bacterial carbon dioxide may be present in solution but not in concentrations likely to constitute a hazard. It does not occur in the saturated zone in gaseous phase. (Factors that limit bacterial hydrogen sulfide and carbon dioxide generation are described in Chapter 3.)

Methane

Methane is generated in environments that are wet, anoxic, rich in labile organic matter, moderate in temperature, and low in sulfates. These environments include fluvial sediments, freshwater lake sediments and anoxic bottom waters, mires, glacial drift incorporating organics, deltas, marine sediments below the sulfate reduction zone, and landfills.

Shallow terrestrial sediments and lacustrine environments are relatively open systems that lack secure gas retention mechanisms. Most of the methane they generate escapes to the atmosphere or to subsurface oxic environments where it is consumed by methanotrophs. Gaseous phase methane escapes soft or permeable sediments and anoxic bottom waters by ebullition. Solution phase methane within local flow systems may be dispersed by groundwater flow. These open systems retain relatively small amounts of methane for short periods (in

geologic time), but they can retain enough methane to pose a hazard to nearby excavations.

Rapid burial of methane-generating environments isolates them somewhat from their surroundings, making gas accumulation and long-term retention more likely. Modes of rapid burial include sedimentation, glaciation, and human activities such as landfilling and paving. Progressive burial below the water table raises the solution phase retention capacity of pore waters. Burial in fine-grained sediments protects solution phase methane from being flushed out in migrating groundwaters, and it promotes the formation of seals to trap gaseous phase methane.

Bacterial methane generated in marine sediments may be retained for millions of years, in conventional and unconventional gas reservoirs (Rice and Claypool 1981). Bacterial methane is generated below the sulfate reduction zone, which may extend some tens of meters or more below the sediment surface. Hydrostatic pressure from the overlying water column retains large amounts of solution phase methane in pore waters, and fine-grained sediment helps to retain a gaseous phase. These retention mechanisms hold methane while traps and seals form with continued sedimentation. Subsequent lowering of sea level, uplift and erosion of sediments, or upward migration of groundwater causes hydrostatic pressures to decline, which may allow gaseous phase exsolution. A gaseous phase in permeable strata may migrate and accumulate in conventional reservoirs. A gaseous phase held in unconventional reservoirs may be underpressured with respect to normal hydrostatic pressure gradients, as a result of sediment cooling and dilation associated with uplift and erosion (Barker 1987; Rice 1992).

Carbonaceous deposits, such as lignite and subbituminous coal, may retain bacterial methane by adsorption on organic surfaces. Gas retention in coal is described in a following section on coal gases.

Hydrogen Sulfide

Hydrogen sulfide is generated in environments that are wet, anoxic, rich in labile organic matter, moderate in temperature, and high in dissolved sulfates. The most common of these environments are upper marine sediments and anoxic bottom waters, where sulfates are available from seawater. A few continental environments satisfy the conditions for sulfate reduction; among them are marine sedimentary rock or rock sequences containing evaporites, such as gypsum and anhydrite.

Sulfate reduction is the principal process of organic matter decomposition in marine sediments. Because the sulfate reduction zone is a relatively open system, marine sediments do not retain bacterial hydrogen sulfide for geologic time periods, as they may retain methane. Generation and consumption of bacterial hydrogen sulfide is shown in Figure 6-7. In medium- to fine-grained organic-rich marine sediments, aerobic bacteria and benthic organisms consume all the

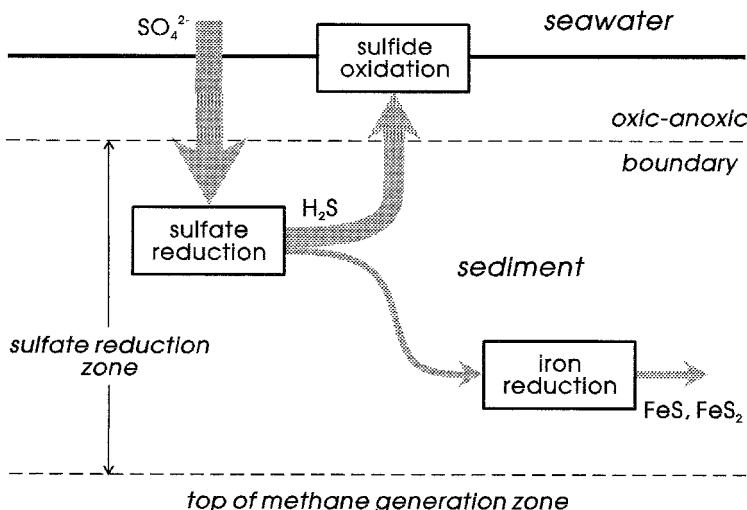


Figure 6-7. Bacterial hydrogen sulfide generation in marine sediments. Thickness of sulfate reduction zone varies from centimeters to tens of meters. (Adapted from Jørgensen 1977.)

dissolved oxygen within the upper few centimeters of sediment, establishing the oxic–anoxic boundary. The rate of sulfate reduction is greatest just below this boundary, and declines rapidly with increasing depth. Most or all of the hydrogen sulfide generated diffuses upward into the oxic zone, where it is biochemically or geochemically oxidized. Some is consumed in iron reduction reactions in the sediment. Iron is not limiting in marine sediments, except for those consisting almost entirely of biogenic carbonates and silicates (Berner 1985). Hydrogen sulfide generated in marine environments can become a hazard if pore waters are drawn from an active sulfate reduction zone into an excavation.

Continental environments can generate hazardous concentrations of hydrogen sulfide but, like marine environments, do not appear to retain ancient accumulations. Hydrogen sulfide in continental environments is likely to be found close to its source: it would be consumed in iron-bearing sediments and oxic waters before it could migrate long distances. Hazardous concentrations have been encountered in marine carbonates containing evaporites and organic matter.

COAL GAS FLOW AND RETENTION

Gases found in coals are commonly thermogenic, consisting mainly of methane with small proportions of carbon dioxide and higher hydrocarbon gases. By the

time coal has reached high volatile bituminous rank, it has generated far more thermogenic methane than the coal can retain. Excess methane expelled into surrounding strata may constitute a more serious hazard to underground construction than gas held within the coal.

Gas is retained in coal in three phases: 1) in solution in bulk water, 2) in gaseous phase within pores and fractures, and 3) in an adsorbed phase on organic surfaces. Solution and gaseous phases are common to inorganic reservoir soils and rocks. The adsorbed phase is unique to carbonaceous deposits. Adsorption capacity enables coal to retain several times more gas per unit volume than any other natural reservoir at comparable pressures.

Porosity and Permeability of Coal

The behavior of coal as a gas reservoir depends to a large degree on the nature of its pores and fractures. Small pores contribute most of the organic surface area that holds gas in the adsorbed phase. Large pores and fractures hold gas in gaseous and solution phases, and channel bulk flow. The nature of pores and fractures varies with rank, mineral content, and geologic history of the coal bed.

Pores originate from the remnant cellular structure of organic matter, and spaces between maceral and mineral particulates (Gamson, Beamish, and Johnson 1993). They occur in a range of sizes, from macropores (greater than 500 Å) to mesopores (20 to 500 Å) to micropores (less than 20 Å). Micropores are comparable in dimension to gas molecules (diameter of CH₄ = 4.36 Å; see Figure C-1, Appendix C), they are accessible to gas but are generally inaccessible to water. Macropores make up most of the pore volume in low-rank coals; their volume declines with physical compaction. Micropores make up an increasing proportion of total pore volume with coalification; in high rank coals they make up most of the pore volume (Gan, Nandi, and Walker 1972).

The internal surface area of coal is derived from organic matter; it ranges from about 150 to 250 m² g⁻¹ among lignites and subbituminous coals, to 50 to 100 m² g⁻¹ for high volatile bituminous coals, to 100 m² g⁻¹ for anthracites (Grimes 1982). The decline in surface area in middle rank coals is due to plugging of micropores by wet gases and heavier hydrocarbons generated at that stage of coalification. Micropores become more accessible in high rank coals as these hydrocarbons are thermally cracked to gas (Levine 1993).

Coal permeability is derived from a network of fractures and from cavities associated with original plant fragments (Gamson, Beamish, and Johnson 1993). Fracturing is induced by compaction, by contraction associated with expulsion of water and gases, and by tectonic displacement (Close 1993). Bright, high rank coals, low in mineral content, exhibit well developed fracture networks. Dull coals, high in mineral content, are more resistant to fracturing. The nature of coal permeability is shown in Figure 6-8.

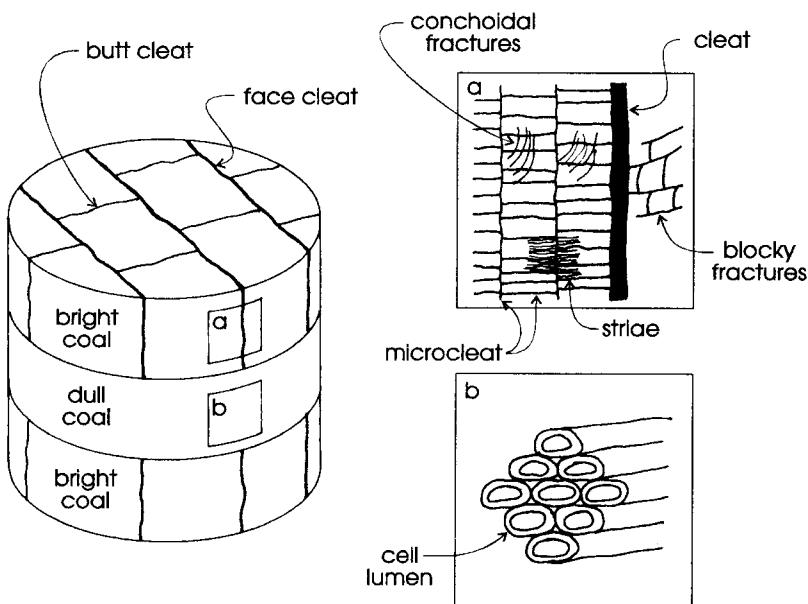


Figure 6-8. Conceptual fracture network in core sample of coal. Not to scale. (Adapted from Gamson, Beamish, and Johnson 1993.)

Visible fractures in coal are called *cleats*. The primary fracture network is made up of two sets of orthogonal, essentially vertical fractures called *face cleats* and *butt cleats*. Face cleat is more prominent and more likely to be continuous. Face cleat often strikes perpendicular to major fold axes and faults, forming a regional fracture pattern. Butt cleat is discontinuous, usually terminating at a face cleat. Primary cleat spacing typically ranges from a few centimeters to a few millimeters (Close 1993; Rogers 1994, p. 99–106). Blocks of coal defined by face and butt cleats and bedding surfaces are further broken by subordinate cleats and microfractures, which develop subsequent to the primary fractures. In this text, microfractures are defined as fractures too small to be visible. Subordinate cleat and microfracture spacings are on the order of 0.1 to 100 μm (Gamson, Beamish, and Johnson 1993).

Macropores and fractures constitute most of the effective porosity of coal; they hold water and gas in the same manner as pore space in conventional reservoirs. Effective porosity estimated from water contents of coal in place varies from a high of over 30% in lignites, to a low of about 1% to 5% in medium volatile bituminous coals, to about 10% in anthracites (Grimes 1982). Fracturing contributes to the rise in porosity from middle to high rank coals (Das et al. 1991). Cleat porosity generally ranges from less than 1% to about 2% (Close 1993).

Gas Retention Capacity of Coal

Retention capacity is the maximum amount of gas that a particular coal can hold under specific temperature and pressure conditions. It includes solution, gaseous, and adsorbed phases. Retention capacity is influenced mainly by pressure, rank, and water and mineral matter contents.

Adsorption and Adsorption Isotherms

Adsorbed phase gas is predominant in all coals; it accounts for 90% to 98% of the total amount of gas held in high rank coals (Gamson, Beamish, and Johnson 1993). Adsorbed phase gas molecules attach to organic surfaces by van der Waals forces, forming a single layer, or monolayer. Gas molecules in the monolayer can become so closely packed that their density approaches that of a liquid.

Micropores contain both adsorbed and gaseous phases in dynamic equilibrium; there is a constant exchange of molecules across the phase interface. This is the same exchange that occurs between a volatile liquid and its vapor phase in a closed headspace. The state of equilibrium is determined by temperature and pressure. The influence of temperature and pressure on gas adsorption in coal is shown in Figure 6-9. The curves in the figure are *adsorption isotherms*. The adsorption curves flatten at high pressures as adsorption sites become filled. Maximum adsorption capacity is reached at pressures below 100 atm (Jolly, Morris,

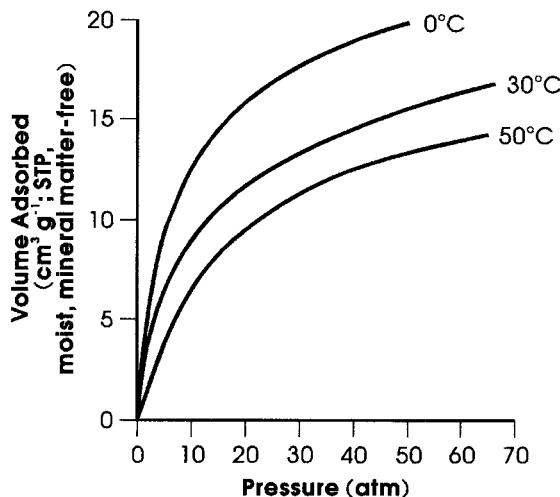


Figure 6-9. Typical adsorption isotherms for methane in coal. (From Kim 1977.)

and Hinsley 1968). Adsorption isotherms can be defined by the Langmuir equation (Yee, Seidle, and Hanson 1993):

$$V = V_{max} \left(\frac{B p}{1 + B p} \right) \quad (6-23)$$

where V is adsorbed gas content (volume of gas per unit weight or per unit volume of coal), p is total pressure on the gaseous phase, and V_{max} and B are empirical constants. The term V_{max} represents maximum gas adsorption capacity, and B represents the initial slope of the isotherm at very low pressures (units of reciprocal pressure).

Adsorption isotherms are determined from laboratory tests on wet or dry samples of coal that have been crushed and placed in a sealed container. The container is evacuated to remove residual gases from the coal. The container is then charged with gas, at constant temperature, over a range of pressures, and the amount of gas adsorbed by the coal is measured. The constants V_{max} and B are determined by curve-fitting the experimental data (for example, Rogers 1994, p. 125–129).

Adsorption isotherms do not account for gaseous and solution phases held in macropores and fractures. The relative contribution of these phases to total gas content depends on effective porosity, water content, and pressure. In tests on dry samples of British coal, from subbituminous to anthracite ranks, the gaseous phase averaged about 25% of maximum adsorption volume at pressures from 35 to 80 atm. At pressures below 10 atm the amount of gas held in the gaseous phase is relatively insignificant (Jolly, Morris, and Hinsley 1968). Gaseous and solution phases may make a small but significant contribution to total gas content in low-rank coals and in highly fractured coals.

Water reduces the gas adsorption capacity of coal by occupying adsorption sites and blocking access to pores. Gas adsorption capacity is inversely related to water content, up to a critical water content—the *adsorbed-water saturation capacity*. Water in excess of critical water content (bulk water) is contained mostly in macropores and fractures, is mobile, and has no influence on gas adsorption. Coal in place is commonly assumed to be at or above critical water content (Yee, Seidle, and Hanson 1993).

Water has a strong tendency to adsorb to oxygen in coal matrix macromolecules; consequently, the critical water content is related to oxygen content of coal. The reduction in gas adsorption capacity of coal in place can be expressed on the basis of oxygen content, as shown in Figure 6-10. Gas adsorption capacity of low-rank coals is considerably diminished by adsorbed water. The oxygen content of lignite is about 20% (wt.), and of subbituminous coal is about 10% (Mukhopadhyay and Hatcher 1993). The oxygen content of coal can be determined from ultimate analysis (ASTM D 3176).

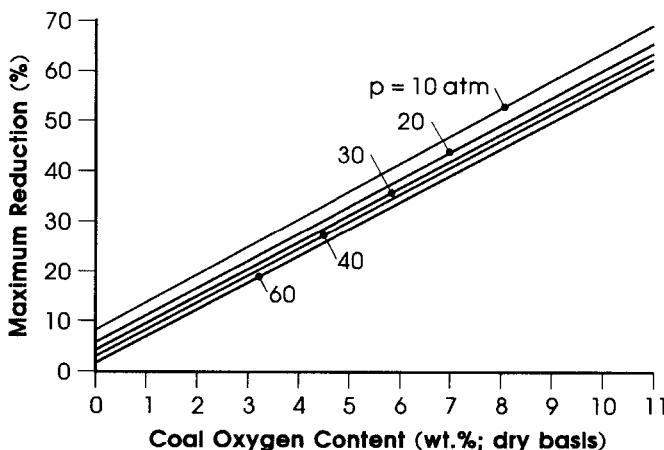


Figure 6-10. Reduction in methane adsorption capacity in coals above critical water content, in relation to dry coal, at 30°C. From tests on high volatile B to low volatile bituminous coals. (From Joubert, Grein, and Bienstock 1974. © 1974 Elsevier.)

The reduction in methane adsorption capacity at water contents below the critical water content can be estimated using the Ettinger equation:

$$\frac{V_w}{V_d} = \frac{1}{1 + A \omega} \quad (6-24)$$

where V_w and V_d are the amounts of methane adsorbed in wet and dry coal, respectively; ω is bed moisture content of coal (%); and A is an empirical constant equal to about 0.3 for low volatile to high volatile bituminous coals (Joubert, Grein, and Bienstock 1974).

Mineral matter has virtually no capacity to adsorb gas; it diminishes gas adsorption capacity by diluting the concentration of carbonaceous material. The effect is shown in Figure 6-11. The figure was developed from tests on samples of a coal seam and its floor and roof strata, all containing carbonaceous material of the same rank. Coaly particles distributed in a predominantly mineral matrix exhibit the same gas adsorption characteristics as solid coal, on a mineral-matter-free basis (Barker-Read and Radchenko 1989; Yee, Seidle, and Hanson 1993).

The adsorptive properties of coal enable it to capture any gas that migrates through it, up to its adsorption capacity. Thermogenic gases generated with petroleum may migrate to and become adsorbed in coal in the same basin. Carbon dioxide has been reported in coal in concentrations up to nearly 100% (Rice 1993). Coal preferentially adsorbs carbon dioxide over methane by a volume ratio of nearly two to one, at pressures below 100 atm (Yee, Seidle, and Hanson 1993).

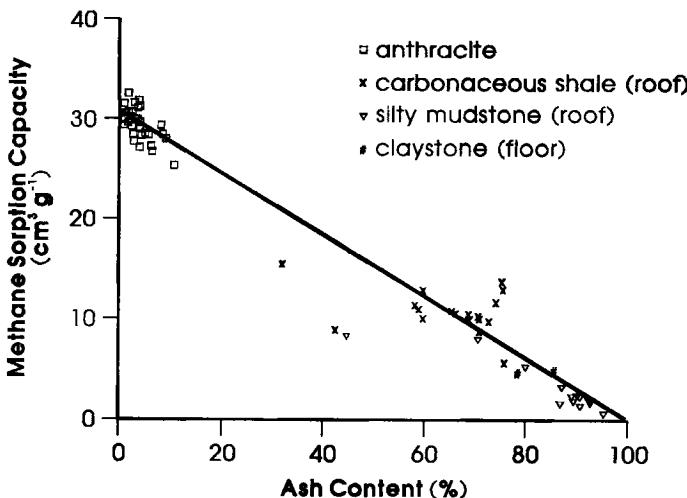


Figure 6-11. Effect of mineral matter content on methane sorption capacity of coal bed and adjacent strata, at 25°C and 40 atm. The rank of carbonaceous material in each stratum is identical. “Sorption capacity” includes adsorbed and gaseous phases. (Adapted from Barker-Read and Radchenko 1989. © 1989 Elsevier.)

Estimating Adsorption Capacity

The U.S. Bureau of Mines has developed a method for estimating methane adsorption capacity of coal on the basis of rank (Kim 1977). Two factors that influence adsorption, accessibility to micropores and water content, are rank-related. The method was developed using data on vitrinite-rich high rank coals.

The relationship between adsorption capacity and rank is based on the equation:

$$V = k p^n - b \theta \quad (6-25)$$

where V is the volume of gas adsorbed ($\text{cm}^3 \text{ g}^{-1}$; on a dry, mineral-matter-free basis), p is pressure on the gaseous phase (atm), and θ is temperature ($^\circ\text{C}$). The terms k , n , and b are empirical constants:

$$k = \left(0.8 \frac{FC}{VM} + 5.6 \right) \frac{\text{cm}^3}{\text{g atm}}$$

$$n = 0.4 - 0.013 k \quad (\text{dimensionless})$$

$$b = 0.14 \frac{\text{cm}^3}{\text{g } ^\circ\text{C}}$$

where FC is fixed carbon content and VM is volatile matter content, determined from proximate analysis (ASTM D 3172 to 3175).

Equation 6-25 can be modified to account for the condition of coal in place:

$$V = \left(\frac{100 - \omega - MM}{100} \right) \left(\frac{V_w}{V_d} \right) \left[k (0.097 h)^n - b \left(\theta_s + \frac{2.5}{100} h \right) \right] \quad (6-26)$$

The first bracketed term represents the organic matter fraction of the coal; ω is gravimetric water content and MM is mineral matter content (%), expressed on basis of total sample weight. The second bracketed term accounts for the reduction in methane adsorption capacity due to adsorbed water; tests showed a factor of 0.75 to be a reasonable approximation for high rank coals. In the third bracketed term, h is depth below ground surface. Gas pressure in the coal bed is assumed to equal hydrostatic pressure, and the water table is assumed to be close to ground surface. Temperature is assumed to equal annual average ground surface temperature θ_s plus an increase due to a geothermal gradient of 2.5°C per 100 m depth. Methane adsorption capacity of coal in place, based on Equation 6-26 and a ground surface temperature of 11°C , is shown in Figure 6-12. Low-

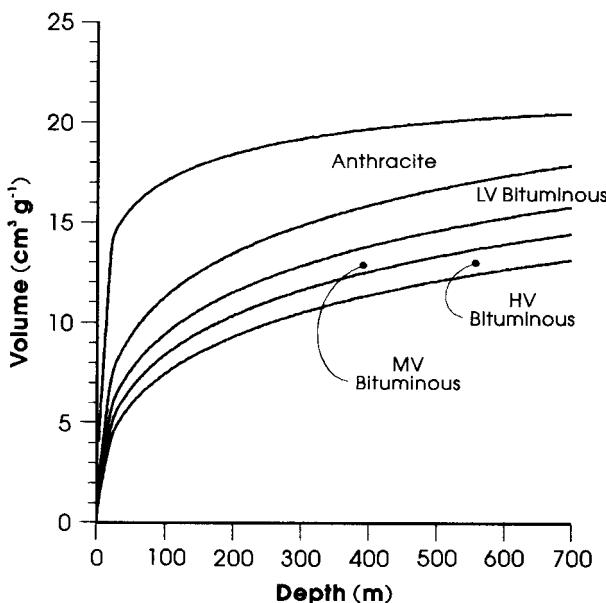


Figure 6-12. Estimated methane adsorption capacity of coal in place, from U.S. Bureau of Mines method. Basis of estimate described in text. Rank boundaries per ASTM, except upper anthracite boundary based on $FC = 95\%$ and $VM = 5\%$. (Adapted from Kim 1977.)

rank coals, not represented in the figure, can be estimated to contain as much as $2.5 \text{ cm}^3 \text{ g}^{-1}$ of adsorbed methane (Rice, Law, and Clayton 1993).

Actual Gas Content of Coal

The gas content of coal can vary significantly over short distances within the bed because of variations in moisture and mineral matter content, permeability and porosity of the coal and adjacent strata, and degree of fracturing. Heat from intrusive dikes and sills or geothermal groundwater flow can increase rank locally, increasing adsorption capacity. In estimating the gas content of coal beds using the Bureau of Mines methods summarized in Figure 6-12, it is commonly assumed that pressure on the gaseous phase in micropores is equal to hydrostatic pressure in surrounding strata. Often the gaseous phase pressure is significantly less, as shown in Figure 6-13. The coal is then said to be undersaturated with gas. Factors that contribute to underpressuring are described in Chapter 8.

The actual gas content of coal in place can be measured using a procedure known as the *direct method* (Kissell, McCulloch, and Elder 1973; Diamond and Levine 1981). In this method, the total gas content is equal to *lost gas + desorbed gas + residual gas*. A core sample of coal, 15 cm in length more or less, is placed in a sealed container as soon as it is retrieved from the core barrel. Desorbed gas is periodically released from the container through a valve, and the volume re-

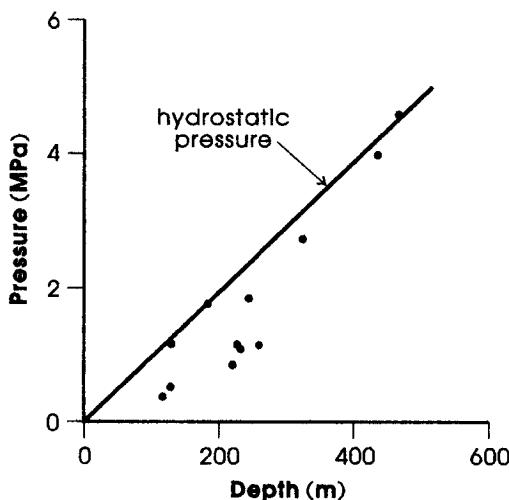


Figure 6-13. Gaseous phase pressure in coal beds. (Adapted from Zabetakis, Deul, and Skow 1973.)

leased is measured by water displacement. Lost gas is the volume of gas desorbed from the coal from the moment the coal was cored to the time it was placed in the sealed container. It is estimated by graphical projection of the rate of desorption over the core retrieval time, as shown in Figure 6-14. Residual gas is measured after desorbed gas ceases to be expelled from the sealed container. The coal sample is crushed in a sealed ball mill and the volume of gas released is measured. Residual gas represents gas that will not be released from coal into an excavation, following a reduction in pressure on the coal. Total gas content is expressed as volume of gas at STP conditions, per unit weight or unit volume of coal. The results are generally considered to be accurate within 30% (Kim 1977). Average gas contents of a variety of U.S. coals in place are shown in Table 6-5.

The direct method may underestimate the gas content of low-rank coals. They are highly porous and probably will lose much of their adsorbed gas during sampling and recovery (Choate, Johnson, and McCord 1984).

Gas Flow Through Coal and Surrounding Strata

Adsorbed phase gas in the coal matrix maintains an equilibrium with gaseous and solution phases in the macropore and fracture network; any upset in this equilibrium causes gas to flow. Gas flow in coal involves three interdependent

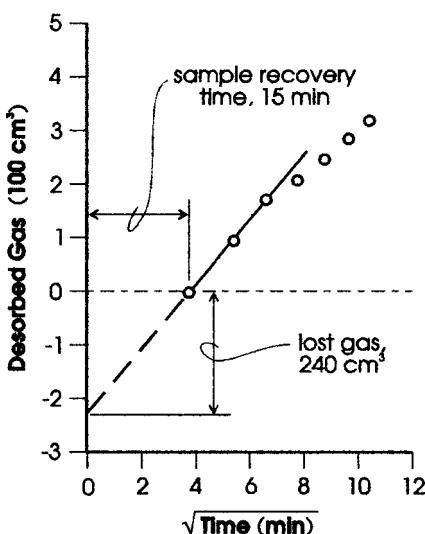


Figure 6-14. Lost gas curve for sample of Pittsburgh coal. (From McCulloch et al. 1975.)

Table 6-5 Gas Contents of Various U.S. Coalbeds

Coalbed	County, state	No. of samples	Depth (m)	Average gas contents ($\text{cm}^3 \text{ g}^{-1}$)			
				Lost and desorbed	Residual	Total	Rank
Anderson	Big Horn, Montana	7	120–150	0.1	0.0	0.1	Sub-A, HV-C
Wall	Big Horn, Montana	7	180–240	0.3	0.0	0.3	Sub-A, HV-C
Lower Fruitland Form.	San Juan, N. Mexico	9	180–260	1.2	0.3	1.5	HV-C, HV-B
Indiana No. V	Posey, Indiana	4	180–210	1.5	0.3	1.8	HV-B
Herrin No. 6	various, Illinois	10	210–300	1.7	0.4	2.1	HV-B
Castlegate "A"	Carbon, Utah	5	180–300	0.6	0.9	1.5	HV-A
		6	300–610	2.5	1.4	3.9	HV-A
		4	610–910	7.0	1.1	8.1	HV-A
Pittsburgh	Doddridge and Monongalia, W. Virginia	6	150–270	2.1	2.4	4.5	HV-A
Upper Kittanning	Barbour, W. Virginia	11	150–210	2.9	1.8	4.7	HV-A
Lower Kittanning	Barbour, W. Virginia	17	150–240	4.0	1.6	5.6	HV-A
Colorado "B"	Gunnison, Colorado	8	120–130	4.3	1.8	6.1	HV-A
Anderson	Garfield, Colorado	6	1010–1070	8.7	0.5	9.7	HV-A
Mary Lee	Jefferson, Alabama	8	300–304	10.3	0.4	10.8	HV
		13	300–340	14.3	0.3	14.6	LV
Lower Kittanning	Indiana, Pennsylvania	4	180	6.1	1.6	7.8	MV
Hartshorne	Leflore, Oklahoma	8	110–180	10.8	0.7	11.5	LV
		2	430	15.7	0.9	16.6	LV
Pocahontas No. 3	Buchanan, Virginia	11	400–550	13.6	0.8	14.4	LV
		11	550–700	15.0	1.1	16.1	LV
Various	Schuylkill, Pennsylvania	6	180–250	15.2	1.1	16.3	Anth.
		4	410–520	0.3	0.2	0.5	Anth.

Source: Adapted from Kertis, Ulery, and King 1983.

actions: 1) desorption of gas from organic surfaces into the gaseous phase in micropores, 2) diffusion of the gaseous phase through the micropore network, and 3) bulk flow of gaseous and solution phases through macropores and the fracture network. The manner and timing of gas flow into surrounding strata depends on gas content, retention capacity, and depth of burial of the coal, on the character of surrounding strata, and on the geologic history of the coal-bearing strata. Inorganic strata of coal-bearing sequences—the sandstones, siltstones, mudstones, and limestones—that possess matrix or fracture porosity can become highly charged with methane from conterminous coal beds and coaly shales, or entrained lenticular coal.

Coal begins to expel gas into surrounding strata at high volatile bituminous rank, when coalification has generated more thermogenic methane than the coal can retain. Strata surrounding the coal bed may be charged with large amounts of gas. A general relationship between methane generation and retention capacity for high rank coals is shown in Figure 6-15. Gas expulsion begins in coal micropores. As adsorption sites fill with gas, the gaseous phase concentration in micropores rises. Gaseous phase methane diffuses from micropores into the fracture network, saturating pore waters and extending the gaseous phase into macropores and fractures. The process is shown in Figure 6-16. The gaseous phase eventually fills the cleats, and is driven by bulk flow into surrounding strata. Pressures that drive gas from the coal bed dissipate rapidly in surrounding strata, limiting gaseous phase bulk flow to short distances.

Methane is also expelled from high rank coals in response to a drop in confining pressure, such as is associated with uplift and erosion of overlying strata. Gaseous phase methane moves from the fracture network into surrounding strata by bulk flow, followed by methane diffusion from micropores into the fracture network, then by methane desorption from organic surfaces into micropores, to reestablish equilibrium.

The rate of gas flow through high rank coal is controlled by diffusion and bulk flow, as the exchange between the adsorbed and gaseous phases in micropores is almost instantaneous. Diffusion in coal is a combination of Fickian diffusion, dominated by molecule-to-molecule interactions as described earlier in this chapter, and *Knudsen diffusion*, dominated by molecule-to-pore surface interactions. The effective diffusion coefficient for most coals ranges from about 10^{-7} to $10^{-14} \text{ cm s}^{-1}$ (Kolesar, Ertekin, and Obut 1990). The relative influence of diffusion and bulk flow on overall flow rate depends on the permeability of the coal. Bulk flow is the rate-limiting step in the near-surface underground, where close spacing of the fracture network limits diffusion distances (Kissell and Bielicki 1972).

Bulk flow of gaseous phase methane from coal is opposed by pressure mobilized in conterminous strata, the sum of hydrostatic and capillary pore water pressures. Coals overlain by permeable sandstone often contain less gas than

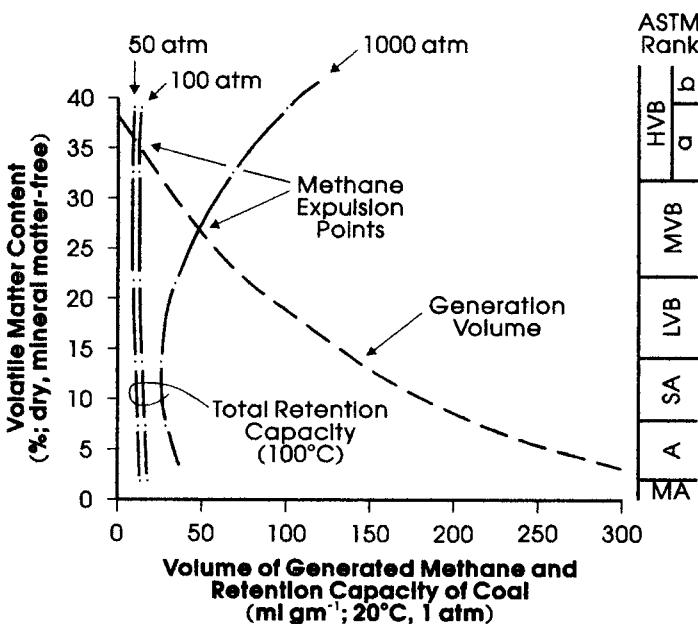


Figure 6-15. Methane generation and retention capacity of humic coal. Total retention capacity is sum of adsorbed and gaseous phases. The difference in retention capacity between 100 and 1000 atm confining pressures is largely due to gaseous phase storage in macropores and cleat. Generation volume based on mass balance analysis by Jüntgen and Karwell 1966, assuming start of “significant” methane generation at a volatile matter content of 37.8%. (Adapted from Meissner 1984.)

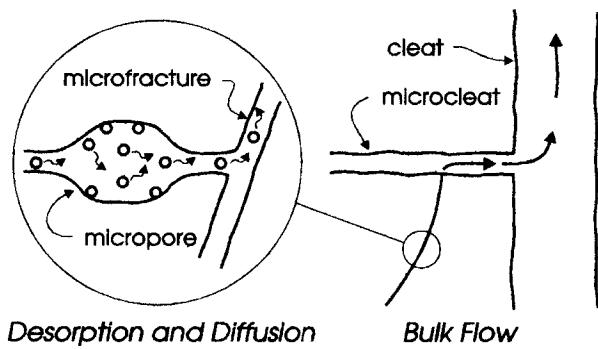


Figure 6-16. Conceptual illustration of methane flow in hard bright coal.

coals of equal rank and depth overlain by shales (Kertis, Ulery, and King 1983). Fractured coals tend to have lower gas contents than unfractured coals, as fracturing increases the permeability of the coal and surrounding strata. Gas that cannot escape through conterminous strata may migrate updip through fractures in the coal bed, possibly to outcrop. Low-rank coals may contain excess methane that has migrated from higher ranking coals lying underneath or downdip (Meissner 1984).

Gas that escapes the coal bed into surrounding permeable strata may migrate in gaseous phase by buoyant flow, and in solution in groundwater by bulk flow. It may also accumulate in gaseous phase in stratigraphic or structural traps. Low permeability strata conterminous to the coal bed, or containing coaly inclusions, may retain a gaseous phase in unconventional reservoirs.

PETROLEUM GAS FLOW AND RETENTION

Petroleum gases consist principally of methane, with subordinate amounts of higher hydrocarbon gases and carbon dioxide. Petroleum (crude oil and gas) is expelled from its source rock into surrounding strata during thermogenesis. Petroleum can migrate long distances from the source to be retained in soils, rocks, and groundwater in the near-surface underground. Petroleum gas that remains in source rock can be brought to shallow depths by uplift and erosion of overlying strata.

Primary Migration

Primary migration is the movement of petroleum from source rock into surrounding strata. Most gas escapes the source rock in solution in crude oil. In thermally mature, organic-rich source rocks ($\text{TOC} > 2.5\%$), the oil forms a continuous phase. It moves through kerogen, and through fractures or pore space in inorganic matrix, by bulk flow driven by pressure from overlying strata (Palciauskas 1991). Organic-poor source rocks ($\text{TOC} < 0.5\%$) or source rocks of low thermal maturity may generate too little oil to support bulk flow. Gas may also escape organic-rich or organic-poor source rocks by bulk flow in gaseous phase, in late stages of petroleum generation. This gaseous phase may include liquid-range hydrocarbons, which can dissolve in gas at high temperatures and pressures (Hunt 1996, p. 263–265). Bulk flow of oil or a gaseous phase through source rocks is directed toward an area of lower hydraulic head. In either case, primary migration may be directed up or down into conterminous strata.

Primary migration mechanisms of lesser importance include migration in solution in groundwater moving through the source rock, and diffusion through water-saturated pores (Hunt 1996, p. 257–263). These migration mechanisms are

significant only for methane and, to a lesser extent, ethane. Diffusion is limited to very short distances even over geologic time periods, such as into inorganic beds within source strata.

Secondary Migration

Secondary migration is the movement of crude oil and gas through water-saturated permeable strata outside the source rock. Oil migrates mainly by buoyant flow. Gas migrates in solution in oil, by buoyant flow in gaseous phase, by bulk flow in solution in water, and by diffusion.

In migrating by buoyant flow, crude oil and gas follow a tortuous path of least resistance through the largest interconnected pores until becoming trapped in a conventional reservoir, escaping to the surface, or being dissipated in solution in groundwater. Buoyant flow may be mainly lateral through carrier beds, or mainly vertical through faults and fractures (Perrodon 1983, p. 114–120). Oil may migrate vertically several hundred meters or more, and laterally 100 km or more through favorable strata. Buoyant flow of oil and gas is shown in Figure 6-17.

Oil and gas tend to separate along the migration route. As oil rises through strata, temperature and pressure decline. The gas solubility limit declines, and gas exsolves. Oil and gas are further separated by differential trapping. Individual traps encountered along the migration route may hold gas and spill oil out the bottom, or they may hold oil and leak gas through the seal (Perrodon 1983).

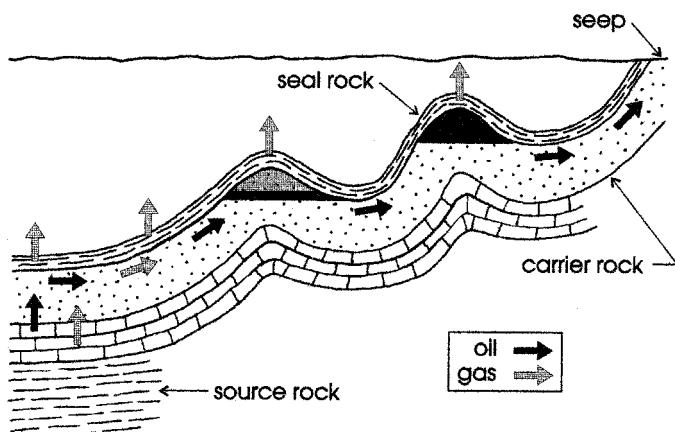


Figure 6-17. Secondary migration of oil and gas by buoyant flow through water-saturated strata.

Buoyant flow of gas occurs in a continuum of bubble sizes, from filaments extending several centimeters or meters through interconnected pores, to micro-bubbles. Filaments of gas tend to migrate through networks of large pores, fractures, and unconformities in a combination of lateral and vertical moves. Micro-bubbles are able to migrate through comparatively finer-grained sediments and microfractures. This *microseepage*, not constrained to high-permeability pathways, has a mainly vertical component. Microseepage is responsible for very low concentrations of petroleum gas (typically 10^{-6} to 10^{-4} mole ratio) often found directly over oil and gas reservoirs, in unsaturated soils within a few meters of ground surface (Klusman 1993, p. 42–47).

Petroleum gas also migrates by bulk flow in solution in groundwater. Circulating groundwaters may acquire gas deep in sediments and later release it from solution upon approaching the surface, as temperature cools and hydrostatic pressure declines (McAuliffe 1980). Groundwaters updip of the source may be saturated with gas, and the carrier bed may contain isolated bubbles of gas in pores. Enough gas may exsolve from rising groundwaters to coalesce into a gaseous phase capable of buoyant flow. Gaseous accumulations in conventional reservoirs have been attributed to gas exsolving from groundwater migrating updip (England, Mann, and Mann 1991).

Diffusion flow of gas can be important over short distances. Gas may diffuse into sealing strata from conterminous source rocks or from reservoirs. Diffusion flow cannot form gaseous accumulations in conventional reservoirs.

Gas Migration Through Oil and Gas Wells

Gas can migrate from deep petroleum reservoirs and carrier beds into the near-surface underground through oil and gas wells, as shown in Figure 6-18. In a common method of constructing oil and gas wells, the well is drilled into competent rock, and a surface casing is set and grouted in place. A borehole of smaller diameter is then drilled through the surface casing to the pay zone, which may be 1000 m or more deep. A production string is installed, and the annulus at the bottom of the production string is grouted to some distance above the pay zone. Much of the annulus remains open to strata between the surface casing and the bottom seal.

If the surface casing is sealed such that gas pressure can build in the annulus, the annulus provides a conduit for balancing hydraulic heads between lower and upper strata (Harrison 1985). Gas from lower strata can then enter upper strata. The annulus is pressurized by a gaseous phase escaping either porous or fractured ground above the bottom grout seal, or by leaking through the bottom seal. Some of this gas may go into solution in water in the annulus. Hydraulic head at any particular depth in the annulus is equal to the hydrostatic head of

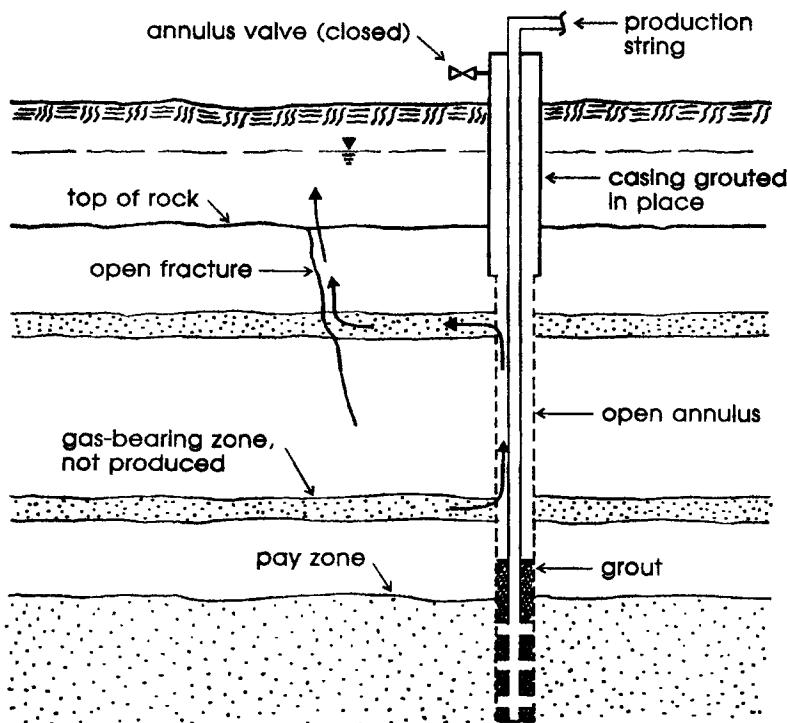


Figure 6-18. Gas migration through an oil or gas well into overlying strata. (Adapted from Harrison 1983.)

the water column above that point, plus the gage pressure head of gas in the surface casing. Gas or gas-charged water will flow from the annulus into any permeable strata where hydraulic head in the annulus exceeds that in the strata.

Oil and gas fields developed prior to enactment of government regulations addressing well abandonment procedures pose a risk of gas migration through deep wells. For example, more than 500 oil wells penetrating the Salt Lake Oil Field, a small field in Los Angeles, California, were improperly abandoned after the field was virtually depleted in 1937 (Cobarrubias 1992). Most wells in that field were severed 2 to 3 m below grade, and plugged with wood posts or debris. In another example, methane migrating through oil and gas wells has contaminated household water supply wells 1000 m or more away. Groundwaters from some wells were charged with combustible concentrations of gas (Harrison 1983; Harrison 1985). Higher than normal methane concentrations have also been ob-

served in coal mines, in the vicinity of oil and gas wells (Zabetakis et al. 1972; Wasson and Whieldon 1973).

Retention

Petroleum gas in the near-surface underground is most likely to be retained in solution in groundwater but may also be retained in conventional and in unconventional gas reservoirs.

Conventional petroleum gas reservoirs are rare in the near-surface underground. Factors working against the preservation of shallow conventional gas reservoirs include fractured ground and active groundwater circulation. Accumulations are usually far too small to be of commercial value, but even small accumulations pose a risk to excavations.

Unconventional reservoirs may be found in petroleum source rocks, or co-terminous low-permeability rocks that were charged with gas during petroleum generation. These reservoirs can be brought into the near-surface underground by uplift and erosion of overlying sediments.

Weathering of Petroleum

Petroleum retained in the near-surface underground is subject to weathering processes that tend to eliminate gaseous and gasoline-range hydrocarbons. Water washing and biodegradation are important, and generally concurrent, weathering processes.

Water washing is the progressive flushing of the most water-soluble compounds from crude oil (Lafargue and Barker 1988). Its effects are most severe on oil that is reservoired or has seeped to the surface. Its effects on migrating oil are generally minor. Water washing can occur independently of biodegradation in anoxic environments.

Biodegradation is the progressive elimination of low-molecular-weight hydrocarbon compounds, mainly by aerobic bacteria (Leahy and Colwell 1990; Palmer 1991). Biodegradation of crude oil occurs at the oil–water contact. Sulfate reducers and methanogens can utilize intermediate products of aerobic degradation of oil. Sulfate reducers and methanogens have very limited capabilities to decompose hydrocarbon compounds directly (Bossert and Bartha 1984). Biodegradation effects on crude oil are generally more severe than water washing.

Water washing and biodegradation tend to reduce if not eliminate gas dissolved in crude oil in the near-surface underground, even though gas is several times more soluble in oil than in water. Crude oil encountered in an excavation is a strong indicator that petroleum gas may be present in surrounding ground, but the oil alone would generally not contribute to an explosion hazard by releasing gas and gasoline-range hydrocarbons.

GAS RETENTION IN OIL SHALES

Thermally immature petroleum source rocks, also known as oil shales, may contain small amounts of methane, on the order of $1 \text{ cm}^3 \text{ g}^{-1}$ or less (Matta, LaScola, and Kissell 1977). Oil shale gas may be of bacterial or early thermogenic origin. Mechanisms of gas retention are not clear. Evidence indicates that at least some of the gas is adsorbed. Gas content appears to vary with organic matter composition, rather than organic matter content (Schatzel and Cooke 1994). This gas can pose a risk to an excavation made in the rock, as it is released with hydrostatic pressure reduction and breakup of the rock at the face.

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7

Natural Gas Inflow to Excavations

INTRODUCTION

An excavation in the near-surface underground introduces steep hydraulic energy and chemical gradients to a zone of variable extent around the excavation perimeter. These construction-induced gradients overcome existing gradients to draw gases toward the excavation. This chapter focuses on the forces that control gas inflow to tunnels and shafts during construction. These principles of gas inflow can be applied to other types of excavations and completed structures in the near-surface underground.

Gas in the ground constitutes a hazard to construction only if the gas is concentrated and mobile enough to enter an excavation in quantities that can generate a hazardous atmosphere. Gas inflowing at a low rate can generate a hazardous atmosphere in poorly ventilated areas of an excavation, often the tunnel heading. Gas inflowing at a high rate can overcome a ventilation system performing as intended. This chapter describes the relationship between the amount and mobility of gas in the ground, ventilation, and development of hazardous atmospheres.

Carbon dioxide and hydrogen sulfide in solution in groundwater can accelerate corrosion of metal. Hydrogen sulfide is odorous, and toxic to living organisms; its discharge into the atmosphere (with ventilation air) or waterways (in tunnel water) may raise environmental concerns. These problems are considered briefly.

HAZARDOUS CONCENTRATIONS OF GAS IN THE GROUND

For the purposes of this text, natural gases in the ground will be considered a geologic hazard where they can move from the ground to form concentrations in an excavation atmosphere that exceed allowable limits. This definition assumes that the volume of the contaminated atmosphere is relevant; that is, it is capable of injuring workmen by combustion, asphyxiation, or toxic reaction. There are two aspects to the eventuality of gas forming a geologic hazard: the concentration of gas in the ground, and its ability to move into the excavation.

Assume for the moment that gas can move freely through permeable ground into an excavation. Concentrations of gas in the ground that can generate maximum allowable concentrations in the excavation atmosphere are shown in Table 7-1. The gaseous phase concentrations are equal to maximum allowable concentrations in air, from Table 1-2. The solution phase concentrations will equilibrate to maximum allowable concentrations in air. Gas in the ground in concentrations exceeding these limits is considered here to be potentially hazardous.

Compare these potentially hazardous concentrations with gas concentrations most likely to occur in sediments. The following is a list of gases by manner of origin. For each gas, potential solution and gaseous phase concentrations are noted.

Bacterial methane. Solution concentrations can reach saturation concentrations to generate a 100% gaseous phase. Either phase can be a hazard.

Bacterial hydrogen sulfide. Solution concentrations can reach up to about 400 mg L^{-1} . This is well below saturation concentration, so a gaseous phase is not generated. The solution phase can be a hazard.

Bacterial carbon dioxide. Gaseous phase in unsaturated sediments may reach concentrations up to about 19%; it can be a hazard. Generation in saturated environments is limited by the solubility of oxygen, as noted

Table 7-1 Minimum Gas Concentrations Capable of Generating Maximum Allowable Concentrations in Air

Gas	Gaseous phase concentration (%)	Solution phase concentration ^a	
		(ml gas/ml water) ^b	mg L ⁻¹
Methane	1 ^c	3.48×10^{-4}	0.249
Hydrogen sulfide	0.001 ^d	2.57×10^{-5}	0.0396
Carbon dioxide	0.5 ^d	4.37×10^{-3}	8.63

^a Solution phase in water at 20°C and 1 atm.

^b Gas volume at 0°C and 1 atm.

^c OSHA limit (20% LEL).

^d ACGIH TWA.

in Chapter 3. Maximum solution concentrations are only about 50% greater than concentrations defined as potentially hazardous. It seems unlikely that environments containing maximum solution concentrations of bacterial carbon dioxide would be extensive and capable of generating heavy groundwater inflows to an excavation. Therefore, bacterial carbon dioxide in solution phase is not considered here to constitute a serious hazard.

Thermogenic methane. Solution concentrations can reach saturation concentrations to generate a 100% gaseous phase, even under relatively high hydrostatic pressure. Either phase can be a hazard.

Geothermal carbon dioxide. Solution concentrations can reach saturation concentrations to generate a 100% gaseous phase. Either phase can be a hazard.

Now consider the second aspect of a gas hazard, the ability of gas to move into the excavation. To pose a real hazard, gas in excess of concentrations shown in Table 7-1 must be capable of moving from the ground to the excavation in amounts that can occupy a significant portion of the atmosphere, a portion large enough to pose a combustion hazard, or an asphyxiating or toxic hazard to workers. To illustrate the significance of the ability of gas to move, consider the pore water in an organic clay stratum: it almost certainly contains bacterial methane in solution in excess of potentially hazardous concentrations. Yet very little gas can escape this impermeable material to enter the excavation. In a narrow sense, the organic clay poses no hazardous gas risk. (Taking a wider view, the clay can contribute dissolved organic substrates to groundwater in adjacent granular deposits. Bacterial methane generated in these deposits may easily enter the excavation. Organic clays, then, cannot be summarily dismissed as a source of hazardous concentrations of gas.)

HAZARDOUS GAS INFLOWS AND VENTILATION

The risk of a hazardous atmosphere developing during underground construction is reduced by ventilating tunnels and shafts. Ventilation dilutes incoming gas and removes it from the excavation, preventing it from forming a hazardous accumulation. But ventilation is commonly not entirely effective. It may be interrupted during overnight or weekend work stoppages, or periods of equipment breakdown or servicing. The tunnel face is sometimes poorly ventilated because of the difficulty of extending ventilation ducts through equipment congested there. Wheel chambers of soft ground TBMs, and hard rock TBMs lacking dust collectors, are typically not ventilated. In addition, a considerable portion of ventilation capacity can be lost to leakage and friction along far-reaching ducts. These common conditions allow low to moderate gas inflows to form hazardous accumulations over

a relatively short period of time. A rapid gas inflow can briefly overcome even a ventilation system performing as intended.

The amount of air that the ventilation system can deliver to the face of a tunnel or shaft is *effective ventilation capacity*. It can be expressed as a volumetric airflow rate, or average airflow velocity across the excavation opening. The effective ventilation capacity necessary to safely dilute gas inflowing at a particular rate can be determined from:

$$q_{ta} = \frac{q_g}{\phi_a} \quad (7-1)$$

where q_{ta} is volumetric airflow rate at the face ($\text{m}^3 \text{ min}^{-1}$), q_g is hazardous gas inflow rate at 100% concentration ($\text{m}^3 \text{ min}^{-1}$), and ϕ_a is allowable gas concentration (volume fraction) in the underground atmosphere. The relationship between ventilation capacity, hazardous gas inflow rate, and hazardous gas concentration in the excavation atmosphere is shown in Figure 7-1. Current U.S. Occupational

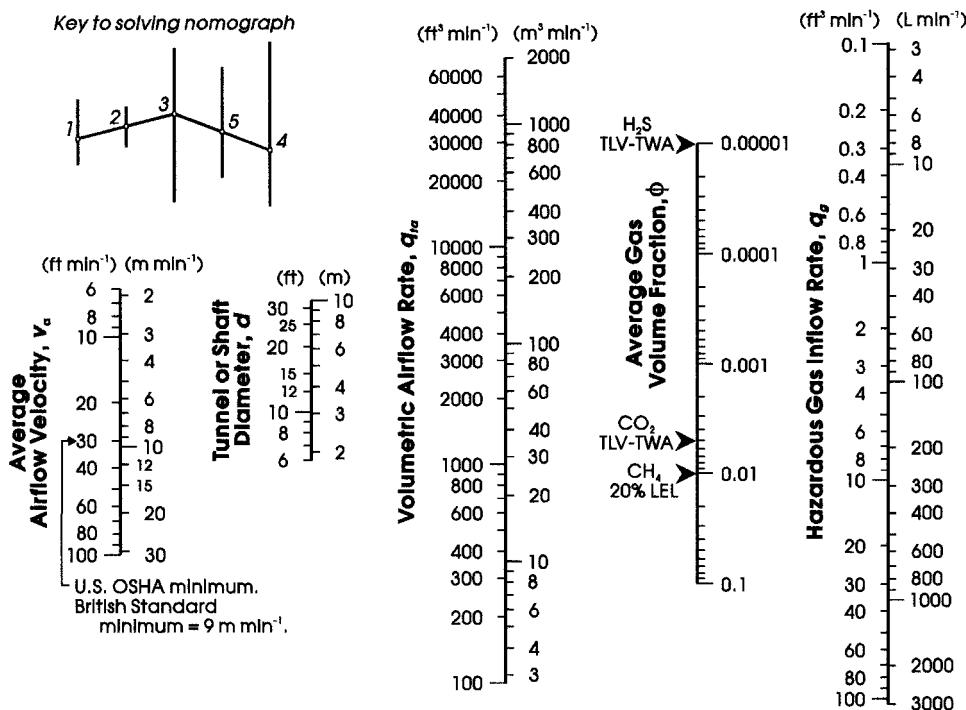


Figure 7-1. Relationship between tunnel ventilation capacity, hazardous gas inflow rate, and contaminant concentration in the tunnel atmosphere.

Safety and Health Administration Standards require a minimum airflow velocity of 30 ft min⁻¹ for normal tunnel and shaft construction (OSHA 1999, 29 CFR 1926.800.k.3). This compares closely with the British Standard minimum requirement of 9 m min⁻¹ (BSI 1990, BS 6164.15.2). For a given airflow velocity, a small reduction in excavation diameter reduces the volumetric airflow rate considerably, whereas the hazardous gas inflow rate is not as affected by excavation diameter. Consequently, the risk of developing a hazardous atmosphere is somewhat higher for smaller openings than for larger ones. The figure assumes that the ventilation system is entirely effective, an optimistic assumption.

Gas inflowing above explosive, asphyxiating, or toxic concentrations is hazardous until adequately diluted in the ventilating airstream. Rapid dilution minimizes the duration and volume of the hazardous concentration. Methane commonly enters an excavation in concentrations approaching 100%; adequate dilution requires lowering the concentration through the explosive range. Rapid dilution requires a turbulent airstream (Bielicki and Kissell 1974). To achieve it, it may be necessary to augment the main ventilation system with a simple blower fan directed at the gas inflow area.

Hazardous gas entering an excavation tends to stratify in the excavation atmosphere, another factor to consider in establishing ventilation requirements. This is called *layering* and is caused by the difference in densities between the incoming hazardous gas and normal air. Methane is lighter than air, so it tends to stratify in the roof of the excavation. Carbon dioxide and, to a lesser extent, hydrogen sulfide tend to stratify on the floor. Layering can be predicted using the empirical relationship (McPherson 1993, p. 429):

$$LN = \frac{v_a}{\left(G |\Delta SG| \frac{q_g}{W} \right)^{1/3}} \quad (7-2)$$

where LN is *layering number* (dimensionless), v_a is average airflow velocity in the excavation (m s⁻¹), G is gravitational acceleration (m s⁻²), $|\Delta SG|$ is the absolute difference in specific gravity between the inflowing gas and air, q_g is gas inflow rate (m³ s⁻¹), and W is width of the airway (m). For circular tunnels, W may be estimated as three-quarters of the diameter. Layering in a horizontal airway does not occur when the layering number is greater than or equal to 5. A gaseous phase inflow may consist of a mixture of gases, and its specific gravity should be based on the composition of the mixture. For methane inflowing at 100% concentration, in SI units, Equation 7-2 may be simplified to:

$$LN = \frac{v_a}{1.6} \left(\frac{W}{q_g} \right)^{1/3} \quad (7-3)$$

In a horizontal airway receiving even small inflows of hazardous gas, airflow velocities significantly higher than minimum required velocities may be necessary to prevent layering. Alternatively, layering can be prevented by directing a turbulent airstream at the area of inflowing gas. Once mixed in the excavation atmosphere, hazardous gas will not stratify.

GAS INFLOW TO EXCAVATIONS

Gas can enter an excavation in several ways: by bulk flow of groundwater; by gaseous phase bulk flow from the unsaturated zone, conventional gas reservoirs, or unconventional gas reservoirs; by excavation and physical disruption of porous ground containing gas; and by diffusion. Gas inflow from coal-bearing strata is considered a special case and will be described in a separate section.

Gas Inflow with Groundwater

Rate of Solution Gas Inflow

Most gas below the water table is held in solution. The principal mechanism of entry of this gas to an excavation below the water table is by bulk flow of groundwater. Pore water pressures on the perimeter of a freely draining excavation are reduced to zero. This reduction in pressure head causes steep hydraulic energy gradients to develop in ground surrounding the excavation. Groundwater moving into the excavation along these gradients carries solution gas with it. Gas inflow rate to the excavation can be estimated from:

$$q_g = q_{gw} L_{gw} \quad (7-4)$$

where q_g is gas inflow rate (L min^{-1}), q_{gw} is groundwater inflow rate (L min^{-1}), and L_{gw} is the Ostwald coefficient solution concentration of gas in groundwater outside the excavation (ml gas/ml water), at ground temperature and gas pressure of 1 atm. Estimating groundwater inflows to tunnel and shaft excavations is beyond the scope of this text, but understanding the character of these inflows is important to understanding gas inflows.

A flow net depicting groundwater flow to a tunnel in a homogeneous, anisotropic porous medium is shown in Figure 7-2. Tunnels are rarely constructed in such a medium; nonetheless, the figure illustrates important characteristics of groundwater flow in permeable strata, including fractured rock. An excavation draws groundwater from a wide area, altering and even reversing the direction of normal groundwater flow. The width of influence increases with the ratio of horizontal to vertical permeability. In sedimentary deposits, this ratio typically ranges from about 2 to 10 (Fitzpatrick, Kulhawy, and O'Rourke 1981). A subsurface exploration program focused on conditions along a narrow tunnel alignment may not identify solution gas reservoirs above, below, or laterally from the align-

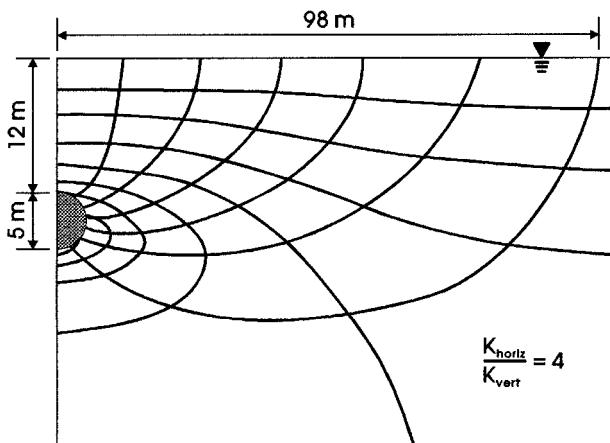


Figure 7-2. Flow net around tunnel in anisotropic porous media. (From Fitzpatrick, Kulhawy, and O'Rourke 1981.)

ment and may seriously underestimate the risk of gas entering the excavation from these distant reservoirs.

Distribution of Gas Inflows in Excavations

Groundwater inflows at the heading of an excavation in permeable strata are typically higher than steady state inflows, 2 to 5 times higher in rock having an equivalent hydraulic conductivity greater than about 1×10^{-4} cm s⁻¹ (Heuer 1995). Initial inflows are higher because flow at the heading is three-dimensional, hydraulic gradients there are steeper, and stored water is being drained. As the gas inflow rate is proportional to groundwater inflow rate, the highest local rate of gas inflow is at the heading, typically the most poorly ventilated area of a tunnel.

Total solution gas inflow rate to an excavation is proportional to total groundwater inflow rate. In a long, continually wet tunnel, gas inflow behind the heading may constitute a significant portion of total gas inflow. Under these conditions a blowing ventilation system would result in rising gas concentrations with distance from the heading; an exhausting system would result in rising gas concentrations with distance from the portal.

Exsolution of Gas From Groundwater

Gas entering the excavation in solution in groundwater is out of equilibrium with its gaseous phase in the excavation atmosphere, so tends to come out of solution. The rate of dissolution is directly proportional to the difference in concentrations

between gas in solution and in the atmosphere, the area of the air/water interface, and the diffusion coefficient of the gas in water (Thibodeaux 1979, p. 141; Benefield and Randall 1980, p. 281–285). Dissolution is especially rapid from deep groundwaters containing gas in excess of saturation concentration at 1 atm, and from groundwaters entering the excavation in a turbulent manner. Gas dissolution in tunnels is a complex phenomenon, and it appears no detailed studies of it have been reported in the literature. As an analogy, an investigation of the radon content of stream water showed that in turbulent streams, half of this solution gas was lost to air over a distance of about 30 m (Hawkes and Webb 1962, p. 71). Given this evidence of the rapidity of dissolution from turbulent waters, and the magnitude of the air/water interface for waters inflowing to tunnels, it seems reasonable and conservative to assume that equilibrium conditions between gas in tunnel water and in the tunnel atmosphere is established within a short period of time after the water enters the tunnel. This approximation should introduce insignificant error to predictive calculations, given the qualitative nature of groundwater inflow estimates to tunnels, and the potentially wide variation in gas concentrations in natural groundwaters.

The amount of gas retained in water in the excavation, after equilibrium conditions have been established with the excavation atmosphere, is generally negligible. Consequently, for the usual case it can be assumed that all gas entering in solution escapes to the excavation atmosphere. The following derivation shows why. A mass balance equation for gas flow through a section of tunnel is (Peterson 1997):

$$q_{gw} \rho_{ggw} = q_{gw} \rho_{gtw} + q_{ta} \rho_{gta} \quad (7-5)$$

where q_{gw} is groundwater inflow rate to the tunnel, ρ_{ggw} is mass concentration of gas in groundwater outside the tunnel, ρ_{gtw} is mass concentration of gas in groundwater that has entered the tunnel, q_{ta} is volumetric airflow rate in the tunnel, and ρ_{gta} is mass concentration of gas in tunnel air. Under equilibrium conditions, the gas concentration in tunnel water is related to that in tunnel air by:

$$\rho_{gtw} = K \rho_{gta} \quad (7-6)$$

where K is a partition coefficient related to Henry's constant. Solving Equation 7-6 for ρ_{gtw} and substituting into Equation 7-5:

$$q_{gw} \rho_{ggw} = q_{gw} \frac{\rho_{gta}}{K} + q_{ta} \rho_{gta} \quad (7-7)$$

Rearranging terms:

$$\rho_{ggw} = \left(\frac{1}{K} + \frac{q_{ta}}{q_{gw}} \right) \rho_{gta} \quad (7-8)$$

Solving for gas concentration in tunnel air:

$$\rho_{gta} = \frac{\rho_{ggw}}{\left(\frac{1}{K} + \frac{q_{ta}}{q_{gw}} \right)} \quad (7-9)$$

The partition coefficient K can be derived using Henry's law, $p_i = H_i x_i(aq)$ (Equation C-25). As an initial step, note that mass concentration of gas in water is proportional to its mole fraction $x_i(aq)$, where $x_i(aq) = n_i(aq)/n_w$ (Equation C-27):

$$\rho_{gw} = x_i(aq) \frac{M_i}{M_w} \rho_w \quad (7-10)$$

where M_i is molar mass of gas i (g mol^{-1}), M_w is molar mass of water, and ρ_w is mass density of water (g cm^{-3}).

The mass concentration of gas in air is:

$$\rho_{gta} = \frac{n_i}{V_i} M_i \quad (7-11)$$

where n_i is moles of gas in gaseous phase, and V_i is total volume of air. From the ideal gas law (Equation C-8), $n_i = p_i V_i / RT$. Substituting this into Equation 7-11 yields:

$$\rho_{gta} = \frac{p_i M_i}{R T} \quad (7-12)$$

Solving Equation 7-12 for p_i , and Equation 7-10 for $x_i(aq)$, then substituting each result into Henry's equation yields:

$$\rho_{gta} \frac{R T}{M_i} = H_i \frac{\rho_{gw}}{\rho_w} \frac{M_w}{M_i} \quad (7-13)$$

Solving for the concentration of gas in air:

$$\rho_{gta} = \left(\frac{H_i}{\rho_w} \frac{M_w}{R T} \right) \rho_{gw} \quad (7-14)$$

where the term in brackets is the dimensionless constant K from Equation 7-6. So at 20°C :

$$K = (H_i \text{ atm}) \left(\frac{\text{L}}{1000 \text{ g}} \right) \left(\frac{18.02 \text{ g}}{\text{mol}} \right) \left(\frac{\text{mol K}}{8.206 \times 10^{-2} \text{ L atm}} \right) \left(\frac{1}{293 \text{ K}} \right) \quad (7-15)$$

Partition coefficients for the subject gases calculated using Equation 7-15, and Henry's constants from Table B-3, are: $K_{CH_4} = 26.7$; $K_{H_2S} = 0.362$; and $K_{CO_2} = 1.065$. Returning to Equation 7-9, the q_{ta}/q_{gw} term for a ventilated tunnel will be a relatively large number. By inspection, the $1/K$ term has little significance, and can be dropped. Equation 7-9 then simplifies to:

$$\rho_{gta} \approx \rho_{ggw} \frac{q_{gw}}{q_{ta}} \quad (7-16)$$

which shows that under equilibrium conditions, gas concentration in tunnel air is a function of gas concentration in groundwater outside the tunnel, groundwater inflow rate, and ventilation capacity.

Gas Inflow with Barometric Pressure Fluctuations

The gaseous phase held in unsaturated permeable ground can be induced to flow to an excavation by a drop in barometric pressure. Flow rates are relatively low, of little consequence in a properly ventilated excavation. But in an unventilated excavation, pore gases can accumulate to hazardous concentrations within a matter of hours.

Barometric pressure changes are associated with a change in weather. Cold weather or warm weather fronts are preceded by migratory low pressure systems. During their passage, pressures may drop by 10 to 30 mb over a 24-hour period (1 standard atmosphere is 1013 mb.) The rate of pressure drop may reach about 2 mb h⁻¹. Low pressure systems in advance of a cold front are typically more severe, and they are more severe and more numerous in winter than in summer. A low pressure system may pass under clear conditions or may be accompanied by precipitation. Migratory low pressure systems occur everywhere in the world, though are most frequent in the middle latitudes, between about 30° and 70° latitude.

Pore gases in the unsaturated zone tend to equilibrate to barometric pressure at the ground surface. A rapid change in barometric pressure causes a temporary pressure imbalance, with equilibrium gradually reestablished by vertical flow of gas into or out of the ground. Resistance to gaseous phase flow through porous media opposes equilibrium; equilibrium is achieved more rapidly in highly permeable ground. A relationship between barometric pressure at the ground surface and pore gas pressure at depth is shown in Figure 7-3. The response in pore gas pressure to a change in barometric pressure can be significantly attenuated and somewhat delayed. At any point in time during a barometric pressure change, the difference between barometric pressure and pore gas pressure increases with depth (Massmann and Farrier 1992).

The effect of barometric pressure changes on pore fluids can be observed in an open standpipe piezometer set in an unconfined aquifer (Weeks 1979).

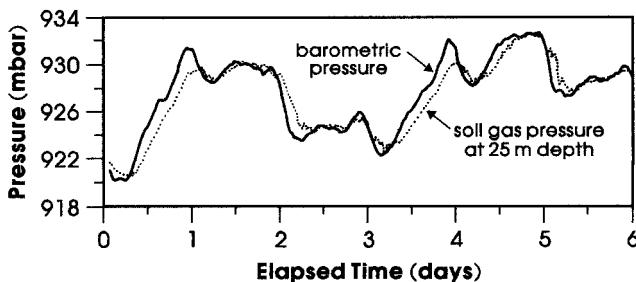


Figure 7-3. Subsurface pore pressure response to variations in surface barometric pressure. In basin fill alluvium in a semi-arid region. (From Stephens 1996, p. 299. © CRC Press, Boca Raton, Florida.)

Whereas the change in barometric pressure is delayed in the unsaturated zone, it is transmitted instantaneously down a standpipe. The difference between gaseous phase pressure on the water table and on water in the standpipe, caused by a rise or fall in barometric pressure, is balanced by a respective fall or rise in water level. Hydrogeologists use the term *barometric efficiency* to describe the static water level response to change in barometric pressure. For the purpose of this text, barometric efficiency is defined as:

$$BE = \frac{\text{barometric pressure} - \text{pore gas pressure}}{\Delta \text{barometric pressure}} \quad (7-17)$$

Barometric efficiency varies with duration of the pressure change (Rojstaczer 1988) and the permeability of the unsaturated medium to vertical gaseous phase bulk flow. It typically ranges from about 0.2 to 0.75 (Freeze and Cherry 1979, p. 234).

As in a piezometer standpipe, a change in barometric pressure is transmitted instantaneously to an excavation open to the atmosphere. A drop in barometric pressure causes pore gases to flow from the unsaturated zone into the excavation, until a pressure balance is reestablished. Gaseous phase flow to an excavation in response to a change in barometric pressure is analogous to groundwater flow through a confined aquifer; barometric pressure changes are so small relative to atmospheric pressure that compressibility of the gaseous phase has little influence on flow rate. Flow to a shaft can be modeled using an equation for radial flow to a fully penetrating well, derived from the Darcy equation for steady state flow of an incompressible fluid (Slider 1976, p. 20–22):

$$q_g = \frac{2 \pi k b}{\mu} \frac{(p_1 - p_2)}{\ln(r_e/r_s)} \quad (7-18)$$

where q_g is gas flow rate, k is effective horizontal permeability of the unsaturated porous medium, b is thickness of the unsaturated zone exposed to the excavation, μ is absolute viscosity of pore gas, p_1 is gaseous phase pore pressure, p_2 is barometric pressure in the excavation, r_e is effective radius of influence, and r_s is radius of the shaft.

The effective radius of influence can be estimated within an order of magnitude from (derived from Powers 1993, Equation 6.13):

$$r_e = r_s + \sqrt{\frac{k t}{\phi \mu \beta}} \quad (7-19)$$

where t is time, ϕ is porosity, and β is compressibility of the pore fluid. Compressibility is defined as (Freeze and Cherry 1979, p. 52):

$$\beta = \frac{-\Delta V_f/V_f}{\Delta p} \quad (7-20)$$

where V_f is volume of the pore fluid, and Δp is change in pressure. From Equation 7-20, the compressibility of gas in the range of barometric pressure fluctuations is about $1 \times 10^{-3} \text{ mb}^{-1}$.

The following example problem demonstrates gas inflow to a shaft in the unsaturated zone, induced by a drop in barometric pressure. Shaft dimensions and ground conditions are shown in Figure 7-4. Barometric pressure is assumed to drop gradually to 10 mb below the previous average, over a period of 10 hours. This is modeled as an instantaneous drop in pressure of 5 mb. Assuming the barometric efficiency is 0.6, the average difference between pore gas pressure

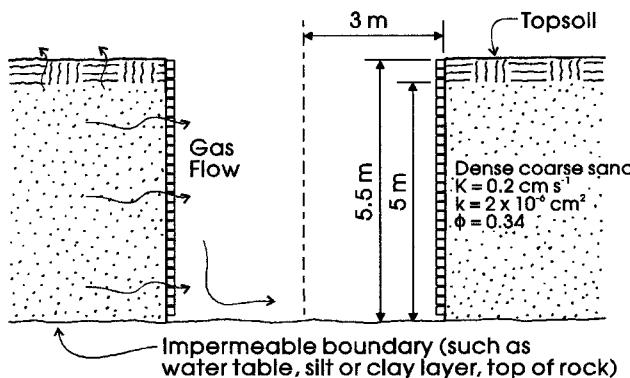


Figure 7-4. Example of gas flow to a shaft, induced by a drop in barometric pressure.

and barometric pressure in the shaft is 3 mb for 10 hours. Assuming that pore gas consists of atmospheric gas (air) somewhat depleted in oxygen by aerobic bacterial activity, absolute viscosity is approximately 1.8×10^{-4} P, from Table 6-2. Applying Equation 7-19, the effective radius of influence for gaseous phase flow to the shaft is:

$$r_e = 3 \text{ m} + \sqrt{\frac{(2 \times 10^{-6} \text{ cm}^2)(10 \text{ h})}{(0.34)}} \left(\frac{\text{cm s}}{1.8 \times 10^{-4} \text{ g}} \right) \left(\frac{\text{mb}}{1 \times 10^{-3}} \right)$$

$$\left(\frac{1 \times 10^5 \text{ g}}{\text{m s}^2 \text{ mb}} \right) \left(\frac{\text{m}}{100 \text{ cm}} \right)^3 \left(\frac{3600 \text{ s}}{\text{h}} \right) = 346 \text{ m}$$

Applying Equation 7-18, the rate of gas flow to the shaft is:

$$q_q = 2 \pi (2 \times 10^{-6} \text{ cm}^2) (5 \text{ m}) \left(\frac{\text{cm s}}{1.8 \times 10^{-4} \text{ g}} \right) \frac{(3 \text{ mb})}{\ln \left(\frac{346 \text{ m}}{3 \text{ m}} \right)}$$

$$\times \left(\frac{1 \times 10^5 \text{ g}}{\text{m s}^2 \text{ mb}} \right) \left(\frac{\text{m}}{100 \text{ cm}} \right)^3 \left(\frac{3600 \text{ s}}{\text{h}} \right) = 79 \text{ m}^3 \text{ h}^{-1}$$

Pore gas enriched in carbon dioxide, upon seeping into the shaft, would tend to drift to the bottom. This rudimentary analysis shows that within a few hours, hazardous gas could occupy a volume in the shaft bottom capable of enveloping a workman. Barometric pressure fluctuations have been responsible for discharge of bacterial methane from unsaturated coarse alluvial deposits, through groundwater supply wells (Hayashi and Ishii 1989). In one case, gaseous phase discharge from a well into a building measured $9.4 \text{ m}^3 \text{ h}^{-1}$.

Gas Inflow from Conventional Reservoirs

Conventional gas reservoirs are porous soils or rocks, of moderate to high permeability, that retain a gaseous phase below the water table. The gas is trapped below a sealing layer and is pressurized by groundwater under the seal. Should an advancing excavation disrupt the sealing layer, or relieve hydrostatic pressure in groundwater under the seal, the gaseous phase may discharge into the excavation, possibly at a very rapid rate. Conventional gas reservoirs in the near-surface underground are most likely to contain bacterial or thermogenic methane, or geothermal carbon dioxide. They are rare, usually small, and difficult to locate. A gas reservoir containing on the order of 0.1 to 1 m^3 of methane (at 1 atm) could pose a serious risk to a small-diameter tunnel or shaft. Gas discharge from con-

ventional reservoirs into excavations cannot be predicted quantitatively. Its basic mechanics are described here to offer some understanding of the problem.

Gaseous phase flow from a conventional gas reservoir into an excavation is unsteady state bulk flow. The discharge rate is highest at the start of discharge, and declines as gas pressure is released. In a reservoir consisting of porous media or finely fractured or bedded rock, groundwater underlying the seal does not maintain constant hydrostatic pressure on a discharging gaseous accumulation. The high viscosity of water relative to gas prevents groundwater from encroaching on the gaseous phase at a rate approaching that of gas discharge.

Short periods of unsteady-state flow can be modeled as steady-state flow. From Chapter 6, steady-state flow of gas through a porous medium is:

$$q_g = \frac{k A}{\mu} \frac{\Delta p}{\Delta x} \quad (6-9)$$

Gaseous phase discharge from a conventional reservoir is usually modeled as single-phase flow, with effective permeability k equal to absolute permeability (Slider 1976, p. 9, 16).

A gaseous phase experiencing a severe decrease in pressure expands as it progresses along the flowpath, so its volumetric flow rate is not constant. Its mass flow rate is constant, however. Utilizing Equation 6-9, mass flow rate is (McPherson 1993, p. 416–418):

$$q_m = q_g \rho = \frac{k A}{\mu} \rho \frac{\Delta p}{\Delta x} \quad (7-21)$$

where q_m is mass flow rate, and ρ is mass density of gas. From Appendix C, mass density of a gas is:

$$\rho = \frac{M p}{R T} \quad (C-23)$$

where M is molar mass. Substituting Equation C-23 into Equation 7-21:

$$q_m = \frac{k A}{\mu} \frac{M p}{R T} \frac{\Delta p}{\Delta x} \quad (7-22)$$

For gas discharge from a conventional reservoir along a linear flow path, Equation 7-22 can be integrated over the length of the flowpath to yield:

$$q_m = \frac{k A}{\mu} \frac{M}{R T} \frac{(p_1^2 - p_2^2)}{2 x} \quad (7-23)$$

where p_1 is initial total pressure, p_2 is final total pressure, and x is length of the flowpath. For gas flow to an excavation, p_2 is 1 atm. Volumetric flow rate into an excavation can be derived by dividing Equation 7-23 by the mass density of the gaseous phase at pressure p_2 , resulting in:

$$q_g = \frac{k A}{\mu} \frac{(p_1^2 - p_2^2)}{2 p_2 x} \quad (7-24)$$

Equation 7-24 has little practical application because the permeability, area, and length of the flow channel cannot be predicted. But it does show the relative significance of the variables involved. A conventional reservoir deep below the water table would be under high pressure, and could discharge into a nearby excavation at a rate high enough to overcome a fully functional ventilation system. Discharge from highly permeable ground is most likely to be initiated at the face. Some gas discharging from an accumulation in porous media remains trapped behind the advancing water front. This residual gas may occupy from 20% to 50% of reservoir pore volume (Ikoku 1984, p. 9).

Gas Inflow from Unconventional Reservoirs

Unconventional reservoirs are porous soils or rocks of low permeability that retain gas in gaseous and solution phases below the water table. Organic-rich unconventional reservoirs also retain an adsorbed phase. In general, the gas is relatively tightly held and widely distributed throughout the formation, in matrix porosity and fractures. Unconventional reservoirs release a gaseous phase into an excavation via bulk flow. Gaseous phase discharge rate cannot be quantitatively estimated because of the heterogeneous permeability of these reservoirs. Discharge rate tends to be lower than for conventional reservoirs, though it may be sustained for a much longer period of time.

Gaseous phase discharge from unconventional reservoirs is mainly controlled by fracture permeability, with some contribution from matrix permeability, such as from sandstone laminae and lenses. Initial discharge may be high as gas is drained from the immediate fracture network but gradually subsides to a low rate. Gas production from wells drilled into chalk of the Niobrara Formation, Rocky Mountains region of the United States, reportedly declines rapidly within the first 30 to 60 days, followed by a sustained decline of 3% to 10% per year (Pollastro and Scholle 1987). These wells range in depth from about 300 to 800 m. Discharge from organic-rich reservoir rock, including coal, may be sustained even longer by gas desorbing from organic matter in the matrix. Gas production from wells drilled into organic shales of the Appalachian Basin reportedly declines to steady-state flow after 2 to 10 years, followed by a long period of production (de Witt 1987).

Gas discharge from an unconventional reservoir is in part controlled by its degree of saturation. Effective permeability to gas rises as water drains from the formation. An openly fractured unconventional reservoir would tend to drain readily; it may discharge gas most rapidly at the face. A reservoir lacking open fractures would tend to drain slowly through the matrix; it may discharge gas some time after being exposed, behind an advancing face. In either case the discharge may be of long duration.

Gas Inflow with Bulk Excavation

Gas held in pores in soil or rock, in gaseous, solution, or adsorbed phases, is released into the excavation atmosphere directly from ground broken up at the face of the excavation. The gas inflow rate is:

$$q_g = c_{bulk} E_r A \quad (7-25)$$

where c_{bulk} is bulk gas concentration (cm^3 gas per cm^3 soil or rock), E_r is bulk excavation rate (m min^{-1}), and A is area of the excavation face (m^2). In inorganic porous media saturated with water, $c_{bulk} = \phi c_{fluid}$, where ϕ is porosity and c_{fluid} is solution gas concentration in terms of Ostwald coefficient. In inorganic porous media only partially saturated with water, $c_{bulk} \approx \phi_e c_{fluid}$, where ϕ_e is effective porosity (defined in Equation 6-3), and c_{fluid} is gaseous phase concentration expressed as volume fraction. In organic media, c_{bulk} is total gas concentration, consisting mainly of adsorbed gas. The bulk excavation rate refers to peak advance rate during active excavation, not to average advance rate over a shift period. So gas inflow with bulk excavation is in effect a pulsed flow.

This inflow mechanism appears significant only for TBM-excavated tunnels. Inflows from inorganic porous media would be relatively low but may generate hazardous atmospheres in TBM muck chambers closed to ventilating air, and they may be sufficient to periodically set off gas monitors while advancing the face. Inflows from organic strata retaining adsorbed gas may be considerably high.

The following example demonstrates the significance of gas inflow during bulk excavation. In this example, a TBM is used to excavate a thermally immature shale (oil shale) that retains a bulk gas concentration of 0.5 cm^3 methane per g shale. This bulk gas concentration converts to 1.2 cm^3 methane per cm^3 shale, assuming a shale saturated unit weight of 2400 kg m^{-3} . Bulk excavation rate is assumed to equal 1 m per 10 min . Allowable methane concentration in the tunnel atmosphere is $0.01 (\phi_a;$ volume fraction). The average airflow velocity necessary to reduce methane inflow from excavation to the allowable concentration can be estimated by applying Equations 7-1 and 7-25, in the following manner:

$$\begin{aligned} v_a &= \frac{q_{ta}}{A} = \frac{q_g}{\phi_a A} = \frac{c_{bulk} E_r}{\phi_a} \\ &= \left(\frac{1.2 \text{ cm}^3}{\text{cm}^3} \right) \left(\frac{1 \text{ m}}{10 \text{ min}} \right) \left(\frac{1}{0.01} \right) = 12 \text{ m min}^{-1} \end{aligned}$$

This airflow velocity is above the normal minimum requirement of 9 m min^{-1} . This example assumes that all methane will escape the shale to enter the excavation atmosphere, a conservative assumption for low-permeability rock.

Gas Inflow through Concrete Lining

Concrete linings are generally not completely impervious; gas can flow through the concrete matrix at low rates. Potential inflow rates are so low as to be of little concern for methane or carbon dioxide, but they can be a concern for hydrogen sulfide because allowable concentrations of hydrogen sulfide are about three orders of magnitude lower than for the former gases. This section applies to gas flow through the concrete matrix, not to flow through leaking joints and fractures in the lining.

Solution phase gas flow across a pervious barrier is a combination of diffusion flow and solution phase bulk flow, described by (Lerman 1988, p. 58):

$$J = -D_{eff} \frac{\Delta c_{fluid}}{\Delta x} + u c_{fluid} \quad (7-26)$$

where J is flux ($\text{mg cm}^{-2} \text{ s}^{-1}$), D_{eff} is effective diffusion coefficient through the barrier ($\text{cm}^2 \text{ s}^{-1}$), c_{fluid} is gas concentration in groundwater behind the barrier (mg cm^{-3}), Δx is distance across the barrier, and u is specific discharge across the barrier (cm s^{-1}). Specific discharge is calculated from the Darcy equation (Equation 6-5):

$$u = \frac{q}{A} = K \frac{\Delta h}{\Delta x} \quad (7-27)$$

where K is hydraulic conductivity of the barrier material to water, and Δh is head loss across the barrier. Substituting Equation 7-27 into Equation 7-26 yields:

$$J = -D_{eff} \frac{\Delta c_{fluid}}{\Delta x} + K \frac{\Delta h}{\Delta x} c_{fluid} \quad (7-28)$$

The following example demonstrates application of Equation 7-28. Consider a concrete-lined tunnel below the water table, with hydrostatic head at springline of 10 m. Tunnel lining thickness is 30 cm, diameter is 5 m, and length is 1 km. The hydrogen sulfide concentration in groundwater outside the tunnel

is 100 mg L^{-1} . Porosity and permeability of the ground is significantly higher than of the lining, so that gas concentration and hydrostatic head outside the lining remain constant—that is, they are not drawn down by flow through the lining. The hydraulic conductivity of concrete normally ranges from about 1×10^{-10} to $1 \times 10^{-8} \text{ cm s}^{-1}$ (Collins, Derucher, and Korfiatis 1986); for this example we will use $1 \times 10^{-9} \text{ cm s}^{-1}$. The porosity of concrete ranges from about 0.1 to 0.2 (Neville 1996, calculated estimate from Tbl. 10.1); for this example we will use the lower value.

An effective diffusion coefficient for the lining can be estimated using Equation 6-17:

$$D_{\text{eff}} \approx \frac{\phi}{\tau} D = \left(\frac{0.1}{2} \right) \left(\frac{2 \times 10^{-5} \text{ cm}^2}{\text{s}} \right) = 1 \times 10^{-6} \frac{\text{cm}^2}{\text{s}}$$

where the diffusion coefficient for hydrogen sulfide in water is from Table 6-4. We will assume some degree of ventilation in the tunnel, so that gas concentration on the inside face of the lining is essentially zero. The change in gas concentration across the lining, Δc , then becomes 100 mg L^{-1} .

Gas flux through the concrete lining is:

$$\begin{aligned} J &= \left[- \left(\frac{1 \times 10^{-6} \text{ cm}^2}{\text{s}} \right) \left(\frac{-100 \text{ mg}}{\text{L}} \right) \left(\frac{1}{30 \text{ cm}} \right) \right. \\ &\quad \left. + \left(\frac{1 \times 10^{-9} \text{ cm}}{\text{s}} \right) \left(\frac{10 \text{ m}}{30 \text{ cm}} \right) \left(\frac{100 \text{ mg}}{\text{L}} \right) \left(\frac{100 \text{ cm}}{\text{m}} \right) \right] \left(\frac{\text{L}}{1000 \text{ cm}^3} \right) \\ &= \left[3.33 \times 10^{-6} + 3.33 \times 10^{-6} \frac{\text{mg cm}}{\text{L s}} \right] \left(\frac{\text{L}}{1000 \text{ cm}^3} \right) \\ &= 6.66 \times 10^{-9} \frac{\text{mg}}{\text{cm}^2 \text{ s}} \end{aligned}$$

Gas exiting the lining would enter the tunnel atmosphere almost immediately. Converting mass flux to gaseous phase volumetric flux, at 20°C:

$$\begin{aligned} J_v &= \left(\frac{6.66 \times 10^{-9} \text{ mg}}{\text{cm}^2 \text{ s}} \right) \left(\frac{\text{g}}{1000 \text{ mg}} \right) \left(\frac{\text{L H}_2\text{S}}{1.54 \text{ g H}_2\text{S}} \right) \left(\frac{293}{273} \right) \left(\frac{100 \text{ cm}}{\text{m}} \right)^2 \left(\frac{60 \text{ s}}{\text{min}} \right) \\ &= 2.78 \times 10^{-6} \frac{\text{L}}{\text{m}^2 \text{ min}} \end{aligned}$$

At this flux, total volumetric gas inflow rate through 1 km of tunnel lining would be:

$$q_g = \left(\frac{2.78 \times 10^{-6} \text{ L}}{\text{m}^2 \text{ min}} \right) (\pi) (5 \text{ m}) (1000 \text{ m}) \left(\frac{\text{m}^3}{1000 \text{ L}} \right)$$

$$= 4.37 \times 10^{-5} \frac{\text{m}^3}{\text{min}}$$

The volumetric airflow rate necessary to dilute this hydrogen sulfide inflow to an allowable concentration of 10 ppmv is:

$$q_{la} = \left(\frac{4.37 \times 10^{-5} \text{ m}^3}{\text{min}} \right) \left(\frac{1 \times 10^6}{10} \right) = 4.37 \frac{\text{m}^3}{\text{min}}$$

which is equal to an average airflow velocity of 0.22 m min^{-1} .

In this example, hydrogen sulfide inflow through the tunnel lining would have little influence on construction. However, it may have a major influence on design if the tunnel were to be occupied by the public, who would likely object to the odor of a 10 ppmv hydrogen sulfide concentration. To reduce this hydrogen sulfide inflow to the odor threshold concentration of about 0.01 ppmv, it would be necessary to ventilate the tunnel with an average airflow velocity of about 220 m min^{-1} , which would be impractical. Hydrogen sulfide inflow through the tunnel lining was a major consideration for design of the Los Angeles subway tunnels, and costly measures were taken to construct an impervious lining (Proctor and Monsees 1985; Murthy 1988).

The sample calculations above are rudimentary; the result is greatly influenced by values used for effective diffusion coefficient and hydraulic conductivity. Design requiring a high degree of accuracy would warrant detailed evaluation of these critical parameters.

GAS FLOW FROM COAL-BEARING STRATA

The behavior of adsorbed gas makes gas flow from coal unique. This section summarizes the characteristics of gas flow into excavations in coal-bearing strata, as described in coal mining literature. Few civil works tunnels in coal-bearing strata will encounter a full face of commercial grade coal. They are more likely to encounter thin seams of coal in a predominantly mineral matrix. Nevertheless, coal mining experience offers insight into evaluating gas flow to an excavation in coal-bearing strata. With few exceptions, the subject gas in coal mining literature is methane.

Gas in coal is retained in solution phase in bulk water, in gaseous phase within pores and fractures, and in an adsorbed phase on organic surfaces. Most

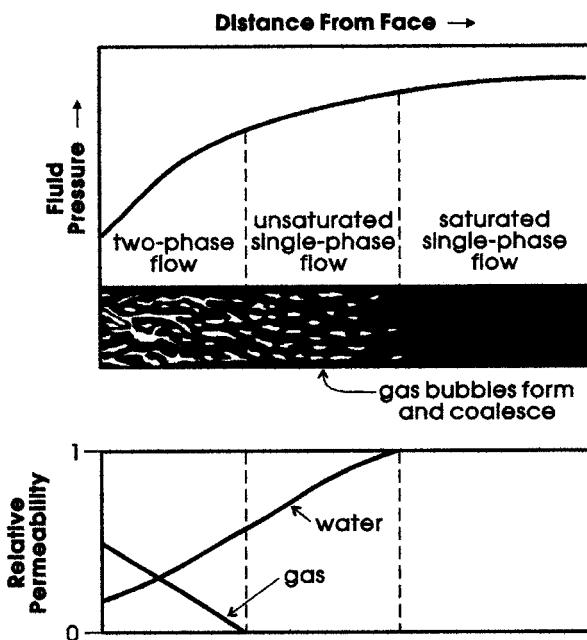


Figure 7-5. Three stages of coal bed dewatering and methane flow. (Adapted from McKee and Bumb 1987. Copyright Society of Petroleum Engineers.)

gas by far is in the adsorbed phase. The amount of gas adsorbed, and correspondingly the gas content of coal, is a function of pressure on the gaseous phase. Where gaseous phase pressure is below hydrostatic pressure in surrounding strata, the coal holds an amount of gas less than its retention capacity. Gas content of coal in place is described in Chapter 6.

Gas is released from adsorbed phase into gaseous phase as hydrostatic pressures around the excavation decline. The gaseous phase moves into the excavation through the fracture network, primarily through cleats. Two-phase flow of water and gas develops on the excavation perimeter, as shown in Figure 7-5. Desorption with decline in hydrostatic pressure is shown in Figure 7-6. If the initial gas content is below retention capacity, little gas is released until hydrostatic pressure falls below the initial gaseous phase pressure. Relative permeability to gaseous phase controls flow rate; relative permeability increases as groundwater drains from coal, as coal shrinks with loss of adsorbed gas, and as coal near the excavation is crushed by overlying strata (Deul and Kissell 1972). Consequently, the gaseous phase flow rate from coal to an exposed face or a dewatered borehole may briefly increase with time before it gradually declines. An openly fractured coal bed can release “blowers” of gaseous phase methane into the excavation. The adsorbed phase may sustain gas flow for a long time.

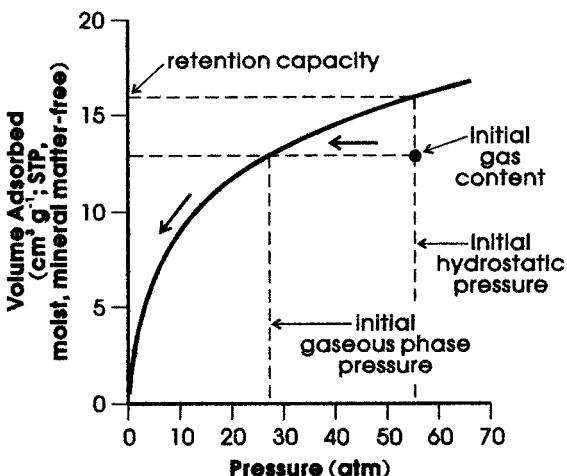


Figure 7-6. Desorption of methane from coal, with declining hydrostatic pressure.

Methane inflow in solution phase is limited by the permeability of the coal bed, which is usually low. However, some fractured coal beds are sufficiently permeable to act as aquifers, with the capacity to deliver solution phase methane inflow to the excavation.

The strike of the cleats can influence gas flow from boreholes drilled into the coal bed. Horizontal holes drilled from the face of the excavation release about 2.5 to 10 times as much gas if directed perpendicular to face cleats, compared to butt cleats (Diamond, Elder, and Jeran 1988). Vertical holes drilled into the seam preferentially drain gas from face cleats.

A small amount of gas is released from coal broken up at the face during excavation, as shown in Figure 7-7. Peak methane concentrations associated with coal breakage can exceed combustible concentrations. Peaks that occur in the immediate vicinity of a source of frictional ignition can constitute an explosion hazard. The size to which coal is broken by the excavating machine is a minor factor in methane emission (Kissell and Deul 1974). The natural fracture network has the greatest influence on gas flow, it is typically much more closely spaced than the size of coal lumps. Not all gas is released from coal exposed in an excavation. A small amount, defined as “residual gas” in the direct method of determining gas content, is retained in the coal, under an absolute pressure of 1 atm.

Gas flow from the face constitutes only a small portion of total gas flow into an excavation in coal-bearing strata. In large, deep coal mines with sustained production, about 6 to 9 times the amount of gas initially contained in the extracted coal is emitted into the mine from exposed ribs, surrounding strata, and gob piles (Kissell, McCulloch, and Elder 1973). In shallow mines, this ratio drops

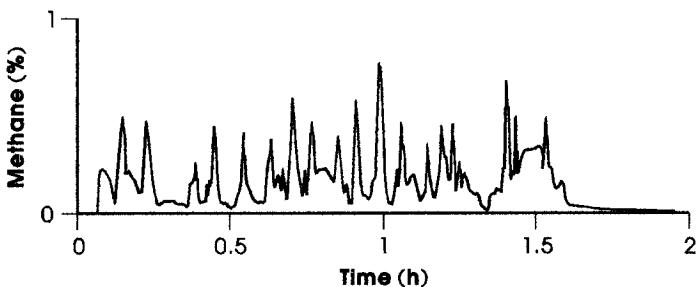


Figure 7-7. Methane concentration in atmosphere near working face of a coal mine. Peaks correspond to mining machine cuts into the face. (From Kissell et al. 1974.)

to about 3 to 4 (Zabetakis, Deul, and Skow 1973). Gas flow from inorganic strata is independent of gas flow from the coal bed. It occurs in the manners previously described for inorganic geologic media, mainly via bulk flow in groundwater, and bulk flow in gaseous phase from conventional and unconventional reservoirs.

Gas discharge rates into an excavation in a coal-bearing sequence vary widely as the heading is advanced. A characteristic of these sequences is that they offer numerous opportunities for stratigraphic trapping. Folded and faulted sequences offer additional opportunities for structural trapping. Gas held anywhere within the zone of hydrostatic pressure reduction may find an avenue to the excavation through poorly cemented sandstones or fracture networks. Sustained flows of methane from behind the heading, such as from coaly strata, unconventional reservoirs, and points of groundwater inflow, may constitute a significant portion of total flow. Observations in coal mines show that vertical clay seams in coal-bearing strata may form cells that trap gas in interjacent rock (Diamond, Elder, and Jeran 1988). Penetration of the clay seam results in rapid discharge of gas. Faults can enhance or inhibit gas flow to excavations, depending on their effect on the permeability of adjacent ground.

It is very difficult to accurately predict gas flow into excavations in coal-bearing strata. This difficulty is typically addressed in coal mines by ventilating the mine workings with a minimum airflow velocity of about 20 m min^{-1} (60 ft min^{-1}), directing a stream of ventilating air across the working face, and using explosion-proof electrical equipment between the face and the main airway (Deul and Kim 1988; MSHA 1987, 30 CFR 75.301-4, and 75.500).

GAS AND COMPRESSED AIR TUNNELING

In using compressed air to stabilize an excavation in soft, water-bearing ground, some air can escape the excavation into permeable geologic features exposed in

the face and walls. This “lost air” migrates generally laterally and upward, by bulk flow driven by working pressure in the excavation, and by buoyant flow. The composition of normal air introduced into the ground can change rapidly, in biochemical and geochemical reactions, and by simple gas exchange with pore waters. Lost air can become a hazard if it migrates back into the excavation following a reduction in working pressure, or if it migrates to an adjacent excavation or structure at a lower ambient pressure.

Lost air can be rendered oxygen deficient via biochemical and geochemical reactions that consume oxygen. Bacteria capable of consuming oxygen include aerobes and facultative anaerobes. They convert the oxygen to carbon dioxide. This process would be most rapid in environments favorable to bacterial growth—porous, wet environments containing labile organic matter. Oxygen is also consumed in geochemical reactions with ferrous iron, a soluble form of iron that is stable in anoxic environments.

Lost air can lose oxygen, and can acquire methane and hydrogen sulfide, simply by exchanging gases with pore waters. Chemical gradients drive the process, with the gas concentration in lost air equilibrating to solution concentrations in pore waters, according to Henry’s law.

The following are examples of the association between compressed air construction methods and hazardous atmospheres:

Structural caissons in Tokyo were often excavated under compressed air. Numerous fatalities have been attributed to oxygen-deficient atmospheres that developed in the working caisson following a decline in working pressure, and in adjacent caissons at lower ambient pressure (Hayashi 1968). Lost air was rendered oxygen deficient by geochemical reactions with ferrous iron. The excavations penetrated unsaturated, confined sand and gravel layers at depths of 10 to 20 m. These layers were infiltrated by groundwaters with dissolved iron concentrations of 3 to 35 mg L⁻¹. The iron originated in overlying deposits derived from volcanic ash.

Construction of a sewer tunnel under compressed air caused high levels of carbon dioxide in nearby basements (Crouse, Gormley, and Campbell 1979). The tunnel was excavated in West Allis, Wisconsin, in glacial deposits free of buried organics. Gas apparently entered the basements through abandoned water wells.

A sewer tunnel being constructed under compressed air, through organic deposits, exploded shortly after air pressure was released. Four workers were killed. The project was constructed in Green Bay, Wisconsin, from 1974 to 1975. The tunnel had been advanced through organic silt estuarine deposits that partially fill the Fox River valley, and into clayey glacial till of the ancient valley wall. A formed concrete lining was placed through the organic deposits into the till, to the end of the TBM trailing gear, and air pressure was then released. Gaseous phase methane migrated along the outside of the concrete lining into the heading, where it ignited. Air pressure had held methane out of the excavation

prior to the explosion. Methane in these deposits is held mainly in solution in groundwater.

NATURAL GAS CORROSION AND DISPOSAL ISSUES

In addition to their adverse effects on human physiology, geothermal carbon dioxide and bacterial hydrogen sulfide can reach concentrations in groundwater high enough to generate corrosion and environmental problems for underground construction. These are noted here, though their solutions are beyond the scope of this text.

Carbon dioxide can accelerate the corrosion of carbon steel and copper alloys in wet, aerobic environments. Carbon dioxide disassociates in water to some extent to form carbonic acid (H_2CO_3); the reaction lowers the pH of the water, which increases corrosion rate. Carbon dioxide solution concentrations above about 850 mg L^{-1} are potentially corrosive (Szilas 1985, p. 305). Geothermal carbon dioxide encountered during construction of the Mono Lakes Tunnel, a water conveyance tunnel in California, corroded dewatering system components (Jacques 1940). Corrosion reaction rates approximately double for each 10°C rise in temperature; this factor may be significant in geothermal systems.

Hydrogen sulfide also reacts with water to form a weak acid and corrosion in a manner similar to carbon dioxide. Hydrogen sulfide solution concentrations above about 40 mg L^{-1} are potentially corrosive (Szilas 1985, p. 305). In the Tumbler Ridge "Wolverine" tunnel, a rail tunnel in British Columbia, Canada, hydrogen sulfide caused severe corrosion of all metal components in the completed tunnel (Hendry, Kimball, and Shtenko 1985). Hydrogen sulfide is extremely corrosive to copper and copper alloys typically used in electrical equipment. Concentrations of a few ppb can be corrosive to sensitive control circuits.

Hydrogen sulfide in groundwater discharged into a body of fresh water may damage the ecology of the aquatic environment by upsetting the sulfur balance. The toxic effects of hydrogen sulfide on freshwater species are exacerbated by long exposure times, low pH, or low oxygen content of the receiving water body. A maximum concentration of 0.002 mg L^{-1} is recommended as a long-term exposure limit for freshwater species (EPA 1986, p. 267–270; National Research Council 1978, p. 67–79). The toxic effects of hydrogen sulfide in well-oxygenated water tend to be localized and transient, due to its rapid oxidation, a characteristic that can be considered in establishing an appropriate discharge standard. Discharge of hydrogen sulfide waters into seawater appears to be generally a minor concern. Discharge into municipal sewer systems may be regulated by local authorities.

Hydrogen sulfide in ventilating air discharged into the atmosphere may generate complaints about odors. Standards for hydrogen sulfide concentrations in ambient air vary widely in the United States and internationally, generally

ranging from 0.005 to 0.2 ppmv for exposure periods of 30 to 60 minutes. Emission standards for effluent air from stationary sources also vary, generally ranging from 3.5 to 1600 mg m⁻³ (National Research Council 1978, p. 81–92).

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8

Geologic Environments of Natural Gas

INTRODUCTION

Hazardous gas incidents in civil works excavations involve so many variables that patterns may seem indiscernible, making meaningful extrapolation appear impossible. On the contrary, gas occurrences in the near-surface underground follow consistent geological patterns, and the consequences of gas in an excavation relate to the effectiveness of atmosphere control measures. This chapter identifies common geologic environments that may contain all the factors necessary to pose a gas risk to construction. It describes environments in which bacterial, thermogenic, and geothermal gases are generated, migrate, are retained, and can enter excavations.

This chapter includes case histories of tunnel projects that encountered hazardous concentrations of gas. Some case histories include interpretations of these incidents, based on limited information available to the author. The interpretations are not intended to represent the conclusions of detailed analyses, but rather are to demonstrate that the effects of gas on tunneling can be explained using basic principles of this text. These same principles can be applied to risk assessments on future projects.

Numerous references are made herein to geologic age of sediments. The geologic time sequence for Phanerozoic time is summarized in Figure 8-1.

Era	Period	Epoch	Age (10^6 yrs)	Developments In Evolution
Cenozoic	Quaternary	Holocene	0.01	modern humans appear
		Pleistocene	2	
	Tertiary	Pliocene	5	
		Miocene	24	
		Oligocene	34	mammals abundant
	Paleogene	Eocene	55	
		Paleocene	65	
	Cretaceous	Late Early	144	angiosperms appear, extinction of dinosaurs at end of period
	Jurassic	Late Middle Early	206	dinosaurs abundant, birds and mammals appear
	Triassic	Late Middle Early	248	forests of gymnosperms and ferns, first dinosaurs
Mesozoic	Permian	Late Early	290	rise of reptiles and amphibians, conifers appear
	Carbonifer	Pennsylvanian	323	forests appear, first reptiles and winged insects
		Mississippian	354	
	Devonian	Late Middle Early	417	first amphibians, earliest trees, rise of fish
	Silurian	Late Early	443	first spore-bearing plants and jawed fish
	Ordovician	Late Middle Early	490	first fish-like vertebrates
	Cambrian		543	marine Invertebrates abundant, external skeletons evolve

Figure 8-1. Major geologic time units of the Phanerozoic. (Adapted from GSA 1999; Duff 1993, Tbl. 7-1; and Raven, Evert, and Eichhorn 1992, App. D.)

BACTERIAL GAS ENVIRONMENTS

This section identifies common geologic environments that actively generate bacterial gas. It describes natural continental and marine environments of organic matter deposition; gas generation in landfills, from which gas can migrate into surrounding strata; and bacterial gas generation in ancient organic-rich sediments, including coal-bearing strata and petroleum source rocks. Carbon dioxide is the

principal gas generated in oxic environments; hydrogen sulfide and methane are principal gases in anoxic environments. A text on sedimentary geology should be consulted for a description of physical processes of sedimentation (for example, Reineck and Singh 1980).

Continental Environments

Fluvial Environments

Rivers are major agents of erosion, sediment transport, and deposition (Reineck and Singh 1980, p. 256–314). Rivers can be classified as straight, meandering, or braided, and all are capable of incorporating organic matter into sediments. The propensity for sedimentation is strong in mature-stage rivers, which form flood plain and lateral accretion deposits; and in old-stage rivers, which develop a distributive channel network in coastal or shoreline regions. Humid climates support vegetation that provides the principal source of organic matter. Particulate organic matter carried as suspended load is deposited with silt and clay. Larger masses such as tree limbs and trunks may be deposited with sand and gravel.

Fluvial deposition occurs in channels, on natural levees, and in flood basins. Organic-rich channel sediments may be deposited on the downstream ends of bars, in pools downstream of bars, and in swales between a series of bars. In lower reaches of rivers where coarse sediment is not available, wood, mud pebbles, and other organic matter may form channel lag deposits. Channels abandoned by meandering rivers become filled with organic-rich sediments. Vegetation growing on alluvial islands in braided streams may become buried in sediment. Channel sediment bodies are characteristically discontinuous. Sediments are deposited outside the channel on natural levees and in flood basins during flood stage. Levees and basins can support lush vegetation, such as backswamps, which may become incorporated in sediments.

Fluvial deposits may contain bacterial methane or carbon dioxide. Methane or carbon dioxide may be generated in unsaturated sediments. Methane may be generated in saturated anoxic sediments, and held in solution in pore waters, or in gaseous phase in stratigraphic traps. Deposits of interbedded organic-rich silts and clays, sands, and gravels may be highly permeable, and capable of discharging groundwater with solution phase gas to excavations. River waters are almost invariably oxic, posing little risk of containing hazardous concentrations of gas in solution.

Lacustrine Environments

Lacustrine environments in general are capable of incorporating relatively high concentrations of organic matter in sediments. Organic matter concentrations of 1% to 5% (dry weight) are common and may range as high as 40% to 50% (Talbot

and Allen 1996). Lacustrine water columns are shallow compared to marine water columns, enabling detrital organic matter to reach the sediment surface before being completely mineralized by aerobic bacteria (Kelts 1988). Lakes may be classified as *oligotrophic*, characterized by low nutrient concentration, sparse primary productivity, and oxygenated waters; and *eutrophic*, characterized by high nutrient concentration, high primary productivity, and oxygen depletion in shallow waters in summer. Hazardous concentrations of methane are likely in eutrophic sediments, but evidence suggests they may also occur in oligotrophic sediments.

Aquatic organic matter is generated in lakes in the *littoral* zone, a shallow zone of rooted vegetation, and in the *limnetic* zone, the deep water area penetrated by light. Rivers and marginal land areas supply terrestrial organic matter. The amount and type of organic matter in lakes is strongly controlled by climate. Sediment distribution depends on hydraulic energy gradients. Ideally, silt and clay are deposited in the center of the basin, grading to sands along the shoreline (Reineck and Singh 1980, p. 241–242). The actual distribution may be considerably affected by other factors including lake size, wind, water depth, water temperatures, and sediment load of inflowing rivers (Talbot and Allen 1996). Terrestrial organic matter may be concentrated in river delta sediments extending into the lake. Aquatic organic matter dominates over terrestrial organic matter in offshore sediments of large lakes such as the Great Lakes of the United States, and in lakes receiving little clastic supply.

Methane is generated in lacustrine environments below the oxic/anoxic boundary. In organic-rich sediments, methane concentration may reach saturation within the upper few centimeters of sediment, leading to bubble formation and ebullition of gas (Whiticar, Faber, and Schoell 1986). Deeper in the sediment, methane concentration may stabilize or decline. The amount of methane that can be retained in solution increases with depth of the overlying water column. Typical methane distributions in lake sediments are shown in Figure 8-2. In some lakes the oxic/anoxic boundary lies above the sediment surface. Thermally stratified lakes have a cool dense bottom layer, the *hypolimnion*, underlying a warm circulating upper layer, the *epilimnion*. The hypolimnion is relatively quiescent and may be anoxic. Most methane in anoxic bottom waters apparently diffuses from sediments (Reeburgh and Heggie 1977).

Lacustrine sediments may contain methane concentrations hazardous to construction. For example, Quaternary lacustrine sediments of the Yamagata gas field of Japan contained enough methane to serve local energy needs (Marsden and Kawai 1965). The gas is in solution in groundwaters and was produced from depths of 40 to 200 m. In another example, methane was encountered during construction of Chicago's first water inlet tunnel into Lake Michigan, in 1861 (Beaver 1972, p. 67–68). The tunnel was constructed in late Pleistocene silty clay sediments of glacial Lake Chicago, which reached a water level of up to

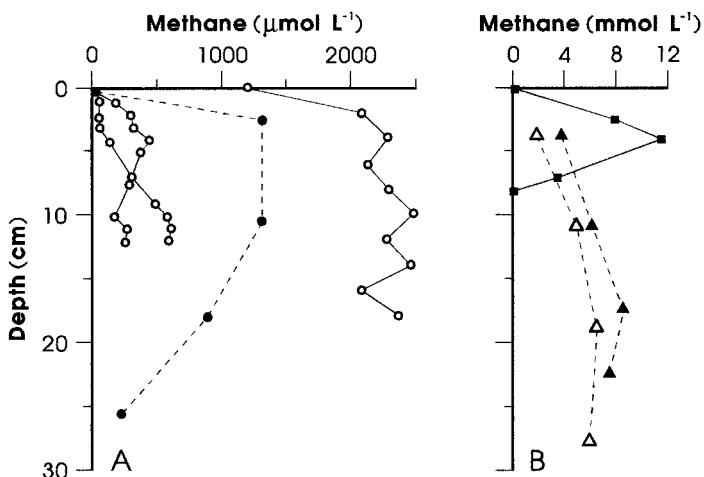


Figure 8-2. Distribution of methane in freshwater lake sediment pore waters. A—Canadian lakes; Ace Lake; Lake Mendota. B—Lake Vechten; Lake Kizaki-ko; Lake Aoki-ko. Note that methane concentrations in excess of $16 \mu\text{mol L}^{-1}$ are potentially hazardous. (By Mah et al. 1977, from various sources. © 1977 Annual Reviews.)

18 m higher than present Lake Michigan. At the inlet shaft, water depth was about 6 m and soil cover over the tunnel crown was 7 m. Methane formed pockets in the clay, which caused the face to sound hollow when struck with a pick. Opening these pockets released gas into the excavation. The gas may have come out of solution to form gaseous voids following reduction in hydrostatic pressure at the heading.

Mires

Mires are freshwater wetlands in which geochemical conditions prevent bacteria and fungi from completely consuming all the organic matter produced (Moore 1989). Consequently, mires accumulate peat. Mires develop in areas of poor subsurface drainage such as topographic depressions formed by glacial processes; oxbow lakes and flood-plain depressions; shoreline interdune hollows and abandoned delta lobes; and depressions formed by solution of carbonate rock. These peat-forming environments range from local to regional extent. Organic matter originates mainly from inside the system (Moore 1987). Mire vegetation survives on mineral nutrients that enter in system waters; it is usually isolated from nutrients of underlying soil or rock by an intervening peat layer.

Peat consists of highly organic detritus (less than 25% ash on combustion, dry weight). Peat can be differentiated by degree of decomposition and by its

botanical composition. Mires subject to flood discharge may accumulate peaty sediments high in mineral matter. Terms used to describe these include clayey peat (25% to 50% ash), and peaty clay (>50% ash); these terms are synonymous with *muck* in the United States (Cameron, Esterle, and Palmer 1989). Geotechnical engineering terms for peaty material include organic silt (slightly plastic), and organic clay (plastic).

Bacterial decomposition in mires is inhibited by a number of factors, including lack of oxygen, lack of mineral nutrients, acidic pore fluids, and low temperature (Moore 1989). Of these, lack of oxygen is perhaps the dominant inhibiting factor in saturated organic deposits. Bacterial activity may be high in the more oxygenated upper layer of peat but declines below the surface as the environment becomes anaerobic. Accumulation of thick peat deposits requires a longstanding high or gradually rising water table.

Shallow-water wetlands that are subject to seasonal aeration of surface sediment do not accumulate peat. These environments are distinct from mires. They include *marshes*, inhabited by herbaceous vegetation, and *swamps*, dominated by trees. Their vegetation is supported by mineral nutrients in soils.

Mire sediments generate methane. Gas that does not ebullate from the sediments is retained either in solution or in gaseous phase in stratigraphic traps. Gas may enter shafts and tunnels constructed in or below the mire, mainly from pore waters drawn into the excavation.

Glacial Environments

Pleistocene continental glaciers advanced over heavily vegetated landscapes formed during the previous interglacial stage or interstadial. These landscapes held organic matter reservoired in peat deposits, soils, fluvial sediments, and lacustrine basin and delta sediments; and in biomass of standing forests. As continental ice overrode the landscape, organic matter was incorporated within or buried partially intact under lodgement till, outwash deposits, and glaciolacustrine deposits. Surficial organics were eroded and incorporated into the till, leaving remaining portions of soil profiles and peat deposits to be buried in place or to be plucked and incorporated into the till in frozen blocks. Organic sediments eroded by meltwater streams were incorporated as particulates in clastic sediments downstream (Stevenson 1969).

The organic richness of these former landscapes was influenced by contemporaneous climatic conditions. An interglacial stage implies regional warming to a temperate climate; an interstadial implies warming to a subarctic (boreal) climate (Flint 1971, p. 391). A cooler, tundra climate may have existed near the ice margin. Prior glaciation leaves surface drainage undeveloped, and permafrost inhibits subsurface drainage, the effect being wet ground in summer. Tundra is vegetated with grasses, mosses, and low shrubs. A boreal forest (taiga) is vegetated mainly with pine, fir, and spruce trees, and ground cover of mosses, shrubs,

and grasses. Surface and subsurface drainage are generally poor in summer. Mires are numerous. At the climax of interglacial warming, a temperate climate supports a deciduous forest, typically a dense growth of broadleaf trees; or grasslands of a prairie or steppe (McKnight 1987, p. 248–251). Interglacial stages last long enough to produce mature soil profiles. Organic remnants of interglacial stages can be identifiable over areas of regional extent. Remnants of interstades, if present at all, may be very localized and may be unreported in regional geology literature. Paleosols (buried soils), peat deposits, and other organics are more likely to be preserved if buried in sediments that subsequently remain poorly drained (Retallack 1991).

A common feature of deglaciated areas are distal lakes fed by outwash streams. These lakes may become thermally stratified, increasing their capability to preserve organic matter in sediments. Ice-contact lakes are generally not thermally stratified, because of continuous supply of cold meltwater (Miller 1996), so have lesser ability to preserve organic matter.

The northeastern portion of the State of Illinois, in the central United States, provides an example of methane production from unconsolidated sediments of a glaciated region. “Drift gas” wells have been drilled in the region since the late 1800s to produce bacterial methane for domestic use. Typical well depths range from about 10 to 100 m; the average is about 40 m (Coleman, Liu, and Riley 1988; Meents 1968). Methane production from these wells averages about $1.5 \text{ m}^3 \text{ min}^{-1}$ but can reach $100 \text{ m}^3 \text{ min}^{-1}$. Wells produce gaseous phase methane from layers of organics, sand, and gravel buried within and beneath silty and clayey till. Well-drillers describe organic sediments recovered from boreholes using terms such as “forest beds,” “black soil,” peat, “driftwood,” “brush piles,” “woodyard,” and “black muck.” Gas-producing areas are concentrated where organics are preferentially preserved: in end moraines of the last glacial phase and in ancient bedrock valleys. A profile through the Tiskilwa drift-gas area is shown in Figure 8-3. Radiocarbon dating of methane samples indicates that most gas is generated from organics in the Robein Member of the Roxana Silt, which accumulated on a poorly drained, low-lying landscape prior to the last glacial episode in the region, which began about 25 ka B.P. (Coleman 1979; Hansel and Johnson 1996). The Robein silt is organic-rich and is locally overlain by peat or muck. Groundwater in the tills is partially perched. Flow gradients carry methane in solution from the Robein layer to underlying sand and gravel layers, where lower hydrostatic pressures allow the gas to exsolve into gaseous phase. Gas in the unsaturated portion of the Sankaty Sand is near atmospheric pressure, and is extracted using vacuum wells. Some methane is also generated from buried organic matter above the Robein silt, apparently from discontinuous peat and muck deposits associated with stagnant ice features.

A second example of methane in glacial sediments is provided by a study of the Alliston aquifer, a regional aquifer located near the south end of Georgian

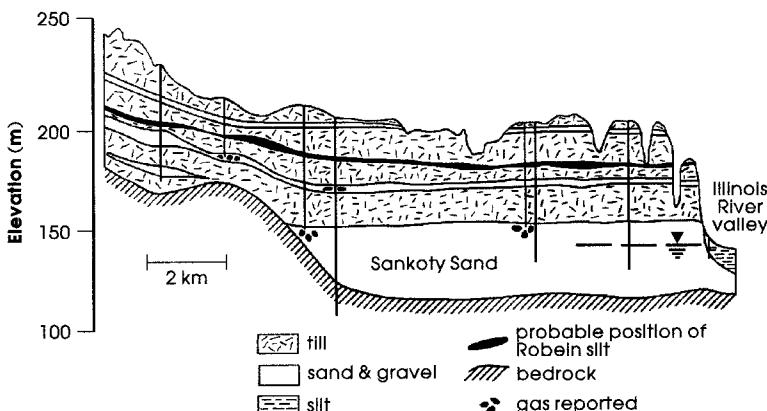


Figure 8-3. Profile from Tiskilwa “drift gas” area, northeastern Illinois, U.S. Sankaty Sand partially fills the Ancient Mississippi River Valley. (Adapted from Coleman 1979. © University of California Press.)

Bay in Ontario, Canada (Aravena and Wassenaar 1993). The aquifer is composed of mid-Wisconsinan (late Pleistocene) glacial and interglacial silt, sand, and gravel. It is confined above by Late Wisconsinan glaciolacustrine clays, and below by Ordovician shales and limestone. Aquifer sediments contain peat from the Plum Point Interstadial and the earlier Port Talbot Interstadial. Groundwaters in the central part of the aquifer contain high concentrations of dissolved organic carbon (DOC), ranging up to 18 mg L^{-1} . Groundwaters containing more than 5 mg L^{-1} DOC appear pale yellow, apparently from humic substances. Some groundwaters contain solution concentrations of methane in excess of $0.024 \text{ ml gas/ml water}$, below saturation concentration at 1 atm total pressure, but high enough to encourage venting of water supply systems to prevent gas explosions. Wells average about 115 m in depth. Radiocarbon dates for methane sampled from the central part of the aquifer range between about 26 and 44 ka B.P., reflecting the age of the source organic matter. Groundwaters are less than 13 ka years old, suggesting that methanogenesis is ongoing in this aquifer.

Marine Environments

Marine sediments deposited under quiescent water incorporate organic detritus from marine organisms. Sediments near the shore may incorporate terrestrial plant matter. Organic matter buried in marine sediments provides a substrate for sulfate-reducing and methanogens groups of bacteria.

Marine waters are high in sulfates, which enable sulfate-reducing bacteria to fill an important role in the decomposition of organic matter. Sulfate reduction

is limited to depths to which dissolved sulfate ions can diffuse into sediments before being consumed in biochemical reactions, a distance of centimeters to a few meters in organic-rich, fine-grained sediments.

Below the sulfate reduction zone, methanogens become the terminal decomposers, and they may generate gas to sediment depths of several hundred meters (Davis 1992). Methane is by far the predominant gas found in marine sediments. Typical bacterial methane distributions in upper marine sediments are shown in Figure 8-4. Marine sediments may also contain thermogenic methane that has migrated up from source rocks or reservoirs deeper in the sedimentary profile.

Gaseous phase methane in marine sediments can sometimes be distinguished on seismic profiles generated by reflecting an acoustic pulse off the seabed. Gas bubbles adsorb or scatter the acoustic pulse, obscuring geologic reflectors within or below the gas zone. The effects on seismic profiles take several forms. Two distinct examples are shown in Figure 8-5. The plumes shown in Figure 8-5a suggest upward migration of gas or gas-charged sediment (Davis 1992). The gas curtain shown in Figure 8-5b suggests gas bubbles, in concentrations as low as about 1%, finely disseminated in low-permeability matrix (Judd and Hovland 1992). Other geologic conditions can cause similar seismic effects, making seismic profiles difficult to interpret.

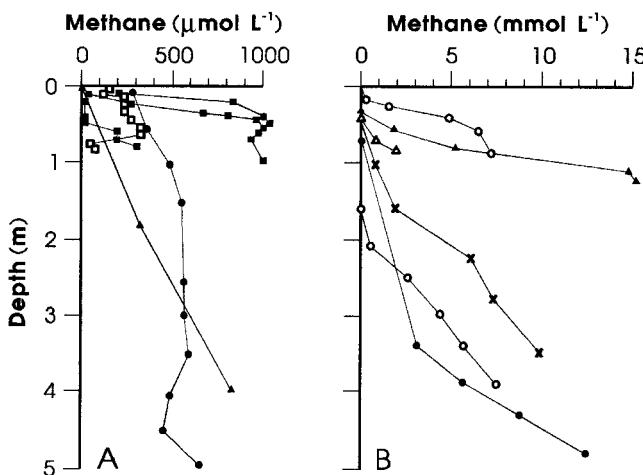


Figure 8-4. Distribution of methane in marine sediment pore waters. A—Long Island Sound; Louisiana salt marsh; Grand Manan basin; Chaleur Trough, Gulf of St. Lawrence. B—Santa Barbara basin; Cariaco Trench, eastern and western basins; Chesapeake Bay. Note that methane concentrations in excess of $16 \mu\text{mol L}^{-1}$ are potentially hazardous. (By Zhang and Chen 1985, from various sources.)

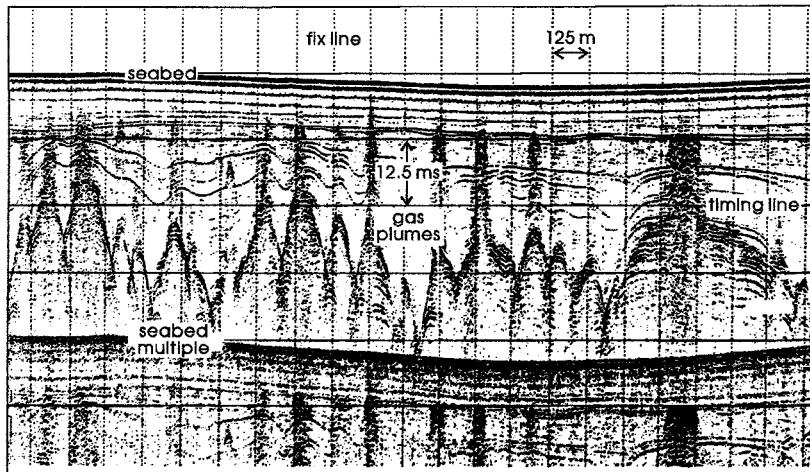
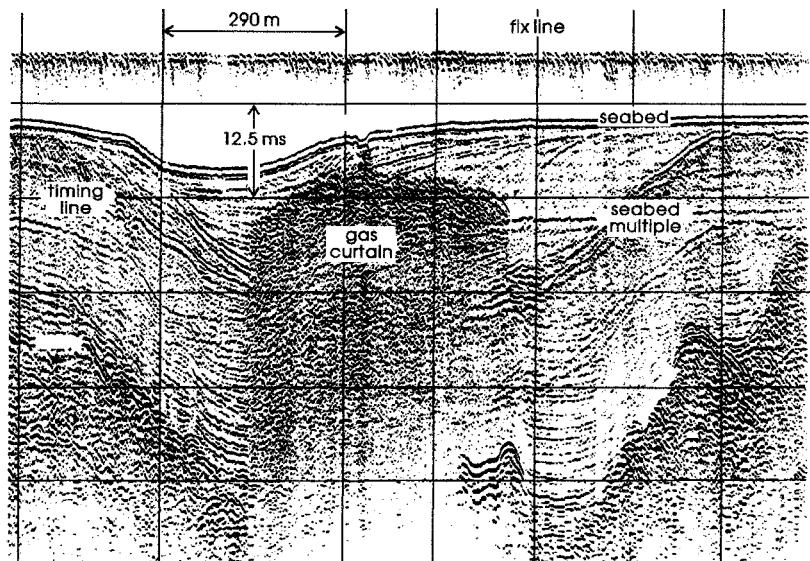
a. Gas plumes, northeast Irish Sea.**b. Gas curtain, Firth of Forth.**

Figure 8-5. Indications of gaseous phase methane on seismo-acoustic profiles of marine sediments. (From Taylor 1992. © 1992 Elsevier Science.)

Estuaries and Fjords

Estuaries and fjords are related geomorphological features. Both are formed by marine transgression into valleys proximate to the coast. Most present-day estuaries and fjords were formed by the 100 to 130 m rise in sea level that occurred during the Holocene, in response to melting of Pleistocene continental glaciers. Estuaries and fjords may also be formed by tectonic coastal subsidence.

An estuary is that portion of a river valley influenced by tidal currents and mixing of fresh and marine waters (Reading and Collinson 1996). Estuaries receive sediments from both continental and marine sources. An estuary is bounded seaward by a high-energy outer zone dominated by marine processes. The outlet may be partially closed by a barrier beach or dune ridge. The head of the estuary is dominated by fluvial processes. A central basin forms in-between. The basin is a relatively low-energy zone, the site with the greatest potential for deposition of organic-rich sediments, particularly during still-stand of the tide (Reineck and Singh 1980, p. 315–320). Some basins may become anoxic. Basin sediments may be heterogeneous, consisting, for example, of lenticular channel sands amid interbedded layers of sand and organic-rich silt and clay. A delta may form at the head of the estuary, capped by mud flats or peat-forming salt mire. Subaerial delta topset sediments may eventually become buried in fluvial sands and gravels or marine sands.

Fjords are generally glacially excavated valleys that open to the sea. Fjords often feature a rock sill on the seaward side, which promotes anoxic conditions in bottom waters (Reineck and Singh 1980, p. 319). Organic-rich sediments are deposited in the deeper parts of the basin.

Examples of bacterial methane in estuarine sediments are common along the coast of China (Zhang and Chen 1985). Accumulations of commercial importance are located near the mouths of major rivers, including the Chang (Yangtze), near the city of Shanghai; the Qiantang, near Hangzhou; and the Zhu (Pearl), near Guangzhou. The main source beds have been dated at 10 ka B.P. and lie at depths of 30 to 40 m. Secondary sources deposited during later transgressions lie at depths of 10 to 24 m. Gaseous phase methane accumulates in sand bodies ranging from 1 to 10 m thick. These form sheet sands and channel sand bodies, and sand bar belts parallel to the coast. A cross-section of estuarine sediments and gas pools in the Shanghai region is shown in Figure 8-6.

Gaseous and solution phase methane in estuarine formations caused considerable difficulty during construction of a sewer outfall into the Chang River in the early 1990s (Cheng 1997). Boreholes drilled prior to tunneling released gaseous phase methane from stratigraphic traps. Discharge volumes from boreholes averaged 30 to 40 m³ and reached a maximum of 140 m³. These traps subsequently recharged, and during tunneling they contributed to gaseous phase discharge into the heading. This difficult situation was aggravated by the absence

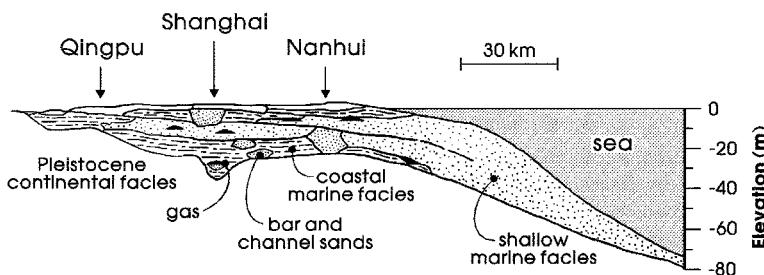


Figure 8-6. Holocene stratigraphy and trapped bacterial methane in estuarine deposits of Chang River, Shanghai region. (Adapted from Zhang and Chen 1985.)

of backfill in boreholes. Gas was detected entering the tunnel through the outlet part of the TBM screw conveyor and around the tail of the shield.

Marine sediments blanketing ancient drainage channels may be highly charged with bacterial methane. The distribution of gaseous phase methane in fine-grained sediments of Chesapeake Bay, U.S. East Coast, is shown in Figure 8-7. The figure was developed from seismo-acoustic reflection records. North of latitude 39°N, methane is generated in recent sediments under low salinity waters. South of 39°N, gaseous phase methane is confined to sediments overlying ancient drainage channels incised during the last (Wisconsinan) glaciation, when sea levels were 80 m lower than present. As sea levels rose, these channels filled with organic-rich sediments and were subsequently blanketed by fine-grained sediments that obscured the drainage basin relief. Tests on core samples indicate that gas bubbles occupy more than 6% of the volume of highly gas-charged sediment and extend to depths of several meters (Hill et al. 1992). Gas-charged marine sediments over ancient buried drainage channels have also been reported on the U.K. coast (Taylor 1992) and in Hong Kong harbor (Premchitt et al. 1992).

Lagoons

A coastal lagoon is a shallow body of water partly or completely separated from the sea by a narrow strip of land such as a barrier island or reef that retains water at low tide. Lagoon waters range from brackish to hypersaline. Fine-grained sediments may be deposited in lagoons subjected to a narrow tide range (Reading and Collinson 1996). Organic matter incorporated in lagoonal sediments includes plant debris washed in by rivers, and benthic algae on the lagoon bottom.

Deltas

Organic matter in delta sediments is derived mainly from terrestrial plants in the drainage basin. Burial is promoted by humid climatic conditions in the drainage

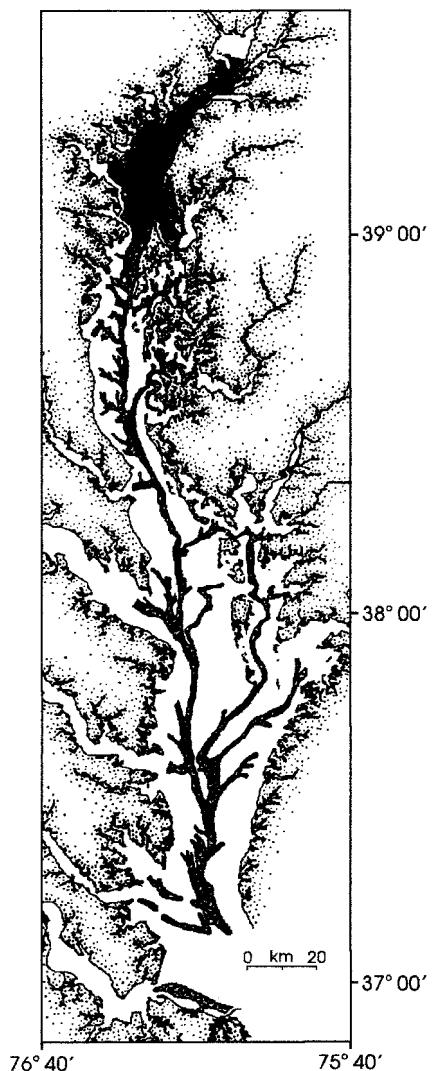


Figure 8-7. Distribution of gaseous phase methane in sediments of Chesapeake Bay, U.S. east coast. (From Hill et al. 1992. © 1992 Elsevier Science.)

basin, sediment load of mainly fine clastics, and low to moderate wave and tidal forces in the receiving basin. The distribution of organic matter in sediments is influenced by water flow gradients across the delta.

The upper delta plain is unaffected by basin hydraulics; it does not differ substantially from fluvial environments (Reading and Collinson 1996). Deposition on the upper delta is both subaqueous and subaerial. As delta lobes prograde into the basin, lakes form in abandoned channels, and embayments form between emergent and near-emergent levees along active and abandoned channels. These shallow lakes and embayments are gradually filled with organic-rich fine sand, silt, and clay, by small distributary channels that feed into them, and by overbank flood waters. Lakes and embayments may eventually develop into wetlands and peat-forming mires, populated by freshwater vegetation nearest the delta head and brackish or saline vegetation toward the basin.

The delta front is the most active area of deposition; it is a transition area between the upper delta plain and the prodelta basinal environment. Delta front sediments consist of coarse to fine sand, silt, clay, and organic matter. The finest sediments are deposited in layers or lenses in basins bounded by subaqueous channels and levees.

Shelf Environments

Shelf environments occur along continental margins and in inland seas. On continental margins the shelf extends from just below wave base to the top of the continental slope (Reineck and Singh 1980, p. 371–381). Water column depths range from 5 to 500 m, averaging from 10 to 200 m (Johnson and Baldwin 1996). Sediment transport on the shelf depends on tidal currents, waves, storm-generated currents, and oceanic currents. On many shelves these water currents are so low in energy as to produce no visible effects on the sediment surface.

Shelves receive most of their mineral sediment from suspension load of rivers. Silty sand to clayey silt are typically deposited in the transition zone from coastal sand to shelf mud. Clayey silt to silty clay are deposited in more distal areas, and in shallow areas along low-energy coasts. Extensive deposits may form off the mouths of rivers carrying a heavy suspension load. Shelf sediments incorporate particulate organic matter of terrestrial and marine origin. Marine organic matter originates from primary production in the euphotic zone, which extends to depths of a few meters in turbid nearshore waters (Calvert 1987).

Bacterial methane generated in marine shelf sediments in the Tokyo region served as a major energy resource for about 40 years, until 1971 (Marsden and Kawai 1965; Hayashi and Ishii 1989). The principal source and reservoir deposits are Pliocene to lower Pleistocene marine basin sediments of the Kazusa Group, which underlie the Kanto Plain. These interbedded siltstones and sandstones were deposited in a relatively deep open sea. They extend over an area of 12,000 km² and have a maximum thickness of 2,800 m. A subsurface profile of the area is

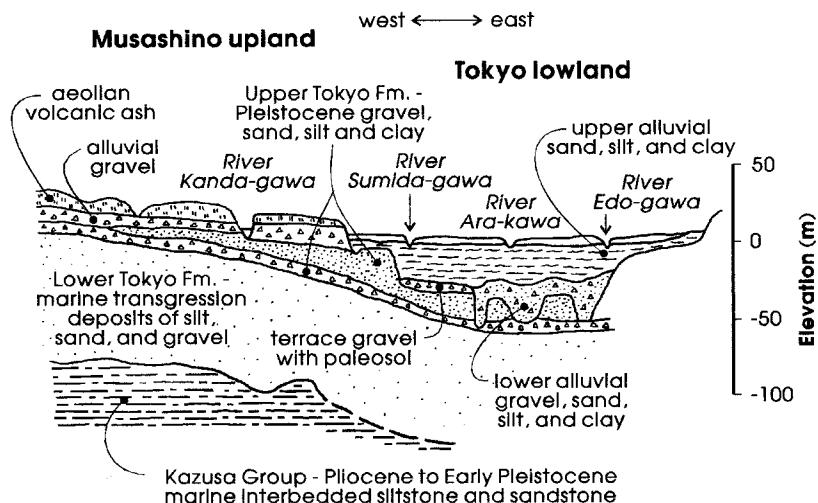


Figure 8-8. Stratigraphy of Tokyo area. Marine basin sediments of the Kazusa Group, a principal source of bacterial methane. Overlying Quaternary sediments contain methane migrated from Kazusa Group and from decomposition of organic matter abundant in alluvial sediments. Gas retained in solution in brine in lower formations, and in freshwater in upper. (Adapted from Hayashi and Ishii 1989.)

shown in Figure 8-8. The main reservoirs are poorly consolidated fine- to medium-grained sands and sandstones at depths of about 450 to 650 m. Porosities are about 30%. Methane in the Kazusa Group is held mainly in solution in pore water, at saturation concentrations, and was recovered by groundwater extraction. Gas was also produced from much shallower depths from upper Pleistocene and Holocene sediments, which contain a mixture of methane that migrated from the Kazusa Group and methane generated from organic matter incorporated in these younger sediments. The scarcity of gaseous phase accumulations suggests a lack of stratigraphic traps. Groundwater extraction was gradually restricted and ultimately banned in 1973 to stay ground subsidence in the area. By that time the groundwater table had been depressed as much as 60 m below the surface. Groundwater levels rose 20 to 50 m over the subsequent 15 years. This forced pore gases out of unsaturated sediments and into basements, causing several fires and explosions.

Landfills

Residential and commercial refuse consists of about 70% to 80% organic material (wet weight; EMCON 1980, p. 15). Bacteria generate gases from organic matter

in municipal landfills in the same manner as in natural environments. Confining layers in the landfill can impede escape of gas to the surface, causing excess pressures to develop in the unsaturated zone. Excess pressures can drive a gaseous phase from the landfill for considerable distances, laterally or downward through permeable ground.

In the early stage of landfilling, the composition of landfill gases changes as conditions in the bacterial environment change from aerobic to anaerobic. Four stages of landfill gas generation are shown in Figure 8-9. Phase I is the aerobic decomposition phase, in which aerobic bacteria utilize oxygen entrained in the waste to generate carbon dioxide (Barlaz and Ham 1993). Phase II is the anaerobic acid phase, in which fermentative bacteria generate carbon dioxide, and methanogenic populations have not yet become well established. Carbon dioxide concentrations can approach 90%. Phase III is the accelerated methane production phase, in which gas generation peaks. Phase IV is the decelerated methane production phase, in which the rate of gas generation stabilizes and gradually declines. The composition of landfill gas in Phase IV generally ranges from 50% to 70% methane, with carbon dioxide making up most of the balance. Phases I through III may take from 6 months to 5 years from start of landfill operation (Farquhar and Rovers 1973; Matsufuji et al. 1993). Methane generation may continue at low rates for 30 to 100 years after landfilling (McBean, Rovers, and

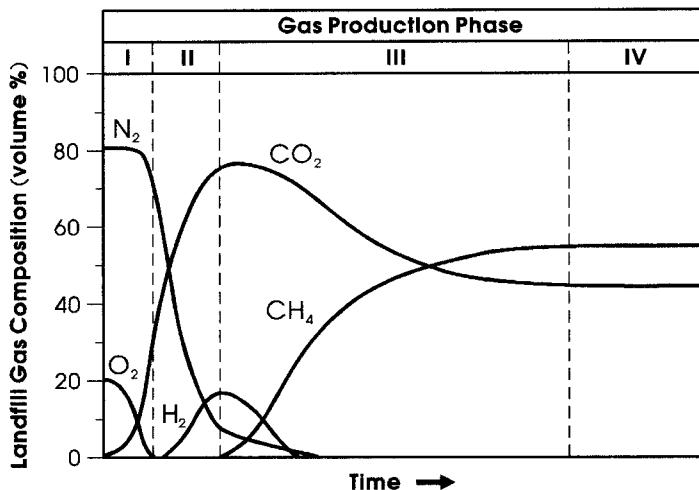


Figure 8-9. Evolution of gas composition in a landfill. (From Farquhar and Rovers 1973. © 1973 Kluwer Academic Publishers.)

Farquhar 1995, p. 73). Bacterial gas generation is enhanced, and shortened in duration, by moist conditions in the landfill, warm temperatures, and aeration.

Excess pressures may develop in the unsaturated zone of the landfill and drive gaseous phase bulk flow out into surrounding unsaturated strata. Gaseous phase pressures of 0.08 atm (80 mb) above atmospheric have been measured in large deep landfills (Campbell 1989). Factors that promote pressure buildup include impermeable layers within the waste, such as dense compaction layers, intermittent covering layers, or perched water; a liner or clay cap; increasing depth of waste; moist conditions in the waste; and a high volume of gas generation (McBean, Rovers, and Farquhar 1995, p. 379–412; Campbell 1989). Gas migrates through localized permeable features such as sand layers, rock fractures, and utility trenches. Confinement of the permeable pathway by overlying clay layers, frozen ground, saturated surface soils, and pavements tend to extend potential migration distances. The groundwater table forms the lower limit of potential gaseous phase migration. Vegetation distress is a common indicator of landfill gas migration and is caused by anoxic conditions in the root zone. Landfill gas has been responsible for a number of building explosions and injuries. Explosive concentrations of methane have been measured in soils 400 m from the landfill. Methane can also be generated from dissolved organics in leachate that has escaped the landfill.

Late-Stage Bacterial Gas Environments

Organic matter incorporated into anoxic sedimentary environments eventually becomes bacterially or thermally decomposed to the extent that it is no longer directly accessible to anaerobic bacteria as an energy source. This organic matter can be decomposed by *aerobic* bacteria if subsequently exposed to oxygenated groundwater flow. Aerobic decomposition may eventually deplete flow system groundwaters of oxygen, enabling anaerobic bacteria to utilize the waste products of aerobic decomposition. Gas generated in this manner is termed *late-stage bacterial gas*. Hazardous concentrations of late-stage bacterial methane and hydrogen sulfide can be generated from lignite and subbituminous coal, thermally immature organic-rich shale, and crude oil.

Geologic conditions favorable for generation of late-stage bacterial gas in coal or organic-rich shale include uplift of the sedimentary sequence, erosion of overlying strata, and infiltration of meteoric waters (Scott, Kaiser, and Ayers 1994). Uplift and erosion promotes active groundwater flow by opening the fracture network. Late-stage bacterial gas can be generated at any time in a strata's history when it becomes exposed to oxygenated groundwater. Late-stage methane found in some coals may have been generated tens of thousands to a few million years ago (Rice, Law, and Clayton 1993). Gaseous phase methane may migrate

out of the strata to be retained in conventional traps. Unusually high methane concentrations in low-rank coals or thermally immature organic-rich shales may indicate late-stage bacterial gas generation.

Groundwaters of southeastern Montana contain bacterial hydrogen sulfide attributed to decomposition of lignite and subbituminous coal (Dockins et al. 1980). Hydrogen sulfide concentrations in groundwaters are generally below 1 mg L⁻¹ but may reach 4 mg L⁻¹. Sulfate originates from oxidation of pyrite, from solubilization of gypsum, and possibly from weathering of rock in this semi-arid region. Of 26 water wells sampled in the study, none exceeded 260 m in depth, and 17 did not exceed 50 m. The shallow depth of hydrogen sulfide suggests that aerobic bacteria may have played a role in making organic substrates available for sulfate reduction.

Commercial gas wells within and adjacent to a subcrop of late Devonian Antrim Shale on the northern margin of the Michigan basin produce methane of more than 80% bacterial origin, the balance being of thermogenic origin (Martini et al. 1998). The Antrim includes black shale members with organic contents ranging up to 24% TOC. The shale is thermally immature on the basin margin (vitrinite reflectance from 0.4% to 0.6%), but it is known to generate petroleum in deeper, more central parts of the basin. The subcrop on the northern margin is overlain by 50 to 250 m of glacial sediments. Gas wells produce from depths of 200 to 600 m. Repeated Pleistocene continental glaciation of the region opened fractures in the shale, increased hydraulic head over the subcrop, and charged the shale with oxygenated groundwater. Recharge with oxygenated waters is ongoing. Chemical effects of meteoric recharge to the Antrim extend 50 km basinward from the subcrop. Bacterial gas in the shale is likely on the order of a few tens of thousands of years old. Bacterial gas has also been reported to make up a significant portion of methane found on the northwest margins of the Appalachian basin, where organic-rich shales occur near the rock surface (de Witt 1987).

Hydrogen sulfide may be found in areas of oil seeps and near-surface shows. Permeable features that allow oil to migrate to the surface also serve as conduits for groundwater moving down through local or intermediate flow systems; the oil then may be subjected to aerobic bacterial decomposition. If sulfates are present in groundwater, sulfate-reducing bacteria can use these decomposition products in areas of the aquifer depleted of oxygen. Bacterial methane may also occur in areas of oil seeps in the absence of sulfates but is not readily distinguishable from thermogenic methane without detailed analysis.

Methane and hydrogen sulfide are generated in some oil reservoirs that have been artificially produced by injection of water. Hydrogen sulfide is particularly associated with injection of seawater (Nazina et al. 1995; Nazina, Rozanova, and Kuznetsov 1985; Odom 1993; Ivanov et al. 1983). It seems unlikely that bacterial hydrogen sulfide generated in a deep oil reservoir would survive migration to

shallow depths: it would tend to be consumed in geochemical reactions with iron in sediments.

Case Histories of Tunnels in Bacterial Gas Environments

Shaft Excavation for Chicago TARP Tunnel

A shaft was excavated in the community of La Grange Park, Illinois, in 1985, for construction of Chicago's TARP wastewater storage/conveyance system. The shaft was excavated through a uniformly graded coarse sand. Excavation had progressed to a depth of about 5.5 m through unsaturated ground, to near bedrock. Ground support consisted of vertical steel I-beams and horizontal timber lagging. At the end of the workday the shaft was covered with steel plates. Work recommenced three days later, on a rainy morning. The cover was removed and three workers descended in a mancage to continue excavating. Conditions appeared normal until the workers bent over to pick up their tools on the bottom of the shaft and had difficulty breathing. One worker felt particularly weak; he stumbled back to the mancage assisted by his companions. He fell from the mancage as it swung away from the top of the shaft and was fatally asphyxiated in the shaft bottom. Two workers participating in a rescue attempt suffered serious respiratory injury. The shaft was again covered overnight. The next day, the cover was removed and air in the shaft sampled. Tests showed an oxygen concentration of about 11% to 12%, and a carbon dioxide concentration of about 3% to 4%.

The available facts of this incident are sketchy. A possible explanation is that oxygen-deficient pore gases were drawn from unsaturated soils into the shaft. Gas inflow could have been driven by a drop in barometric pressure preceding a change in weather. The shaft dimensions, ground conditions, and an estimate of a moderate barometric pressure drop were used in the example calculation of gas inflow with barometric pressure fluctuation presented in Chapter 7. The shaft is depicted in Figure 7-4. The example calculation shows this to be a reasonable explanation, though based on an interpretation of the facts.

Crosstown 7 Collector Tunnel

The Crosstown 7 Collector Tunnel is one element in a large wastewater storage/conveyance system serving Milwaukee, Wisconsin. A portion of this tunnel was constructed in freshwater estuarine and fluvial deposits of the Menomonee River valley. The tunnel was excavated with a TBM, 3.6 m in diameter. Muck entry through the cutter head was controlled with flood doors, and discharge from the muck chamber onto a conveyor was controlled with a door mounted on an inner bulkhead. The tunnel was lined with single-pass concrete segments. On two occasions during excavation, methane entered the tunnel and forced the crew to evacuate. On the second occasion, three workers reentered the tunnel to modify the

ventilation system and clear the atmosphere, and they were killed in the heading by an explosion.

The estuarine and alluvial deposits in which the tunnel was constructed are Holocene valley fill. A river predating the present Menomonee River eroded the valley in Pleistocene glacial deposits following final retreat of Wisconsinan ice from the area. The river discharged to the ancestral Lake Michigan basin, at a level about 100 m below present lake level. As isostatic rebound raised the outlet of the Great Lakes drainage basin, lake levels rose, the lower reach of the river was drowned, and the valley was partially filled with sediment. Subsurface conditions along the tunnel alignment are shown in Figure 8-10. Groundwater levels in the estuarine deposits are close to present river level. Groundwater levels in the channel lag deposits and glacial deposits are about 2 m lower, due to pumping from underlying bedrock aquifers.

Methane was known to be present in the Holocene valley sediment. Tests on groundwater samples showed methane in solution, generally in concentrations less than 70% to 80% saturation (MWPAP 1988). Gaseous phase methane discharged from a borehole along the alignment, noted in Figure 8-10, after the boring was completed and during extraction of the casing. The discharge was apparently from a trap in the channel lag deposits below a seal of estuarine deposits. Gaseous phase discharges from borings in the area are rare.

Findings made in the course of investigations after the accident are as follows. The shift began at 7:00 AM, the tunnel was evacuated at 8:30 AM, and the explosion occurred at 9:03 AM. Ignition was attributed to an electrical pump motor (Stephan and Urosek 1989). The tunnel was ventilated by a main fan on the surface and a main duct that extended to the end of the trailing gear, and a separate smaller fan with a duct that extended the length of the trailing gear. Both ducts

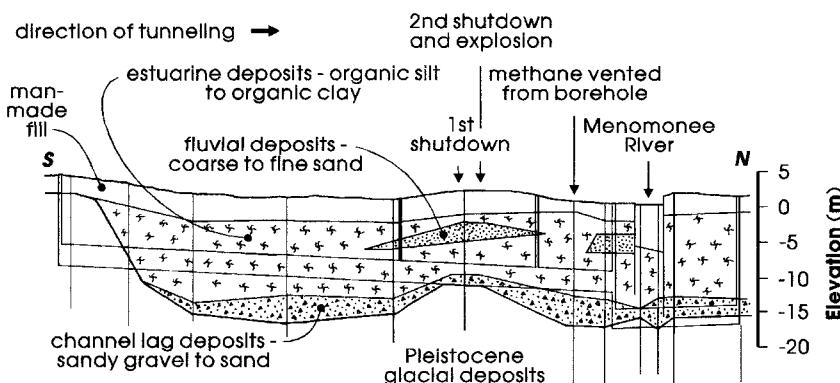


Figure 8-10. Crosstown 7 tunnel alignment through Holocene freshwater estuarine deposits. Bacterial methane retained in channel lag deposits. (Adapted from MMSD 1987.)

were determined to have been delivering air at a rate above the required minimum of about 9 m min^{-1} . The trailing gear had advanced beyond the end of the main duct, opening a gap of about 7 m between the main and forward ducts. Investigators estimated that 10 m^3 of methane contaminated 165 m^3 of tunnel atmosphere, to form a combustible concentration of 6% methane. The victims died of carbon monoxide poisoning. Groundwater inflow at the heading after the explosion was estimated to be about 100 L min^{-1} . The gas monitor on the TBM appeared to have been working properly. Its sensor head was located on the inner bulkhead very near the muck door.

The following is an interpretation of this incident.

There are two potentially significant mechanisms for methane entry to this tunnel. One is solution phase inflow with groundwater, and the other is gaseous phase inflow from a stratigraphic trap. The most likely gas entry point is through the face. A brush seal on the TBM tail-can impeded inflow around the leading edge of the segmented lining. The lining annulus was grouted close behind the TBM, preventing inflow through joints and grout holes in the lining. Methane entering the tunnel through the inner muck door would have to pass the gas sensor undiluted; consequently, the amount of methane that entered the tunnel prior to alarm was probably negligible. Elapsed time between the alarm and the explosion was 33 minutes. An average gas inflow rate of about 300 L min^{-1} would be necessary to produce the estimated 10 m^3 of methane that mixed in the tunnel atmosphere. The saturation concentration of methane in groundwater is 70 ml L^{-1} , at 1.74 atm total pressure at springline (1 atm barometric pressure plus 7.6 m water head) and ground temperature (13°C). Assuming the groundwater was saturated with methane, a groundwater inflow rate of 4300 L min^{-1} would have been necessary to produce a gas inflow rate of 300 L min^{-1} . Such an inflow was not observed at the time the alarm sounded. Gaseous phase discharge from a trap appears to be the only explanation for the estimated inflow rate.

The gap that had opened between the leading end of the main duct and the trailing end of the forward duct essentially cut off 55 m of the heading from the ventilation system. The fan and duct on the trailing gear were merely recirculating contaminated air. An overlap between these ducts equal to at least twice the tunnel diameter is necessary to prevent recirculation (Kissell 1989).

A test boring drilled prior to tunneling, and very near the explosion location (shown in Figure 8-10), did not discharge gaseous phase methane. This boring was drilled with hollowstem augers. It is possible that the trapped gaseous phase was originally off the alignment and was drawn laterally to the heading by transient groundwater flow gradients induced by tunneling.

This was the first tunnel accident due to methane recorded in Milwaukee, despite the fact that this is a highly developed metropolitan area widely underlain by estuarine deposits. Gas inflows on previous tunnel projects may have been prevented by use of compressed air tunneling methods, formerly a common practice.

Furnas Diversion Tunnels

The Furnas diversion tunnels are part of a hydroelectric power station on the Rio Grande, Brazil (Lyra and MacGregor 1967). The two tunnels are 885 m and 806 m long, about 14.2 m in diameter, and run parallel on the left bank. They were excavated through hard quartzitic rock. Closure gates on the inlet portals failed after the reservoir had been filled to 90 m above tunnel invert. The failure occurred before permanent concrete plugs in the diversion tunnels could be sealed. Water flowed past the partially completed plugs, flooding the downstream reaches of the diversion tunnels. To regain access to construct new permanent plugs, galleries were driven above the diversion tunnels, downstream of the plugs. Methane was encountered in these galleries.

On two occasions, methane entering a gallery from the left tunnel had fatal consequences. In the first incident, strong drafts of air pulsated back and forth through a small vertical access shaft connecting the gallery to the tunnel below. Two workers in the gallery were fatally asphyxiated. At the time, the left tunnel was discharging water at a rate of about $90 \text{ m}^3 \text{ s}^{-1}$. This flow was reduced to $26 \text{ m}^3 \text{ s}^{-1}$ by dropping material into the reservoir, over an opening that had been eroded over the closure gates. On resuming work in the access gallery several months later, a methane explosion killed two workers and seriously injured a third.

Methane inflow to the gallery was attributed to exsolution from water flowing through the diversion tunnels. Methane apparently had originated from bacterial decomposition of vegetation in the reservoir. Tests on samples of reservoir water taken from a depth of 84 m showed solution gas to consist of up to 16% methane, with air making up most of the balance. A methane concentration of 5.4 ml L^{-1} was determined from a single test, though investigators acknowledged that some gas was lost due to decompression while raising the sample to the surface.

The following is an interpretation of this incident.

Regarding the measurements of solution gas in reservoir waters, the 16% methane concentration suggests a mixing of oxic and anoxic waters. The solution concentration of methane is well above the 0.35 ml L^{-1} necessary to generate a combustible concentration in air (from Table 7-1).

In this case it would be unreasonable to make the usual assumption that all solution gas entering the diversion tunnels escaped into the tunnel atmosphere. These tunnels were flooded more than half full and were unventilated. Equation 7-9 describes the precise relationship between the mass concentration of gas in inflowing groundwater (ρ_{ggw}) and in the tunnel atmosphere (ρ_{gta}):

$$\rho_{gta} = \frac{\rho_{ggw}}{\left(\frac{1}{K} + \frac{q_{ta}}{q_{gw}} \right)} \quad (7-9)$$

Under flood conditions in the diversion tunnels, the $q_{\text{ta}}/q_{\text{gw}}$ term for volumetric flow rates of air and groundwater is small and may be neglected. Equation 7-9 then becomes:

$$\rho_{\text{gta}} = \rho_{\text{ggw}} K$$

This is equivalent to:

$$\phi_{\text{gta}} = L_{\text{ggw}} K$$

where ϕ_{gta} is the volume fraction of gas in the tunnel atmosphere, and L_{ggw} is the Ostwald coefficient for gas in solution. The term K is the gas partition coefficient introduced in Chapter 7; it is equal to 26.7 for methane at 20°C. Solving for the concentration of methane in tunnel air using the solution concentration test result yields:

$$\phi_{\text{gta}} = \left(5.4 \frac{\text{ml}}{\text{L}} \right) (26.8) \left(\frac{\text{L}}{1000 \text{ ml}} \right) = 0.14 \frac{\text{ml}}{\text{ml}}$$

This result equals a methane concentration of 14%, well below the 71% necessary to cause fatal asphyxiation. Water flowing through the diversion tunnels during the first incident apparently contained more methane in solution than test results indicate.

A situation somewhat similar to that at Furnas developed during closure of the diversion tunnel for the Akosombo Dam on the Volta River in Ghana (MacLauchlan 1967). Closure gates at the inlet portal failed. Reservoir water leaking through the gates exsolved methane into the tunnel atmosphere. A subsequent explosion killed 11 attempting to complete the permanent plug.

Fort Lawton Parallel Tunnel

The Fort Lawton Parallel Tunnel is located in Seattle, Washington. It was constructed as part of an expansion of the Westpoint wastewater treatment plant (Fulcher 1993). The 2.5 km long tunnel was excavated through glacial and interglacial deposits. It was excavated with an earth-pressure balance TBM, 4.7 m in diameter. Muck entry was controlled with flood doors on the cutter head, and doors on the muck chamber bulkhead. Steel ribs and wood lagging provided initial support. The TBM was equipped with a methane monitor set to shut down the machine at methane concentrations in the heading atmosphere exceeding 10% LEL. Periodic methane inflows shut down the TBM for an hour or so. On two occasions the crew was evacuated for 5 to 8 hours to allow the gas to dissipate. The work was completed without injury due to gas.

Seattle lies in the Puget Lowland, which was glaciated several times during the Pleistocene by a Cordilleran continental ice sheet flowing southward from British Columbia (Armstrong et al. 1965). The most recent glaciation, the Fraser glaciation, was preceded by the Olympia Interglaciation, a period of cool, moist

climate. Sediments of the Olympia Interglaciation were deposited in shallow lakes, wooded swamps, and flood plains. Age of organic matter from these deposits in the Seattle area ranges from 18 to 22.4 ka B.P. Advancing ice of the Vashon Stade of Fraser glaciation dammed northward-draining streams, and Olympia sediments in the Seattle area were buried by lacustrine clays known locally as Lawton Clay. As the ice continued to advance, outwash deposited in meltwater streams along the ice front buried the Lawton Clay. These outwash deposits are known as the Esperance Sand. Ground conditions along the tunnel alignment are shown in Figure 8-11.

Bacterial methane is generated from organic matter in the Olympia Interglacial deposits and is retained below the Lawton Clay. Gaseous phase methane issued from two borings drilled along the alignment. Solution phase methane concentrations measured in groundwater samples are shown in Figure 8-12. The saturation concentration for methane in water, at 20°C and 1 atm total pressure, is about 23 mg L^{-1} , indicating that some samples were undersaturated. The higher concentrations of methane found in the deeper portions of the alignment are likely due to a combination of higher hydrostatic pressures and lower groundwater flow gradients. Groundwater flow is more active in shallower areas of the alignment, and may inhibit methanogenesis by oxygenating the environment, by enabling methanotrophs to consume methane, and by carrying methane away in solution.

Öresund Sewer Outfall

Öresund (The Sund, or The Sound) is a narrow seaway separating Denmark and Sweden. It connects the Baltic sea on the south to Kattegat strait on the north. A sewer outfall tunnel was constructed into Öresund in 1941–1942, presumably near Copenhagen, extending to about 4 km off the coast. Hydrogen sulfide exsolving from infiltrating waters caused intense eye irritation and other discomforts

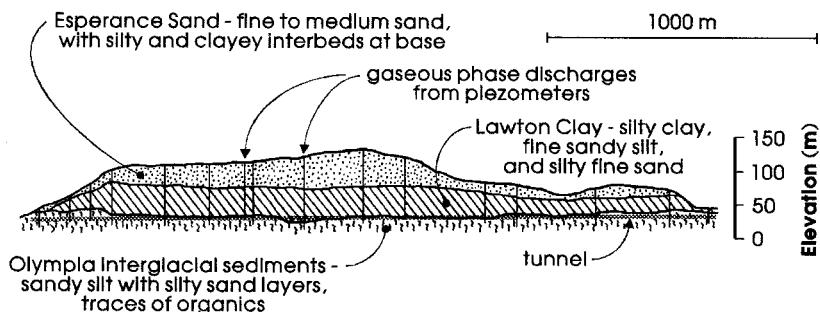


Figure 8-11. Fort Lawton Parallel Tunnel, Seattle. Bacterial methane generated in interglacial sediments is trapped below clayey glaciolacustrine sediments. (Adapted from Fulcher 1993.)

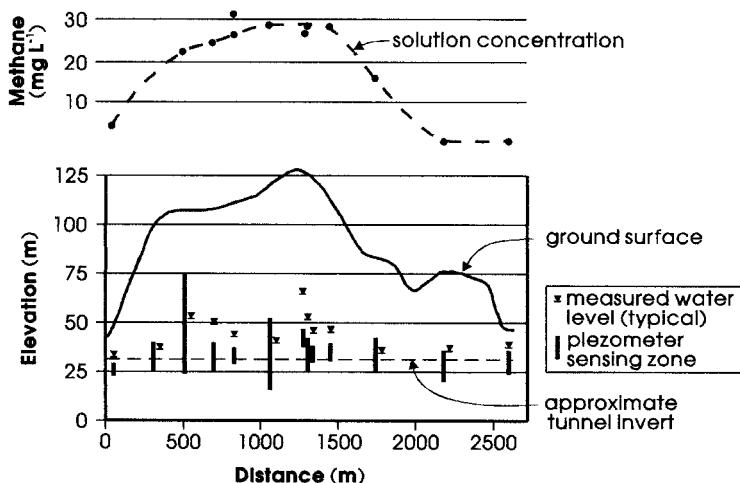


Figure 8-12. Dissolved methane concentrations in pore waters sampled from piezometers along Fort Lawton Tunnel alignment. (Adapted from Fulcher 1993.)

among the workers. War shortages aggravated the difficulty of providing adequate ventilation. The report of this project in a Danish medical journal (Larsen 1944) is apparently the first scientific investigation of hydrogen sulfide in a civil works tunnel ever published.

Most of the year, Öresund waters consist of an upper layer of brackish, Baltic water flowing north, overlying heavier North Sea water flowing south from the Kattegat (Mattsson 1993). Phytoplankton production in the Öresund is relatively low, apparently due to rapid changes in salinity. Waters are shallow, enabling fecal pellets and phytoplankton detritus from the euphotic zone to reach the sediment surface. Bottom waters are oxic, so most of the organic matter that reaches sediments is consumed by benthic feeders. Inorganic matter sedimentation rates are low, in the absence of large rivers discharging into Öresund.

The Öresund tunnel was constructed from an “island shaft,” located 1.75 km off the coast. Bedrock at the shaft was 4 m below sea level. The shaft was excavated in limestone to a depth of about 30 m below sea level. Headings were then driven east (seaward) and west, by drilling and blasting. Excavated size was 2.1 to 3.0 m high by 2.3 to 2.5 m wide. A 0.5 m deep trench was constructed in the invert to collect water inflows. Infiltration was described as a fine rain or as issuing from constant springs. Inflow rates from individual springs ranged up to 1.5 L s^{-1} in the east tunnel, and greater in the west tunnel. Inflows had a salinity of about 20 g kg^{-1} , indicating they originated from Öresund water. The tunnel was ventilated by blowing air into the heading. Ventilation capacities were

gradually increased as hydrogen sulfide problems became more severe. Average tunnel airflow velocities ranged from about 5 to 30 m min⁻¹.

Hydrogen sulfide affected workers only in the east tunnel. Odors there were described as weak. Workers suffered eye irritation including burning pain, abnormal sensitivity to light, and broken vesicles of the cornea. Symptoms appeared one-half hour to several hours after entering the tunnel. Eye irritation increased after workers left the tunnel, apparently due to an anesthetic effect of high concentrations of hydrogen sulfide in the tunnel atmosphere. Workers occasionally suffered slight irritation of the pharynx, and nausea. They also complained that cigarettes and food had a bad taste. The most severe cases occurred among workers employed sealing seepage points and cleaning the trench, not necessarily at the heading. In one instance, two workers violated a prohibition on entering the tunnel while it was unventilated. One collapsed unconscious. The other, though suffering from nausea, cold sweats, shortness of breath, and dizziness, managed to drag his companion to safety.

An investigation was performed to determine the concentration and distribution of hydrogen sulfide, in an attempt to determine its source. Tests on water samples from 68 seepage points along the tunnel showed solution concentrations ranging up to 75 mg L⁻¹. The highest solution concentration was at the point of greatest seepage, inflowing at a rate of 1.5 L s⁻¹. This inflow was centered on a zone of porous rock, 780 m east of the construction shaft. Tests on air samples from along the tunnel showed hydrogen sulfide concentrations ranging up to 165 ppmv, with highest concentrations in an area 600 m to 900 m east of the shaft. The heading at this time was 1050 m east of the shaft. Concentrations in air declined from this area toward the shaft, along the direction of airflow in the tunnel opening. Investigators reasoned that hydrogen sulfide was being oxidized in the tunnel atmosphere.

Investigators concluded that hydrogen sulfide originated from anaerobic bacterial activity in a bed of silt overlying bedrock in the seaward three-quarters of the east tunnel, where the sediment surface ranged from about 8 to 15 m below sea level. The silt bed ranged in thickness up to about 8 m. No serious difficulty with hydrogen sulfide was encountered in the west tunnel, though Öresund water inflows there were greater. Indications are that the rock surface was higher and the silt bed may have been largely absent along the west tunnel.

The following is an interpretation of this incident.

The maximum concentration of 75 mg L⁻¹ found in inflowing waters would equilibrate to a concentration of about 15,000 ppmv in air in an unventilated space, fifteen times the fatally toxic concentration. Concentrations measured in the tunnel atmosphere were consistent with symptoms exhibited among workers.

The sulfate reduction zone in the silt bed may have extended several tens of cm below the sediment surface because of the low rate of sedimentation of organic matter and corresponding low rate of consumption of sulfates in pore waters. In addition, fresh Öresund waters infiltrating through the silt bed along

flow gradients toward the tunnel may have revived sulfate reduction in deeper sediments. The limestone, with its inherently low iron concentration, did little to remove hydrogen sulfide from infiltrating waters via geochemical reactions. There was no mention of methane entering the tunnel atmosphere from silt bed pore waters below the sulfate reduction zone, though it may have been, in concentrations that went unnoticed.

The reported decline in hydrogen sulfide concentrations in the tunnel atmosphere, from the point of greatest groundwater inflow to the shaft, may have been due to oxidation in air as investigators reasoned. At times the average tunnel airflow velocity was so low as to require 2 hours or more for air discharged from the duct to reach the shaft. Hydrogen sulfide in air has a half-life of about 12 hours (Jaeschke et al. 1978).

Niagara Falls Raw Water Intake Tunnel

The Niagara Falls Raw Water Intake Tunnel is located in Niagara Falls, New York. The tunnel extends from a drinking water treatment plant on the north bank of the Niagara River, south to an intake shaft in the river channel (Wiggins 1997). It is about 600 m long and was excavated in dolomite bedrock to 3 m in diameter, using drill and blast methods. Low to moderate groundwater inflows released enough hydrogen sulfide to necessitate extensive grouting to seal permeable features, and upgrade of the ventilation system. Hydrogen sulfide had not been encountered in the project exploration program, though it had been encountered in previous excavations to rock in the vicinity.

A subsurface profile along the tunnel alignment is shown in Figure 8-13. Upper rock formations are sedimentary rocks of the middle Silurian. They dip gently to the south into the Appalachian basin. The tunnel is in the upper Lockport

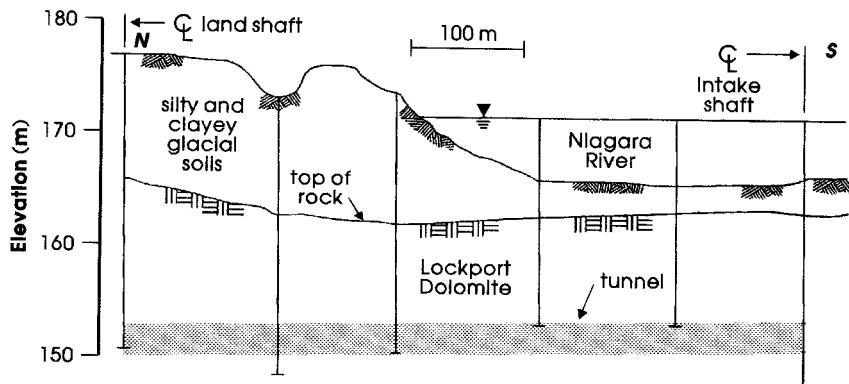


Figure 8-13. Niagara Falls Raw Water Intake Tunnel. Late stage bacterial hydrogen sulfide generated in dolomite below invert. (Adapted from O'Brian & Gere 1993.)

Dolomite, a dark gray to brown, massive to thinly bedded dolomite, about 55 m thick (Miller and Kappel 1987; O'Brian & Gere 1993). Project borings showed the Lockport to contain seams to partings of shale, and occasional seams and nodules of gypsum. Rock at tunnel depth is fresh to slightly weathered. The Lockport is underlain by the Rochester Shale, a dark gray calcareous shale about 18 m thick. Bedrock is overlain by silty and clayey till and glaciolacustrine deposits.

Groundwater movement in the upper Lockport is primarily through abundant vertical joints interconnected with laterally extensive open bedding planes. Jointing is attributed to erosion of overlying rock, and rebound following retreat of Pleistocene continental glaciers. Open bedding planes are attributed to solutioning of gypsum. Open joints in the upper 3 to 8 m of rock give it a hydraulic conductivity of about 2×10^{-3} to 5×10^{-3} cm s⁻¹. Below this zone, hydraulic conductivity declines to about 4×10^{-4} to 7×10^{-4} cm s⁻¹ (Miller and Kappel 1987).

Hydrogen sulfide and methane had been encountered previously in the area. The original water intake tunnel, constructed in 1936 and extended in 1950, lies about 300 m west of the new tunnel. Hydrogen sulfide was encountered in test borings and in shaft and tunnel excavations on both these previous projects (O'Brian & Gere 1993). Gas was encountered in three test borings at about elevation 150 m. On the 1950 project, a workman standing at the top of the bottomed-out intake shaft was overcome by hydrogen sulfide, fell into the shaft, and was killed. The Lockport Dolomite has also been reported to contain methane that has migrated from the underlying Rochester Shale.

Excavation for the new water intake tunnel proceeded from the land shaft toward the river. Hydrogen sulfide was initially encountered during sinking of the land shaft (Wiggins 1997). Hydrogen sulfide concentrations in the shaft and tunnel atmosphere remained at about 4 ppmv for the first 75 m of the tunnel drive. Concentrations peaked locally to several hundred ppmv at points of water inflow, primarily at split set dowel locations. Groundwater pumping rates at the time were on the order of 3.5 L s⁻¹. About 100 m into the drive, groundwater inflow increased, with additional flow now coming from bedding plane openings exposed in the heading. Pumping rates increased to about 10 L s⁻¹, and the ventilation system was frequently unable to maintain hydrogen sulfide concentrations below allowable limits of 10 to 15 ppmv. Grouting conducted from inside the tunnel was marginally effective in reducing groundwater inflows to levels sufficient to maintain a safe atmosphere. About 400 m into the drive, hydrogen sulfide concentrations reached 20 ppmv, temporarily halting the advance. The problem was overcome by pattern grouting the rock ahead of the face, from a barge in the river. Rock was grouted to a depth of 1.5 m below invert. The capacity of the ventilation system was also increased. On resuming excavation, hydrogen sulfide concentrations were generally maintained below 10 ppmv. No methane was reported.

The following is an interpretation of this incident.

Geologic conditions suggest that the hydrogen sulfide is late-stage bacterial gas. It was likely generated in the Lockport Dolomite by sulfate-reducing bacteria inhabiting an anoxic zone below the tunnel invert. Prior aerobic bacterial decomposition of organic matter in this zone would provide a source of organic substrates, and dissolution of gypsum would provide a source of sulfates. The lower Lockport may have been charged with oxic waters at some time in its geologic past, likely during Pleistocene glaciation when overlying ice or ice margin lakes raised hydrostatic pressures at the rock surface. The Lockport is thermally immature, so its organic matter is readily susceptible to aerobic bacterial decomposition. Dolomite is also low in iron, a factor that tends to preserve hydrogen sulfide from consumption in geochemical reactions with iron.

A regional hydrogeologic study showed that groundwater flow in the Lockport is generally toward the Niagara Gorge, northwest of the site (Novakowski and Lapcevic 1988). Geochemical testing showed the groundwater to contain sulfate. The study suggests that at present, groundwater recharge to the Lockport is limited by low-permeability glacial overburden.

Indications are that the oxic/anoxic boundary is at or just below elevation 150 m. Hydrogen sulfide was encountered at that elevation in borings drilled for the 1936 and 1950 projects. Borings drilled for the most recent project did not penetrate much beyond that depth. Subsequent appearance of gas in the excavations can be explained by the much broader spacial hydrostatic influence of excavations compared to borings. The excavations drew some water from deeper depths than those penetrated by the borings, from depths below the oxic/anoxic boundary, from the zone inhabited by sulfate-reducing bacteria.

The minimum hydrogen sulfide concentration in air necessary to cause someone to collapse, as the shaft worker did in 1950, is 1000 ppmv. The minimum hydrogen sulfide concentration in water necessary to produce this concentration in air is about 4 mg L^{-1} . Actual hydrogen sulfide concentrations in groundwater at this site are likely several times higher.

Groundwater inflow to this tunnel would have presented little problem absent the hydrogen sulfide. This project demonstrates hydrogen sulfide's high toxicity, and its influence on construction measures other than ventilation capacity.

Methane may also have entered the tunnel in solution in groundwater but went unnoticed because of the extent of measures necessary to control hydrogen sulfide. Methane may be late-stage bacterial gas generated in the Rochester Shale, or thermogenic methane migrated from deeper strata to the south.

ANCIENT BACTERIAL GAS IN UNCONVENTIONAL RESERVOIRS

Ancient bacterial gas is that remaining trapped in organic-rich rocks or rock sequences after significant anaerobic bacterial decomposition has ceased. The gas

is predominantly methane. It is retained in low-permeability unconventional reservoirs for tens to hundreds of millions of years. Reservoirs are usually of Cretaceous age or younger but may be as old as the Carboniferous (Rice 1992). The distinction between an active gas generating environment and one containing ancient bacterial gas is easier to conceptualize than to define; transition from the former to the latter may take a very long time.

Ancient bacterial gas is found in sedimentary environments of marine and non-marine origin. These include deltaic, shelf (clastic and carbonate), ocean basin (turbidite), evaporating basin, fluvial, lacustrine, coastal plain, and coal swamp environments. Rapid rate of deposition is a common though not universal characteristic of these environments. Rapid deposition promotes incorporation of organic matter in the sediment, and early formation of stratigraphic traps. Sequences often exhibit frequent interbedding of low-porosity organic-rich sediment with porous sediment, on centimeter scale or larger. Thus the reservoir and source/seal are closely associated. Common rock types are interbedded sandstone and organic shale, chalk, and subbituminous coal. Rocks containing ancient bacterial gas exhibit a low temperature history. Burial depths are usually less than 1800 m. Gases may contain up to about 2% higher hydrocarbons (C_2 to C_5) generated in early thermogenesis.

Unconventional reservoirs produce ancient bacterial gas from gaseous phase held in porous beds, and from adsorbed phase held on organic surfaces. The gaseous phase may form by exsolution from pore waters, following a decline in hydrostatic pressure associated with falling sea level, uplift of the strata, or erosion of overlying sediments. The gaseous phase migrates from organic-rich source beds or laminae, such as organic shale, into adjacent porous beds, such as sandstone or siltstone. The adsorbed phase is important in rock or rock sequences composed largely of organic-rich shales or subbituminous coals. Gas in unconventional reservoirs may be underpressured due to dilation of pores and decrease in reservoir temperature following erosion of overlying sediments. Underpressuring helps to retain the gas. Diffusion losses are limited because of the comparatively young age of the reservoirs.

Some unconventional reservoirs contain commercially important accumulations of ancient bacterial gas. Exploitable reservoirs have developed fracture permeability that enables gas in gaseous phase or in adsorbed phase to migrate to the well. The organic matter content of rock containing commercial accumulations of gas is typically greater than 0.5%.

Accumulations of ancient bacterial gas are widespread in the central plains of North America, in Cretaceous clastic and carbonate shelf sediments of the Western Interior Seaway. Some of these are in the Niobrara chalk, deposited in the central portion of the seaway. Unweathered samples of this chalk are colored various shades of gray or black; weathered samples are buff to white (Steece 1989). Gas was generated from organic matter in the chalk and from an overlying

thick sequence of organic shales. Commercial accumulations of gas are found in low-amplitude anticlinal structures where fracturing has improved the reservoir quality of the chalk but has not compromised the sealing properties of overlying shales (Pollastro and Scholle 1987; Rice 1992). Some gas has migrated into glacial deposits overlying the chalk (Steece 1989).

The Powder River basin of Montana and Wyoming produces bacterial gas from a shallow coal-bearing sequence (Choate, Johnson, and McCord 1984; Rice 1993). This is an intermontane basin lying between the Black Hills and the Bighorn Mountains, on the eastern front of the Rocky Mountains. Upper sediments include the Paleocene Fort Union Formation, which contains lignite to subbituminous coal in beds from 15 to 30 m thick. These coals currently range in depth from surface exposures to about 750 m. As much as about 600 m of overburden has been eroded over most of the basin, so coals have not been buried deeper than about 1350 m. Gas is commonly noted in shallow coal beds and adjacent sandstones, and some has been recovered from wells for domestic use. A study showed the gas to be bacterial methane generated by the fermentation pathway, a pathway commonly associated with decomposition of relatively young organic matter (Law, Rice, and Flores 1991). This gas was apparently generated early in the history of the coal. Its entrapment was attributed to the low permeability of coal, retention by adsorption on organic surfaces in the coal, rapid subsidence, and frequent interbeds of shale that formed effective seals. Methane constitutes over 99% of the hydrocarbon fraction. Carbon dioxide constitutes up to 10% of gas desorbed from coal samples, less than 3% of gas produced from coal, and less than 1% of gas produced from adjacent sandstone reservoirs. High gaseous phase discharges have been reported from a number of boreholes drilled into the Fort Union Formation, to depths of 150 m. Methane is discharged from sandstones, from coal beds, and from intervening sandstone–shale beds. Examples include a discharge of $20 \text{ m}^3 \text{ min}^{-1}$ from a poorly cemented sandstone below a coal bed, at a depth of 100 m, which continued for up to 1 hr before being stopped by water inflow. Surface monitoring around the drill casing showed methane concentrations of only 1% to 2% just prior to blowout. Methane discharges of up to $18 \text{ m}^3 \text{ min}^{-1}$ occurred from a coal bed at a depth of about 120 m. Discharge from one borehole formed a 2 m diameter crater at the surface. Groundwaters contain high concentrations of gas in solution. Water discharge from artesian wells is facilitated by bubble expansion as water rises in the well.

Other examples of unconventional reservoirs containing ancient bacterial gas in the near-surface underground include the Molasse basin in Germany (nonmarine/delta/marine); the Apennine foredeep of Italy (deep water clastic); the Carpathian foredeep in Poland (delta/marine); Cherokee and Forest City basins in Kansas (marine); San Luis basin in Colorado (nonmarine/fluvial); and the Caspian Depression in Kazakhstan (Rice 1992).

SEDIMENTARY BASINS—GENERATORS OF THERMOGENIC GAS

Sedimentary basins are crustal regions of thick sedimentary sequences up to several kilometers thick. Basin sediments accumulate over periods of subsidence and deposition that may persist for tens to hundreds of millions of years. Deeply buried organic-rich basin sediments become source strata for coal, petroleum, and thermogenic gases. These gases may migrate tens to hundreds of kilometers within the basin into the near-surface underground, and remain there for millions of years. Basin subsidence is due to stretching, thinning, and bending of the lithosphere, associated with plate tectonics and thermal convection in the mantle. Sediment and water loading in the basin may intensify subsidence. Basin stratigraphy is controlled by subsidence, eustatic sea level changes, climate, and sediment supply. Multiple cycles of continental and marine sedimentation are common. Note that sedimentary basins are defined on the basis of sediment thickness, not topography, and may incorporate mountain chains formed subsequent to deposition (Selley 1998, p. 364). A text on basin mechanics should be consulted for details on basin formation and sedimentation (for example, Allen and Allen 1990). This text follows a basin classification scheme based on the principal formation mechanisms of 1) lithospheric stretching, 2) flexure on continental and oceanic lithosphere, and 3) strike-slip along plate boundaries (Allen and Allen 1990, p. 14). This section identifies basin types commonly associated with accumulations of coal and petroleum.

Gases have been encountered during construction of municipal tunnels in cities located on the margins of the Appalachian and Michigan basins, United States, as shown in Figure 8-14. Both of these basins have generated oil and gas in their lower parts. Vertical migration of gas on their margins has been facilitated by bedrock fracturing from isostatic rebound following retreat of Pleistocene glaciers. Along the south shore of Lake Erie, from about Cleveland to Buffalo, these fractures reach depths of 450 m (de Witt 1987).

Basins Formed by Lithospheric Stretching

Lithospheric stretching leads to subsidence and formation of *intracontinental rifts*, *intracontinental sags*, and *passive continental margins*. These basin types are shown in Figure 8-15.

Intracontinental rift basins form by extensional faulting of continental crust induced by regional uplift or regional shear stress. They are relatively narrow (30 to 50 km wide) and are generally bounded by major normal faults in a stepped arrangement (Duff 1993, p. 671–672). Sedimentation is typically continental in the early stages of development, changing to shallow marine in later stages.

Intracontinental sags are flat, saucer-shaped basins lacking the major extensional faulting of rifts. They represent continental basins that have failed to de-

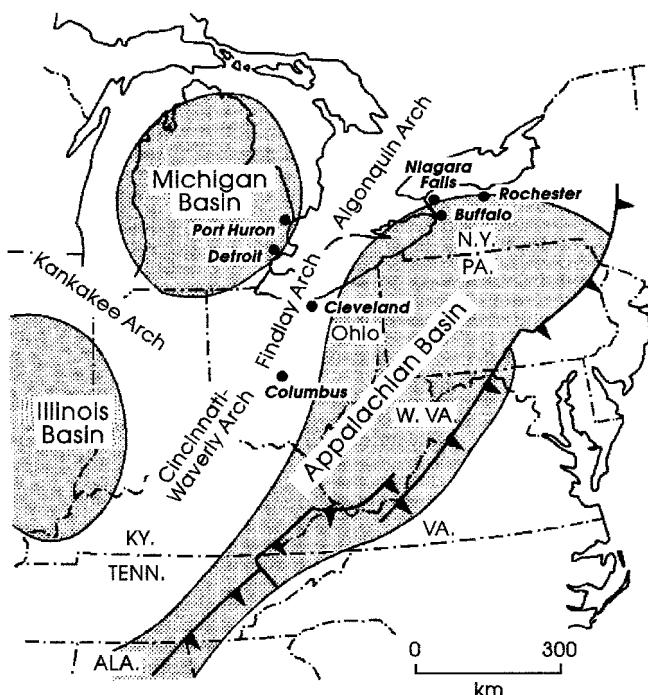


Figure 8-14. Major U.S. cities in which gas has influenced municipal tunnel construction. Appalachian basin is a foreland basin on northwest margin of Appalachian Mountains. Michigan basin is an intracontinental sag basin. (Basin map from Allen and Allen 1990, Fig. 6.8a.)

velop into rift basins or sea-floor spreading centers. Sags can be laterally extensive. The Michigan basin in the United States, for example, is about 600 km in diameter. Sedimentation may be continental or shallow marine. Sediments are characteristically laterally widespread and uniform, favorable for long-distance migration of crude oil and thermogenic gas. Sediments rarely exceed 4 km in total thickness, so only a small portion of sag basin sediments reach thermal maturity (Visher 1990, 346–347).

Rifts that remain active for prolonged periods evolve into ocean basins, and the former margins of the rift develop into passive continental margins. Sediment loads along the continental margin enhance subsidence, resulting in wedge-shaped basin fill thinning seaward. Sedimentation is typically continental in the early stages, evolving to shallow marine. Examples of passive margins include the Atlantic coasts of North America, South America, and Africa.

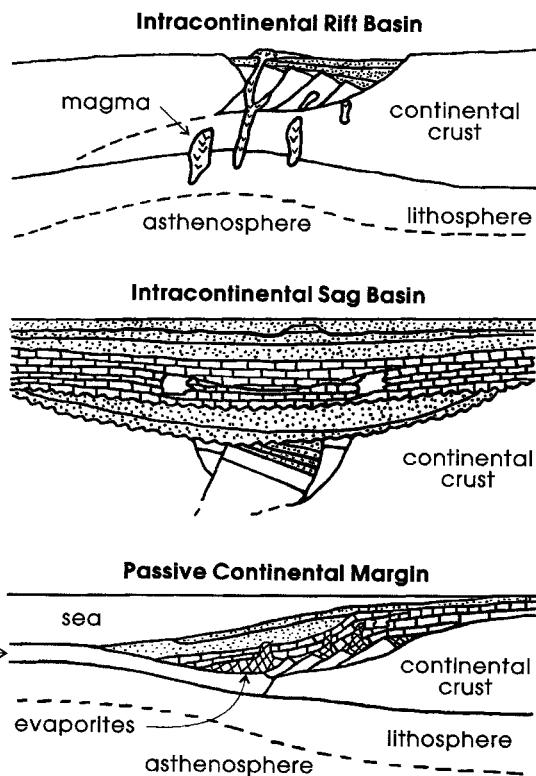


Figure 8-15. Sedimentary basins formed by lithospheric stretching. (Adapted from Wessel 1986.)

Basins Formed by Flexure

Lithospheric plate convergence causes plates to flex along the collision zone, forming elongate or arcuate basins parallel to collision zone margins. Basin types that form along the margins of continent–continent and continent–ocean collision zones include *foreland basins*, *fore-arc basins*, and *back-arc basins*. Foreland basins, also known as foredeeps, include *peripheral basins* and *retroarc basins* (Allen and Allen 1990, p. 94). These basin types are shown in Figure 8-16. In addition, *intermontane basins* form within mountain belts of orogenic zones.

Foreland basins develop in compression zones along orogenic belt margins, on downwarped continental crust. The crust is bent into a wedge-shaped basin under the load of overriding thrust sheets and, to a lesser degree, basin fill. The deepest part of the basin is nearest the belt. Peripheral basins form in continent–

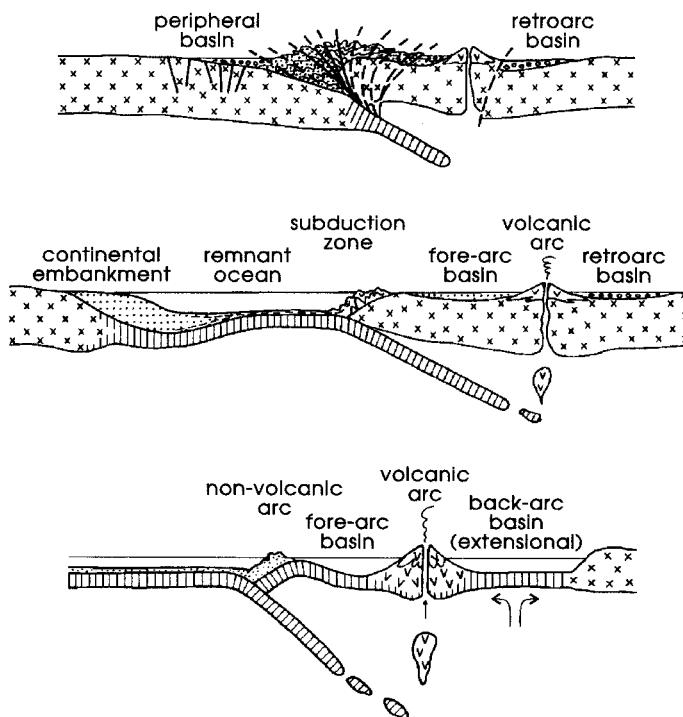


Figure 8-16. Sedimentary basins formed by flexure in collision zones along continental margins. (Adapted from Diessel 1992, Figs. 9.2 A and 9.22; and Duff 1993, Fig. 30.11. © Springer-Verlag.)

continent collision zones along the plate subduction margin. Retroarc basins form opposite the subduction margin, behind a magmatic arc associated with subduction and melting of oceanic lithosphere (Allen, Homewood, and Williams 1986). Basin sediments come mainly from the uplifted orogenic belt. Sedimentation is typically deep marine (turbiditic) in the early stages of basin development, evolving into shallow marine and continental. Sediment thickness may exceed 10 km (Visher 1990, p. 349). As orogenesis advances into the foreland, basin sediments are thrust and folded into nappes and klippen to form the foothills of mountain belts. The Molasse basin, lying north of the Alps and extending through France, Switzerland, Germany, and Austria, is an example of a peripheral foreland basin. Examples of retroarc foreland basins associated with plate subduction along a continental margin include the Rocky Mountain foreland, United States, east of the Rockies; the Appalachian basin, United States, northwest of the Appalachians; and the Apennine basins northeast of the Apennines of Italy, which extend

into the Adriatic Sea (Diessel 1992, p. 520, 555–558; Allen and Allen 1990, p. 110).

Fore-arc and back-arc basins develop along continent–ocean collision zones. Fore-arc basins lie between the accretionary wedge atop the subducting plate margin, and the magmatic arc. Back-arc basins lie on the opposite side of the magmatic arc; they can result from tension in continental or oceanic lithosphere caused by rapid subduction of oceanic lithosphere. Sedimentation may be continental or marine, and may include volcanics. Sediment thickness may reach several kilometers. Examples of back-arc basins occur in the Basin and Range Province of the U.S. Cordillera.

Intermontane basins lie between two marginal chains of an orogenic belt. They commonly contain continental sediments, though they may contain marine sediments, possibly deposited prior to orogenesis (Diessel 1992, p. 559–561).

Basins Formed by Strike-Slip

Strike-slip basins form generally by localized extension along a strike-slip fault system. Some occur along transform plate margins, convergent plate margins with an oblique component, and intracontinental rifts. They include *pull-apart basins* formed at an overstep in a fault trace, and *fault-wedge basins* formed through extension near a fault junction. Strike-slip basins are small in areal extent compared to those formed by lithospheric stretching or flexure, but they can be very deep. Transform plate margins are structurally complex, and this is reflected in sedimentation. Sediment distribution varies considerably, and unconformities may be numerous. Examples of strike-slip basins include the Ridge basin of California, associated with the San Andreas fault system; and the Vienna basin of Austria, associated with the Carpathian thrust belt (Allen and Allen 1990, p. 133–138, 252–255). The Ridge basin contains a thickness of over 13.5 km of continental and marine sediment.

COAL GAS ENVIRONMENTS

Deposition of Coal-bearing Strata

Coals form by compaction and thermal decomposition of concentrated accumulations of organic matter buried deep in sedimentary sequences. Humic coals are derived from peat, which consists of terrestrial plant matter preserved below the shallow water table of a mire. Sapropelic coals are derived from sapropel, which consists of algae, plant spores and cuticles, and peaty detritus deposited as an organic ooze on the bottom of broad, shallow, stagnant water basins. Sapropel forms in lakes of continental mires, abandoned fluvial channels, deltas, and lagoons. Sapropelic coals include cannel coal, derived mainly from plant spores and cuticles, and boghead coal (also known as torbanite), derived mainly from

algae. Sapropelic coals are usually found as thin (< 0.5 m) lenticular layers of limited lateral extent at the top or bottom of humic coal seams (Moore 1965).

The distribution of coal in a sedimentary sequence depends on the environment of peat or sapropel deposition. Principal coal-forming environments are identified in Table 8-1. In most large sedimentary basins, several coal-forming environments are represented, distributed laterally and vertically among the depositional sequences (Diessel 1992, p. 349–459). Coal is an accessory sediment in sequences composed mainly of sandstones, siltstones, mudstones, and occasionally limestones. It may occur as lenses, thin interbeds, or thick layers.

Braid plain environments are associated with elevated sediment sources such as mountainous terrain or rift basins. These environments are high in energy, not conducive to widespread peat deposition. Peat may form in abandoned channels, on margins of fan lobes, and on abandoned lobes. Coals tend to be thin and discontinuous due to lateral migration of channels, high in mineral matter due to overbank flooding, and rich in inertinite due to occasional drying of the peat.

Table 8-1 Principal Coal-Forming Sedimentary Environments

Environments	Subenvironments	Seam characteristics
Gravelly and sandy braid plains	Bars, channels, overbank plains, swamps, raised bogs	Mainly dull coals, generally thin and laterally discontinuous
Alluvial valley and upper delta plain	Channels, point bars, flood plains and basins, swamps, fens, raised bogs	Mainly bright coals, may be thick and laterally continuous, interbedded with overbank flood clastics
Lower delta plain	Delta front, mouth bar, splays, channels, swamps, fens, marshes	Mainly bright coals, thin to thick, may be widespread, may be interbedded with overbank flood clastics
Backbarrier strand plain	Off-, near-, and backshore, tidal inlets, lagoons, fens, swamps, marshes	Transgressive—mainly bright coals; regressive—mainly dull coals, often thick and laterally continuous
Estuary	Channels, tidal flats, fens, marshes	Mainly bright coals, generally thin and discontinuous

Source: Adapted from Diessel 1992, Tbl. 7.1.

Alluvial valley and upper delta plain environments are occupied by meandering rivers. Peat is formed in backswamps that occupy flood plains within the meander belt, and flood basins adjacent to flood plains. The lateral extent of their coals is related to the size and sinuosity of the river channels.

Lower delta plain environments are affected by both fluvial and tidal processes. Peat is formed in abandoned channels, and in interdistributary bays and flood basins. Peat formation on abandoned delta plains may be prolonged by tectonic subsidence or eustatic sea level rise, resulting in thick and laterally extensive coals.

Backbarrier strand plain environments extend along the coast, from the alluvial upper coastal plain seaward to the shoreline. Peat forms in lagoons, and in freshwater and brackish coastal mires occupying a wide belt along the coast. Base groundwater level, which largely controls peat formation, is closely related to sea level. Cyclic rise and fall in sea level causes landward and seaward migration of coastal peat-forming environments, resulting in laterally extensive coals occurring with rhythmic frequency in thick clastic sequences.

Estuarine environments are coastal indentations dominated by tidal energy. Peat is formed on fringe areas. Coals tend to be thin and discontinuous.

Coals are widely distributed in sedimentary rocks. The global areal distribution is shown in Figure 8-17. About 70% of world coal reserves are located in foredeep basins marginal to orogenic belts, 21% are located in shelf basins on cratonic margins, and 8% are located in cratonic interior basins (Diessel 1992, p. 517). Coalfields in shelf basins cover a wider area than in foredeep basins, but foredeeps contain thicker stacks of coal measures due to prolonged subsidence. The temporal distribution of coal is shown in Figure 8-18. Coal formation began in the Devonian, when plants colonized the land. Low reserves in Triassic sediments are related to low sea levels of that period.

Gases in Coal-bearing Strata

Coal-bearing strata may contain gases of one or more of the following origins:

Bacterial gas generated during early stages of coalification (is rarely preserved and limited to low-rank coals)

Thermogenic coal gas generated during catagenesis and metagenesis of coal (most common)

Late-stage bacterial gas from bacterial decomposition of coal associated with a local or intermediate groundwater flow system (usually limited to low-rank coals)

Bacterial, thermogenic, or geothermal gases generated in other source strata and migrated into the coal

Gas content and distribution in coal-bearing sequences can vary widely. They depend on the character of the coal and surrounding strata, hydrogeologic

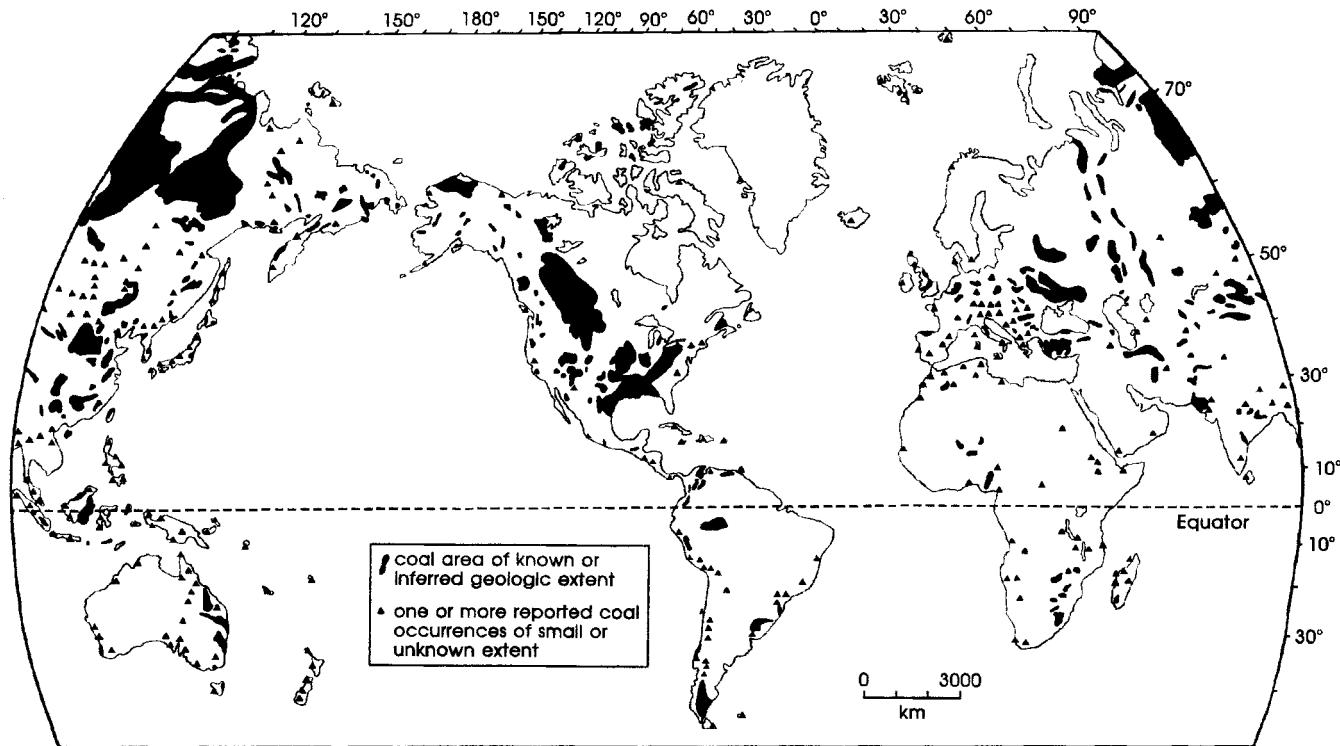


Figure 8-17. World distribution of coal. (From E.R. Landis and J.N. Weaver, U.S. Geological Survey, as presented in Rice, Law, and Clayton 1993.)

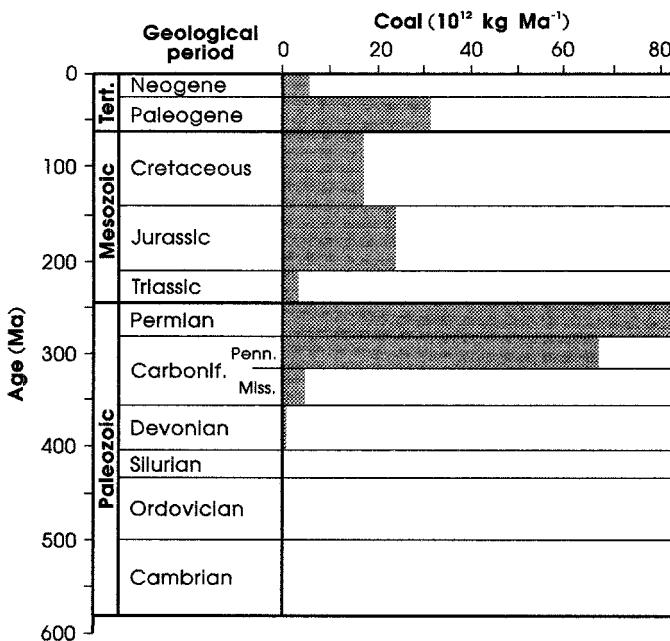


Figure 8-18. Age distribution of coal. Amount of coal corresponding to each period is proportional to shaded area. (Adapted from Killops and Killops 1993, Fig. 5-1. Copyright Longman Group Ltd.)

conditions, and to a considerable degree on the burial, temperature, and pressure history of the deposit.

The gas content of a coal bed is usually assumed to equal its adsorption capacity, unless direct measurements have been made. The actual gas content may be considerably less, in which case the coal is underpressured with respect to gas. Fracturing contributes to underpressuring by opening the coal bed to infiltrating groundwater, which can carry gas away in solution. Coals that have been brought close to the surface or exposed by erosion of overlying strata, then reburied without undergoing further coalification, may become underpressured by their loss of gas at shallower burial depths (Creedy 1988). Recognition of an unconformity in overlying strata is important in assessing the potential gas content of a coal bed. Cooling with erosion of overlying strata contributes to underpressuring, by increasing gas retention capacity.

Methane from coal can migrate to the surface. Methane has migrated into basements through faults and fractures on anticlinal structures (Rice, Law, and Clayton 1993). It has escaped from underground mines to the surface, through collapsed roof strata, abandoned shafts and boreholes, and springs (Harper 1991).

Case Histories of Tunnels in Coal-bearing Sequences

Chingaza Hydro Tunnel

The Chingaza hydroelectric project is located in the Andes mountain range east of Bogotá, Colombia, and was constructed from 1972 to 1983 (ENR 1983). The project included excavation of a tunnel 28.4 km long and 3.7 m in diameter, through shale and claystone with anthracite interbeds. Methane explosions killed 16 workers during excavation of the first one-third of the tunnel. The ventilation system was then upgraded to deliver a volumetric flow rate of $2500 \text{ m}^3 \text{ min}^{-1}$. An additional 12 workers were killed in subsequent explosions. Methane inflow rates were estimated to reach $12 \text{ m}^3 \text{ min}^{-1}$ (Critchfield 1985).

The reported ventilation capacity of $2500 \text{ m}^3 \text{ min}^{-1}$ would produce an average airflow velocity of 240 m min^{-1} in the tunnel, more than 25 times the normal minimum. It would be capable of reducing a methane inflow of $12 \text{ m}^3 \text{ min}^{-1}$ to a concentration of 0.5%, well below the lower explosive limit. It is possible that some ventilation capacity was lost in leakage along the duct. Further, the effective ventilation capacity in the heading would have been reduced considerably if the leading end of the duct had not been maintained close to the face. The project was constructed on the orogenic margin of the Llanos basin of Colombia, a foreland basin east of the Andes, the probable source of coals encountered in the tunnel.

Orange-Fish Tunnel

The Orange-Fish Tunnel is located in southeast South Africa, and was completed in 1975. It conveys water from a reservoir on the Orange River, south through the Zuurberg Plateau to the Great Fish River. The tunnel is 5.3 m in finished diameter, 82.4 km long, and ranges in depth from about 80 to 380 m. In one incident, a blasting round initiated a methane explosion and fire. Investigators estimated the rate of methane discharge during the fire to be $1.8 \text{ m}^3 \text{ min}^{-1}$. The fire was extinguished by constructing a concrete bulkhead about 19 m from the face. Heat from the fire weakened the rock over a length of about 30 m, which required additional support (Olivier 1970; Muir Wood 1975; Keyser and Krige 1978). Apparently no one was injured.

The tunnel was constructed in sedimentary rocks of the Karoo Basin, consisting of horizontally interbedded sandstones, siltstones, and mudstones of late Permian age. The sedimentary sequence contained a network of Jurassic dolerite intrusions, which formed horizontal to semi-concordant sills to transgressive dikes. The sills ranged up to about 100 m thick; the dikes ranged from a few centimeters to 30 m thick. Margins of the intrusions were normally sheared and provided avenues for groundwater and gas migration. Depth to the water table ranged from about 10 to 60 m. The fire occurred in the tunnel between shafts 4 and 5, where methane inflowed from fissures alongside a dike. A profile of this portion of the alignment is shown in Figure 8-19.

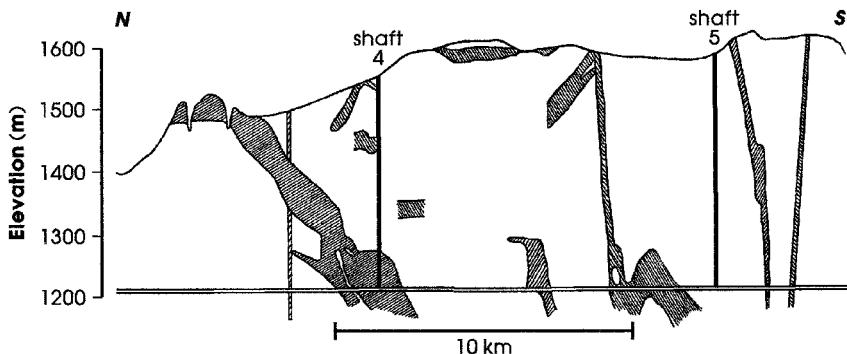


Figure 8-19. Portion of Orange-Fish Tunnel alignment, showing dolerite intrusives in sedimentary sequence. (Adapted from Olivier 1970.)

Characterization of the gas was incomplete. Gas was reported in 9 of 79 boreholes drilled along the alignment during an initial subsurface investigation. In nearly every instance the gas occurred within the dolerite or associated sedimentary rock. Gas discharge from boreholes sometimes caused temporary artesian conditions. Flammable gas was confirmed in a single borehole near a ring dike. Carbon dioxide and hydrogen sulfide, but no methane, were detected in water and gas samples collected from five boreholes during a second phase investigation. Methane was attributed to the underlying coal-bearing Ecca formation (Muir Wood 1975). The source of carbon dioxide and hydrogen sulfide is not apparent from the referenced reports; it may be of geothermal origin.

Hidaka Hydro Tunnel

The Hidaka hydroelectric power station was constructed on the Saru River in Hokkaido, Japan, from 1995 to 1998 (Yokota, Suzuki, and Kasai 1998). The project included excavation of 7.5 km of rock tunnel, about 3.3 m in finished diameter. About 6.1 km of tunnel was excavated using a double-shielded TBM and supported by a concrete lining erected inside the second shield. The site is close to a mountainous coal field in the Furano-Shimukappu region. The detection of methane entering the excavation prompted upgrading of ventilation and tunnel atmosphere control systems, and large methane emissions caused numerous shutdowns and evacuations.

A geologic profile along the alignment is shown in Figure 8-20a. Formations encountered include Cretaceous spilite lava on the east end, Neogene mudstone in the central portion, and Upper Cretaceous mudstone and sandstone on the west end. The alignment crosses numerous fault fracture zones and several steeply dipping sandstone strata. Methane was known to be present in the Neo-

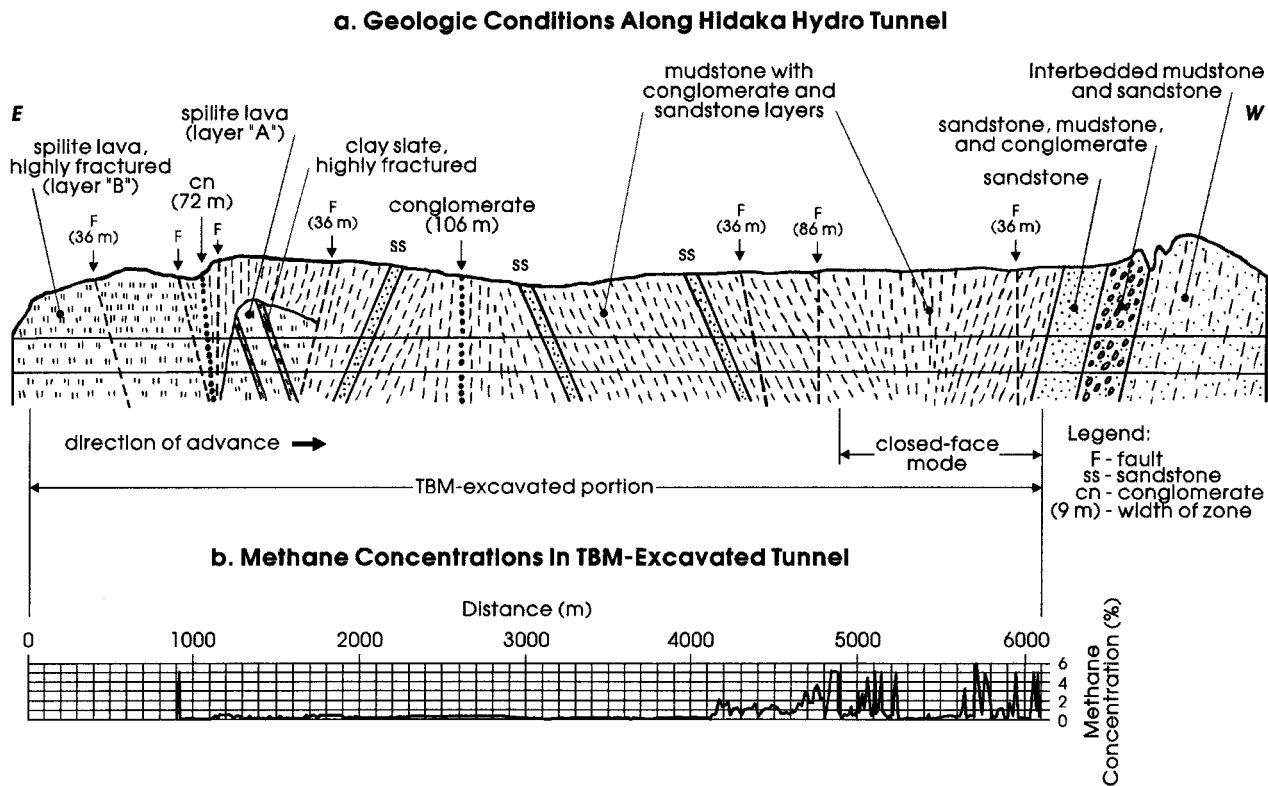


Figure 8-20. Methane inflows to Hidaka tunnel, excavated in coal-bearing strata. (Adapted from Yokota, Suzuki, and Kasai 1998.)

gene mudstone and in coal beds in the region. Groundwater encountered in exploratory borings appeared to contain methane in solution.

A record of methane inflows to the TBM-excavated portion of tunnel is shown in Figure 8-20b. Methane was first encountered at a distance of 917 m in spilite lava, a formation that does not generate gas. The methane apparently originated in Neogene mudstone and entered the excavation through fractures. When this initial inflow occurred, average airflow velocity in the tunnel was about 4 m min^{-1} . The advance was temporarily halted to increase the average airflow velocity to about 30 m min^{-1} and to implement additional atmosphere control measures.

Upon resuming the advance, little additional methane was encountered until reaching a distance of 4100 m, where there were many more fractures. Methane discharges into the excavation were brief and appeared to come from fractures. Groundwater inflows were generally minor. Numerous structural collapses occurred from 4100 m to 4800 m. Structural collapses bound the TBM at 4800 m and again at 4875 m. In this reach of tunnel, 12 shutdowns due to methane were recorded, of average duration 0.9 hours.

To improve face stability the operation was converted to a closed-foam-shield mode, in which the muck chamber was kept filled with a mixture of muck and air foam. This mode was used to complete the excavation from 4875 m to 6100 m distance. While in closed-foam-shield mode, methane inflow to the excavation was concentrated at the screw-conveyor discharge. Use of this mode was credited with reducing methane inflows. Geologic maps indicated that a coal layer was present at 5800 m, though it could not be confirmed in the excavation. This coal layer was believed responsible for the high methane inflows in that area. In this reach of tunnel, 52 shutdowns due to methane were recorded, of average duration 2.3 hours.

A few observations can be made with respect to this experience. The average airflow velocity of 4 m min^{-1} produced by the initial ventilation system is below the 9 m min^{-1} minimum generally accepted in the United States and Great Britain. The initial methane inflow that occurred while in spilite lava at 917 m demonstrates the ability of distant source strata to discharge gas into an excavation. Use of the closed-face mode appeared to reduce overall methane inflows but did not eliminate short-term high methane concentrations in the heading.

PETROLEUM GAS ENVIRONMENTS

Crude oil and hydrocarbon gases that make up petroleum are generated in usually deep, thermally mature source rocks of a sedimentary basin. Part of this petroleum is retained in the source rock. Part escapes into surrounding strata, where it can

migrate several kilometers vertically or several hundred kilometers laterally. Of the petroleum that escapes the source rock, only a small portion becomes trapped in commercially important reservoirs. Most is dispersed along migration routes, is retained in small reservoirs, or escapes to the surface (Hunt 1996, p. 328). Petroleum migration is controlled by sedimentary basin stratigraphy and tectonics. Seeps are surface shows of crude oil or gas that has migrated from mature source rocks or from leaking reservoirs. The mechanics of petroleum migration and seeps can explain how petroleum gases come to reside in the near-surface underground, far from their source rocks. Gases retained in source rocks can also be brought into the near-surface underground by uplift and erosion of overlying strata. Methane is the petroleum gas of principal concern. It may occur in the near-surface underground in gaseous phase in porous ground, in solution phase in groundwater, and in adsorbed phase in organic-rich rocks.

Deposition of Petroleum Source Rocks

Petroleum source rocks originate from bottom sediments in organic-rich, low-energy aquatic environments. Sedimentation typically occurred under anoxic or suboxic conditions, brought on by high organic matter input and low rates of water circulation. Most petroleum source rocks were deposited in marine environments such as epicontinental seas, silled basins, broad continental shelves, deltas, and in highly productive upwelling zones along steep continental slopes. Source rocks from these environments can be laterally extensive. Less extensive source rocks were deposited in embayments, estuaries, fjords, and lagoons. Petroleum source rocks deposited in lacustrine environments are less common but can be laterally extensive. (See, for example, Arthur and Sageman 1994; Jones 1984; Evans and Kirkland 1988.)

Petroleum source rocks are composed predominantly of mineral matter, with moderately to heavily biodegraded organic matter finely disseminated through the matrix. An organic matter content of at least about 0.5% is necessary for petroleum expulsion from thermally mature source rocks. Organic matter is derived mainly from phytoplankton and zooplankton, and from terrestrial plant matter washed into the basin. Mineral matter commonly consists of fine-grained clastics or carbonates. Source rocks include black shales, calcareous shales, argillaceous limestones, chalks, and evaporites.

Petroleum source rocks date back to Cambrian-Ordovician time; most are of Silurian age or younger. Incorporation of terrestrial organic matter into source rocks began in the Devonian, in epicontinental seas, in lakes, and near continental margins. Widespread source rock deposition occurred during periods of marine transgression in the Silurian, Late Devonian-Early Mississippian, Late Pennsylvanian-Early Permian, Upper Jurassic, and Middle-Cretaceous. Major deposition

also occurred during the Miocene and Oligocene (Klemme and Ulmishek 1991). Petroleum that has escaped its source rock is highly mobile, so may be found in sediments of all ages. The world distribution of petroleum-bearing sedimentary sequences is shown in Figure 8-21.

Carrier Beds, Reservoir Rocks, and Seal Rocks

Carrier beds provide permeable pathways for petroleum migration from thermally mature source rocks. Reservoir rocks are porous, permeable rocks that allow crude oil, and gas in gaseous phase, to enter and accumulate. Seal rocks are impermeable strata that overlie and are contiguous with carrier beds and reservoirs. Seals confine fluid movement to more permeable carrier beds and form trap configurations that define reservoirs.

Any rock may serve as a carrier bed or reservoir, provided it is sufficiently permeable. Most commonly they consist of sandstones and carbonates. Sandstones may be of fluvial origin—deposited as braid bars or point bars in braided or meandering rivers; of eolian origin—deposited as dune sands; of lacustrine origin—deposited as delta mouth bars, fluvial channels, shoreface sands, or offshore bars; of coastal origin—deposited as deltaic distributary mouth bars and channel sands, barrier islands, ebb and flood tide deltas, shallow shelf sands, and offshore bars or ridges; or of deep marine origin—deposited as subaqueous fans (Morse 1994). Carbonate carrier beds and reservoirs commonly exhibit secondary porosity formed by dissolution mechanisms. The most porous and permeable carbonate rocks (limestones and dolomites) are associated with shoal environments, reef environments, and tidal flat environments (Jordan and Wilson 1994). The porosity and permeability of carbonate rocks tends to be irregular; they may be less effective than sandstones as carrier beds for long-distance migration. Petroleum is also found in porous chalks deposited in epicontinental seas and shelf areas receiving little clastic input (Scholle 1977). Sedimentary sequence permeability is enhanced by faulting and fracturing, and periodic uplift and subaerial erosion that produces discontinuities.

Effective seal rocks have pore throats too small to allow passage of hydrocarbons, are laterally continuous, are of relative uniform lithology over large areas, and are relatively ductile (Downey 1994). Seal rocks are composed predominantly of evaporites (anhydrite, gypsum, and halite), fine-grained clastics (clays and shales), and organic-rich rocks. These are widespread in most sedimentary basin sequences. Other rock lithologies that perform sealing functions include argillaceous limestones, low-permeability sandstones and conglomerates, cherts, and volcanics, but they are usually of lesser quality and of limited lateral extent (Allen and Allen 1990; p. 366–367). Source rocks are relatively impermeable and can form a seal for underlying carrier beds.

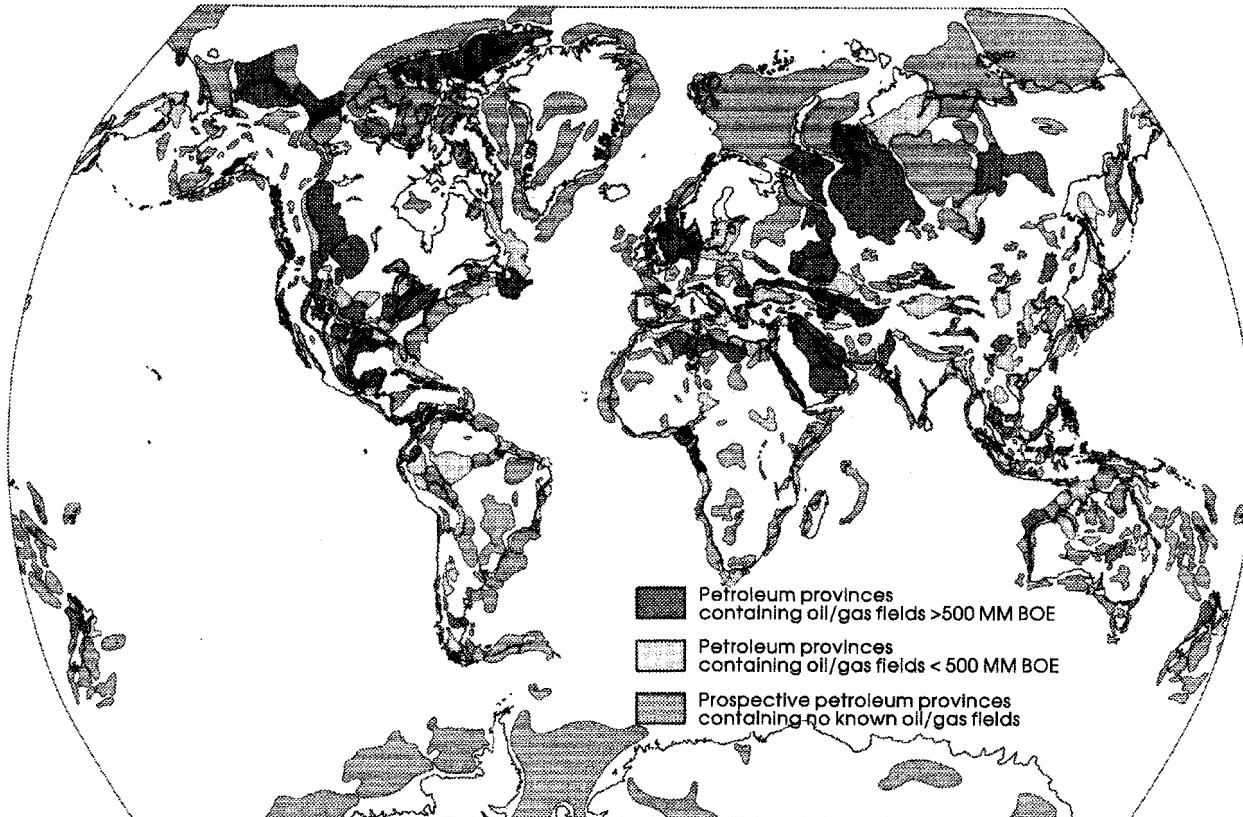


Figure 8-21. Petroleum provinces of the world. MM BOE is 10^9 barrels of oil equivalent. (Adapted from St. John, Bally, and Klemme 1984. © 1984 AAPG.)

Secondary Petroleum Migration, Shows, and Seeps

Secondary Migration

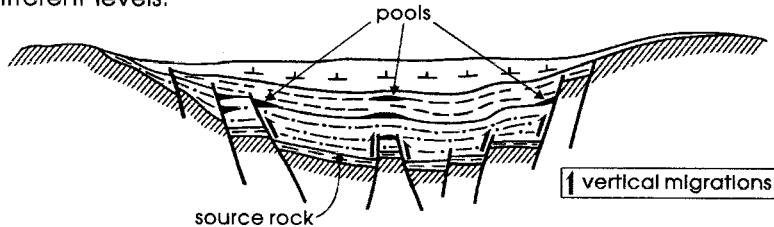
Secondary petroleum migration begins with expulsion of petroleum from thermally mature source rocks. Droplets of crude oil, or gas in gaseous phase, are forced out of source rock into adjacent more porous media. As these droplets coalesce in porous media they develop a buoyant force. The fluid body moves when its buoyancy exceeds capillary pressures in the porous media, always with at least a small upward component. Carrier beds and overlying seals form a route for petroleum fluid migration updip. Seal rocks tend to concentrate petroleum fluids expelled from laterally extensive source rocks into relatively confined flow channels. Without seals, petroleum would be widely dispersed above the source rock. Fluid flow occurs through the most permeable avenues that the migrating fluids have access to. Migration updip through a carrier bed, a predominantly lateral movement, may be interrupted by an intersecting fault, fracture, or other discontinuity in the seal rock that offers a more permeable and more vertical pathway. Petroleum fluids continue to migrate until they reach the surface, become trapped in a conventional reservoir, or become dispersed in an active local groundwater flow system. Much of the gas migrates in solution in crude oil. It gradually exsolves from the oil as pressure declines with upward migration, and continues to migrate or becomes trapped as a separate gaseous phase. Pore waters in carrier beds become saturated with gas. This solution gas may be dispersed with groundwater flow, or it may exsolve from solution as pore waters migrate updip and hydrostatic pressure declines.

Petroleum migration may be classified into three main types of systems, according to dominant characteristics: 1) fault migration, 2) long-range migration, and 3) dispersive migration (Mann et al. 1997). Migration characteristics depend on basin structure, as shown in the examples in Figure 8-22.

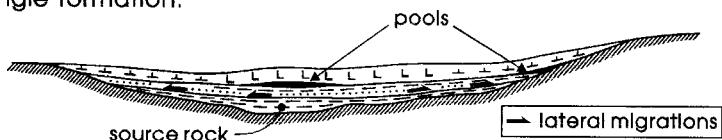
Fault migration systems are generally associated with basins in tension, such as intracontinental rift basins, back-arc basins, and some strike-slip basins. Migration is predominantly vertical along a network of frequently reactivated faults. Vertical migration distances may range from 1 to 5 km, lateral migration is usually limited to less than 30 km (Demaison and Huizinga 1994). Petroleum may be trapped at several levels by faults, horsts, and draping anticlines (Perrodon 1992). Nearly all accumulations occur over or in close proximity to mature source rock.

Long-range migration systems are generally associated with old, stable cratonic basins, such as intracontinental sag basins. Lateral migration occurs through laterally extensive carrier beds overlain by regional seals. Migration distances may reach a few hundred kilometers. Stratigraphic traps are common. Accumulations are generally small and dispersed. They often occur far from mature source rocks, which may be limited to the basin center.

- a. Intracontinental rift basin, with vertical migration and pools at different levels.



- b. Intracontinental sag basin, with lateral migration and pools in a single formation.



- c. Foreland basin, with vertical and lateral migration.

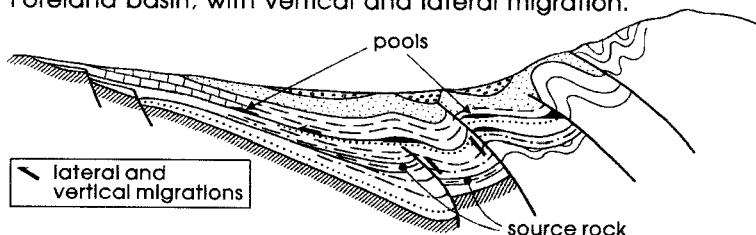


Figure 8-22. Principal petroleum migration systems in various basin types. (Adapted from Perrodon 1992.)

Dispersive migration systems are generally associated with areas of active compression and orogenesis, such as foredeep basins and fore-arc basins. Sedimentation in these basin types tends to be irregular, and the lack of extensive permeable beds limits lateral migration distances. Accumulations frequently are drained by leakage through active faults, or by erosion of seals. Anticlinal traps are common. The degree of dispersion depends on the intensity of tectonic stress; hydrocarbon concentrations tend to increase away from the tectonic zone.

Oil and Gas Shows

Show are any indications of crude oil or gas observed in soils, rocks, or fluids sampled from a borehole or exposed in an excavation. Shows include 1) continuous phase oil or gas in saturated ground, 2) isolated droplets of oil or gas in

saturated ground, or residue on grains or in pores, 3) hydrocarbons dissolved in water, and 4) hydrocarbons adsorbed on kerogen (Schowalter and Hess 1982).

A continuous phase is a filament of oil, or gas in gaseous phase, with continuous connection through a water-saturated pore network. Oil or gas must occupy at least 10% of the pore volume to form a filament. Oil or gas saturations in the pore network may range up to 90%.

Isolated droplets of oil or gas in saturated ground, and oil residue, are referred to as residual shows. Isolated droplets are left behind by petroleum migrating through a carrier bed, or by petroleum produced from a conventional reservoir. Droplet fluids occupy at least 5% to 10% of the pore volume. Average maximum saturations are about 35% in sandstones and 30% to 60% in carbonates and can approach 80% in carbonates with oomoldic porosity. Residue occurs as viscous or solid films of oil chemically adsorbed on mineral surfaces, or droplets in larger pores. Residue may develop from oil migration, from exsolution of gas from oil, or from water washing or biodegradation.

Hydrocarbons dissolved in water may be widespread in petroliferous strata. Solution concentrations can reach saturation values. Pore waters in carrier beds must be saturated with gas to support active gaseous phase migration.

Adsorbed hydrocarbons are retained on kerogen in source rocks. Low-permeability source rocks have little capacity to produce sustained gaseous phase flows. They may release hydrocarbons, particularly gases, by grinding action during drilling.

Seeps and Impregnations

A seep is an area on the earth's surface where crude oil or gas is visibly escaping (an active seep), or which shows visible evidence of escape in the past (a relict oil seep). All gas seeps are active. An impregnation is a surface indication of oil with no evidence of subsurface replenishment. Impregnations that result from erosional exposure of a reservoir or mature source rock may cover very large areas. Oil seeps may be difficult to distinguish from small impregnations (Macgregor 1993). Seeps received a great deal of attention by early petroleum explorationists, as they frequently indicated near-surface accumulations of oil and gas. The value of seeps in petroleum exploration has diminished as prospecting focuses on deeper strata. The world distribution of seeps is shown in Figure 8-23.

Most seeps originate from slow leakage of petroleum from small accumulations in shallow traps. Some may originate from focused secondary migration, with no intervening traps (Clarke and Cleverly 1991). Traps may leak due to fracture of seals or tectonic tilting of beds. Migration from the trap to the seep occurs along fracture planes, permeable beds, and discontinuities. Often there is no apparent connection between the seep and its source. About half of the world's petroliferous basins that produce numerous seeps do not retain commercial accumulations of oil and gas (Macgregor 1993). Their generating capacity may be



Figure 8-23. World distribution of petroleum seeps. (Adapted from Clarke and Cleverly 1991, and Link 1952.)

too little, or they may lack adequate traps. About half of the world's petroleum-rich basins produce no seeps, their deep accumulations are secured by overlying impermeable sediments.

Seeps are most common in geologically young, tectonically active areas, where they are associated with fracturing along continental collision zones, strike-slip zones, or over diapiric intrusions of salt, mud, or igneous rock through sedimentary strata. Seeps are also common along outcrops of long ramped (homoclinal) permeable beds and unconformities that drain traps downdip. Some examples of seep-producing geologies are shown in Figure 8-24.

Seep distribution in a basin is controlled by basin tectonics. In foreland basins, seeps are concentrated on the orogenic margin, and may also occur along outcrops of inclined beds and unconformities on the opposite margin (Macgregor 1993). Strike-slip basins and intermontane basins on active continental margins exhibit numerous seeps. In intracontinental sag basins, seeps occur on basin margins along outcrops of inclined beds and unconformities. In basins deformed by diapirism, seeps may occur over the intrusion in the basin interior. Seeps are rare in tectonically inactive structures draped by undisturbed overburdens, as in some rift basins.

Evidence of seeps is usually most apparent in regions of shallow or outcropping rock. Gas seeps are more common than oil seeps (Link 1952). Petroleum in most fields is predominantly gas by volume at surface conditions, and gas is

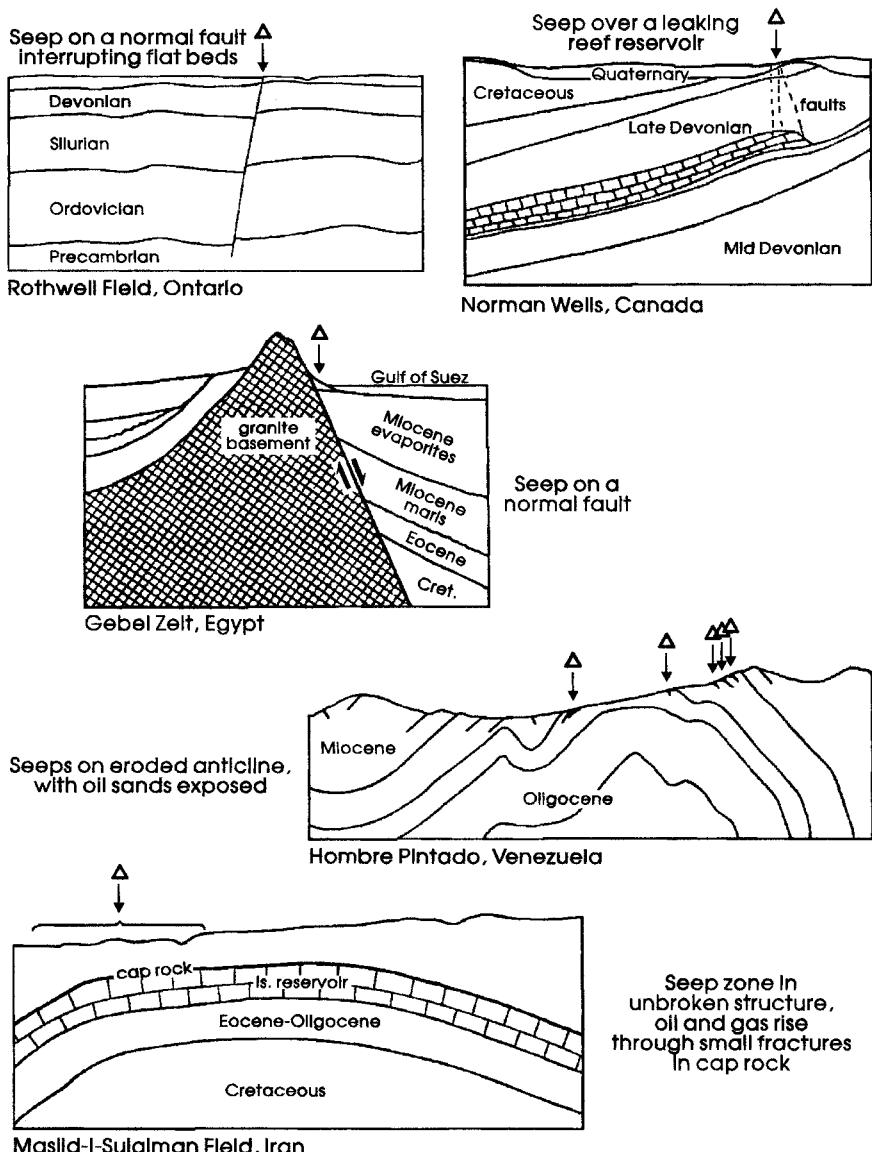
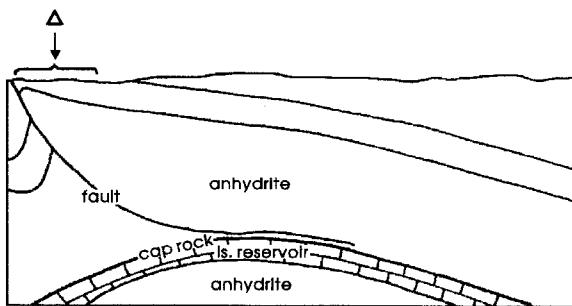
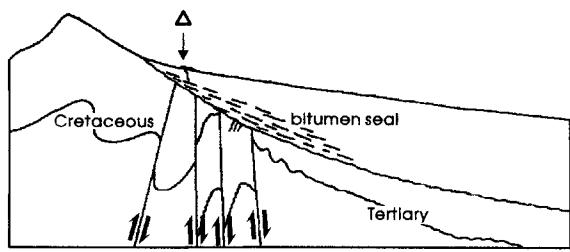


Figure 8-24 (1 of 3). Examples of seep geologies. (Adapted from Link 1952.)

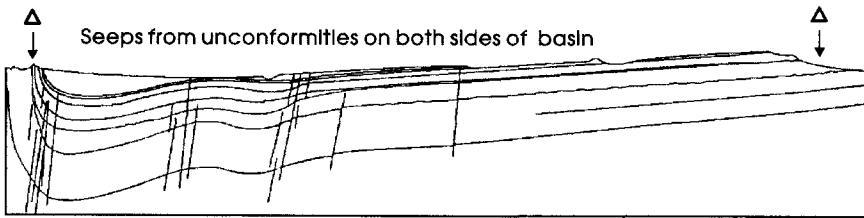


Naft Khaneh Field, Iraq

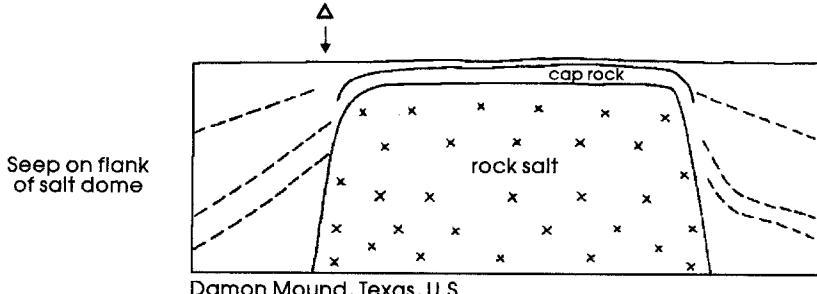
Seep along
low-angle thrust fault
some distance away
from underlying fold



Quiriquire, Venezuela



Uinta Basin, Utah, U.S.



Damon Mound, Texas, U.S.

Figure 8-24 (2 of 3). Examples of seep geologies. (Adapted from Link 1952.)

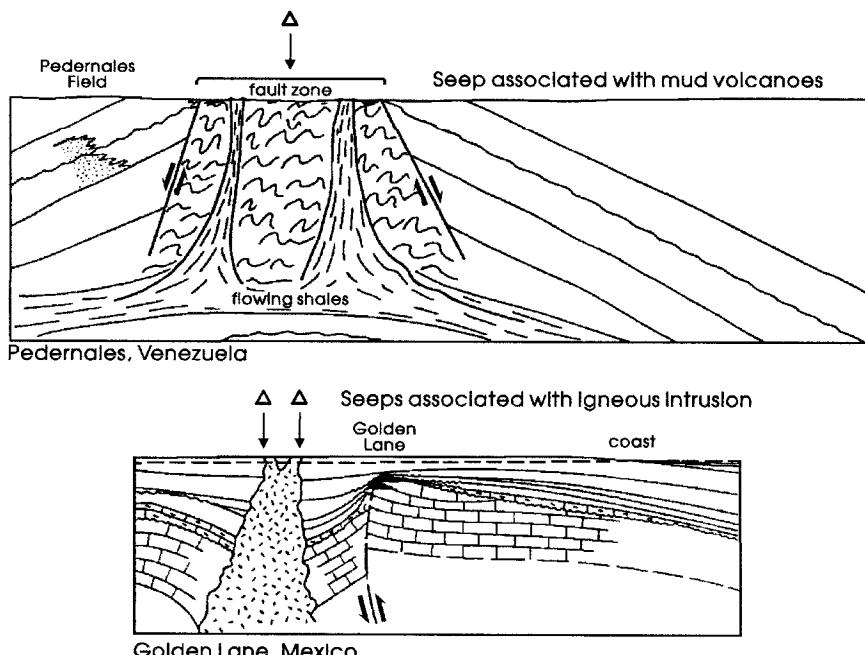


Figure 8-24 (3 of 3). Examples of seep geologies. (Adapted from Link 1952.)

more buoyant than oil (Clarke and Cleverly 1991). Gas seeps may be marked by brown “paraffin dirt,” an agglomeration of fungi that feed on hydrocarbons (Hobson and Tiratsoo 1975, p. 125). Gas seeps are readily observed in saturated ground or pooled water. Oil in seeps may fill fractures, bedding planes, unconformities, and large pores. Oil and gas seeps may be accompanied by salt water springs. Seeps tend to be obscured by thick soils, heavy vegetation, a deep water table, or deeply weathered rock. Oil will flow laterally upon rising to the water table, whereas gas will diffuse upward into overlying unsaturated pores (Clarke and Cleverly 1991).

Seep discharge may be irregular. Obstructions along the migration path temporarily impede filament migration. Seismic activity, even minor events, can cause a rapid surge in seepage rates (Jones and Burtell 1996). Long-term regular monitoring may be necessary to adequately describe seeps.

The composition of petroleum fluids that reach the surface ranges from gas to thick oils. Oils in seeps and impregnations are usually heavily degraded: by water washing in areas infiltrated by meteoric waters, by bacteria, by loss of volatiles, and by inorganic oxidation. Oils lose mobility with degradation; they

may eventually weather into asphalt. Sandy sediments containing degraded oil are referred to as tar sands or oil sands. Degraded oils contain little gas. The Saline Creek Tunnel, constructed in Fort McMurray, Alberta, Canada, was excavated through the Athabasca oil sand, one of the largest deposits of oil sand in the world. No methane was detected within the tunnel during its construction (Chatterji et al. 1979). The ventilation system produced an average airflow velocity of about 11 m min^{-1} .

On rare occasions, seeps are composed largely of gasoline-range hydrocarbons. These very light oils form by progressive condensation from wet gases migrating considerable distances before reaching the surface (Illing 1938). Very light oil was encountered during construction of the Belchen Tunnel, a 3.2 km long double tube road tunnel in the eastern Jura Mountains of north central Switzerland (Fröhlicher and Kehrer 1968). Small amounts were released into the tunnel in two locations, from steeply dipping beds of limestone and from solutioned dolomite. The oil emitted a strong odor, quickly evaporated on the rock surface leaving a greenish yellow residue, and was accompanied by small amounts of methane. Light oil vapors pose toxic and explosion hazards similar to gasoline.

Case Histories of Tunnels in Petroliferous Strata

Missouri River Tunnels

The Missouri River tunnels are two water conveyance tunnels located in Kansas City, Missouri. They were constructed in a sedimentary sequence of shale, sandstone, limestone, and coal, containing abundant oil and gas. The “Missouri Valley Tunnel” was constructed in the mid-1920s using drill and blast methods. It is 4.7 km long, 2.9 m in excavated square, and 85 m deep to invert. Methane inflows during its construction resulted in nine explosions; seven workers were killed in one explosion after failure of the ventilation system, and several were burned in two others. In a separate incident, a fire burned for 5.5 hours before being smothered by bulkheading. An inflow of hydrogen sulfide forced one evacuation. The “Trans-Missouri River Tunnel” was constructed in the early 1990s using a TBM. It lies parallel to and 350 to 600 m east of the original tunnel. This later tunnel is 4.4 km long, 3.4 m in excavated diameter, and 100 m deep to invert. It was constructed without injury due to gas, though methane inflows forced four evacuations (Malone and Retter 1993).

The following description of subsurface conditions is summarized from the geotechnical report for the later tunnel (Woodward-Clyde 1990). A subsurface profile is shown in Figure 8-25a. Soils are alluvial deposits consisting mainly of sand. Fragments of coal are common in the lower alluvium. The rock sequence represents a series of marine transgressions and regressions during the Late Pennsylvanian. Laminated claystones and siltstones (shales) predominate; they appear in various colors, including olive, maroon, brown red, gray, and black. Some

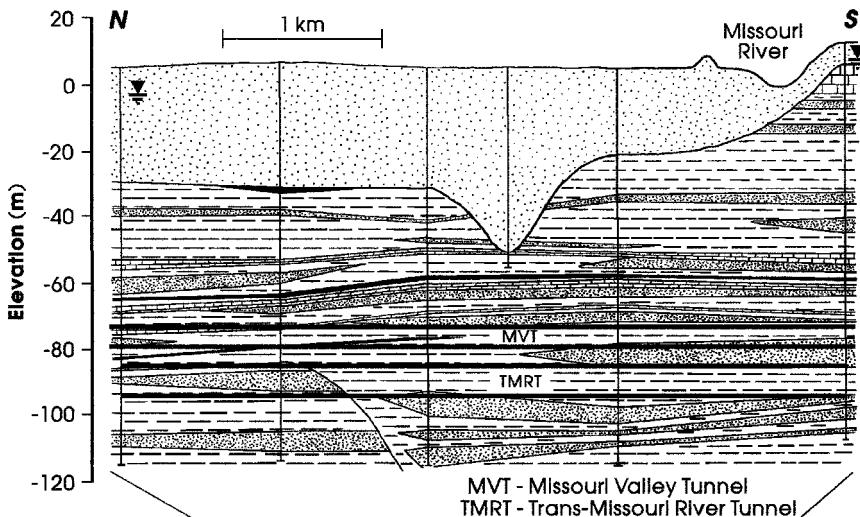
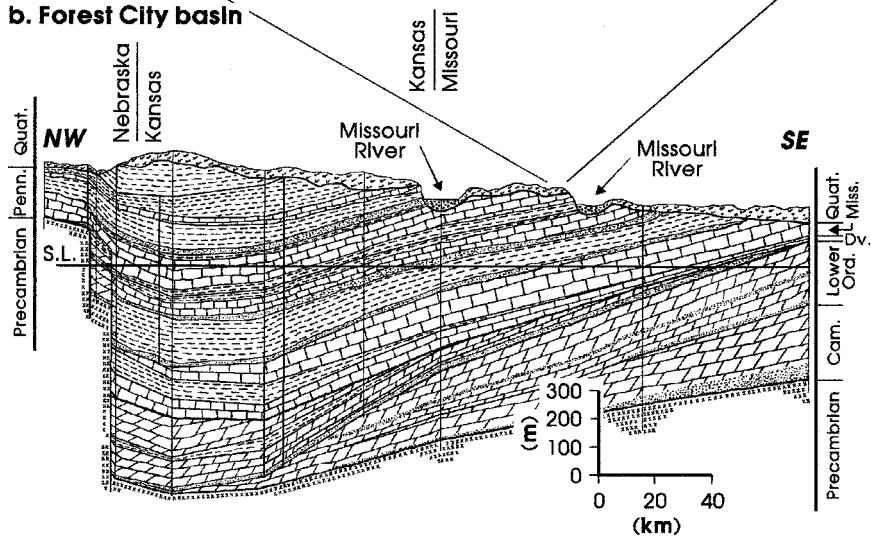
a. Missouri River tunnels**b. Forest City basin**

Figure 8-25. Subsurface profile along Missouri River tunnels, and relationship of site to Forest City Basin. Tunnel site located 3 km southwest of basin profile. (Profile (a) developed from Woodward-Cycle 1990; profile (b) adapted from Wells 1971. © 1971 AAPG.)

shales contain partings of carbonaceous matter or lignite. Sandstones are mainly fine-grained. Limestones are mainly very-fine crystalline, with some shale and sandstone partings. Coal is mainly impure, ranges in color from dark brown to black, and appears dull to lustrous. Joint spacing ranged from 0.3 m in shale to 9 m in limestone. The majority of RQDs (rock quality designations) were 95% or greater. The water table lies from 4 to 8 m below ground surface. A sulfate concentration of 180 mg L^{-1} was measured in one sample from the site, about in the middle of the range of concentrations found in the Kansas City area.

Borings indicated oil and gas in most sandstone layers, in some silt and sandstone partings in shales, and in some porous limestones. In some cases it was present in trace amounts; in others, it saturated pores. Gas was observed bubbling from the surface of some oil-covered sandstone cores. Thermal extraction chromatography (TEC) tests were performed on five samples of oil-bearing rock core, to determine the distribution of hydrocarbon compounds. Results indicated that oil in four of the samples was not significantly biodegraded. Cores were exposed to the atmosphere during sampling, allowing lighter hydrocarbons to escape, so volatile compounds are not fully represented in the results. Numerous oil and gas exploration and production wells have been drilled in the region; some producing strata are represented within the depth of tunneling.

Construction records of the original tunnel indicated that oil and gas were present throughout the formations encountered. There were reported instances of panning oil to keep it from mixing with concrete lining, of gas blowing drill steel and powder from blast holes, and of gas accumulating behind timbering. Gas and water inflows often began a short distance behind the heading. Briny water was reported locally in the tunnel. The average ventilation airflow velocity was about 18 m min^{-1} , in exhaust mode.

Similar oil and gas inflows were encountered in the later tunnel. Oil ahead of the face was always preceded by an odor, eventually followed by staining in the muck. Within about a week of exposing oily strata, a film would cover the walls and produce a sheen on water. The odor never became offensive. In the lower half of each shaft, a sandstone layer about 3 m thick was encountered that discharged gas and oil. The discharge formed a bubbling foam on the shaft wall for about two weeks. Briny water inflow to the lower portion of one shaft. A single intense discharge of gas occurred in the tunnel, from a stratum of fine-grained sandstone. At one point, gas and oil expelled from behind the tail shield formed bubbles 0.3 to 0.6 m in diameter. This forced an evacuation that lasted for about 2 hours. The drive then continued with methane levels in the heading ranging from 10% to 20% LEL for 3 to 4 days. This discharge declined after about 2 weeks but was still making gas during placement of final lining. Total water inflows to the second tunnel never exceeded 60 L min^{-1} . Fluid inflows appeared related to matrix and bedding plane permeability, none appeared related to jointing. A fault reported in the first tunnel was encountered in the second,

but was tight and had no apparent influence on gas discharge. A probe hole was maintained 6 m in advance of the face but in retrospect was not regarded as effective in predicting gas inflows. No hydrogen sulfide was noted. The average ventilation airflow velocity in this tunnel was about 60 m min^{-1} , in exhaust mode. The leading end of the duct was maintained within about 1 m of the TBM bulkhead. Blowers were used as needed in the heading. The work included construction of three intermediate ventilation shafts.

The following is an interpretation of conditions encountered in these tunnels.

Kansas City, Missouri, is located in the Forest City basin, an intracontinental sedimentary basin. This basin's stratigraphy and the relative location of the tunnel site within it are shown in Figure 8-25b. Ordovician shales along the basin's axis are in the initial stages of thermal maturity and probably serve as the main source of oil and gas (Newell et al. 1987). Petroleum migrates to basin margins through sandstones, fractures, unconformities, and porous zones within carbonates. Gas may have migrated as a separate phase, or in solution in brine, or may have exsolved from oil following reduction in pressure with erosion of overlying strata. This basin lacks good regional seals, thick reservoir rocks, and large structural traps, so though it contains numerous commercial accumulations of oil and gas, they tend to be small (Anderson and Wells 1968). Shales within the depth of tunnel construction do not appear to be thermally mature, as evidenced by their multicolors and the presence of lignite, so are not considered here to be a source of petroleum. A relatively insignificant amount of gas may have been generated from thin beds of coal. The wide dispersal of oil along the tunnel alignment suggests that it migrated there through permeable geologic features, not through abandoned wells. The low odor levels suggest that light hydrocarbons have been removed by water washing. Gas entry to the tunnels was mainly by bulk flow in gaseous phase. Gas and water movement through fine-grained sandstones was slow due to their low permeability, so gas tended to inflow behind the heading. Groundwater inflow rates were too low to generate significant solution phase gas flow.

The hydrogen sulfide encountered in the original tunnel may be late-stage bacterial gas associated with aerobic decomposition of oil or organic matter entrained in sediments. Sulfate in groundwater may originate from oxidation of small amounts of pyrite in the shales.

Seelisberg Tunnel

The Seelisberg Tunnel is a twin-tube highway tunnel located in central Switzerland. The tunnel penetrates the High Calcareous (Helvetic) Alps, a high range of mountains built of recumbent folds and nappes of sedimentary rocks. These mountains border the Molasse basin, a peripheral foreland basin to the north, and the Aar massif, part of a chain of largely crystalline mountains to the south. The

Seelisberg Tunnel carries national road N2 through a promontory that forms a constriction between the connected lakes Vierwaldstättersee (Lake Lucerne) and Urnersee. Each tube is 9.3 km long and carries two lanes. The main excavations encountered numerous inflows of methane, a small amount of crude oil, and occasional hydrogen sulfide. Methane inflows forced several evacuations, but adequate control measures prevented injury or accident due to gas.

Geological conditions along the tunnel alignment are shown in Figure 8-26. The tunnel penetrates the Axen nappe and the Drusberg nappe, and the intervening Valangin marl. The nappes are formed of a severely folded and fractured series of sandstones, slates, silicious limestones, pure limestones, and marls (Schneider 1979). The matrix porosity of these rocks is generally low. The Valangin marl is relatively homogeneous, somewhat plastic, heavily compacted, and only finely fractured. Rocks penetrated by the tunnel are mainly of early Cretaceous and Tertiary age. The nappe series are underlain by Tertiary molasse and flysch sediments several thousand meters thick.

Methane was first encountered in the Valangin marl, in an appendant exploratory tunnel that terminated at Huttlegg Station. This prompted further investigation to estimate the risk of encountering gas during excavation of the main tunnel. Laboratory tests showed the Valangin marl contained gas consisting of about 98.8% (vol.) methane and 1% higher hydrocarbons, and liquid hydrocarbons in amounts of about 0.05% (wt.). Investigators concluded that the Valangin marl was an effective petroleum source rock. Tests on core samples showed the porosity of the Valangin marl ranged from 1.3% to 5.5% and averaged 3.3%. Assuming a gas content of 50% to 80%, and a hydrostatic pressure of 4 atm, this marl would contain about 100 L of gas per m³ of rock. All of the marls of the nappe series were considered possible source rocks for gas, as were the underlying molasse and flysch. The silicious limestones were known from other areas to be petroleum carrier beds. For construction of the main tunnel, a minimum average airflow velocity of 30 m min⁻¹ was specified (Pfister 1972; Schneider 1976; Schneider 1979).

The following observations of gas inflow to excavations were reported (Schneider 1976). In the exploratory tunnel in the Valangin marl, a gaseous phase discharged from behind the heading. This formation has a low fracture permeability, which probably slowed the movement of a gaseous phase toward the excavation. Gas and liquid hydrocarbon shows in the main tunnel are shown in Figure 8-26. In the Rütenen section, the Drusberg limestone released a blower that persisted for about 1 hour. Further along the advance, in the Drusberg limestone, small discharges were observed bubbling through water in the invert. Impregnations of crude oil were also observed in the Drusberg strata in the Rütenen section. The most severe methane discharge occurred near the boundary between the Rütenen and Huttlegg sections. Gas discharged from the Valangin limestone at an initial rate of 60 m³ min⁻¹. This subsided to a slow discharge from a finely frag-

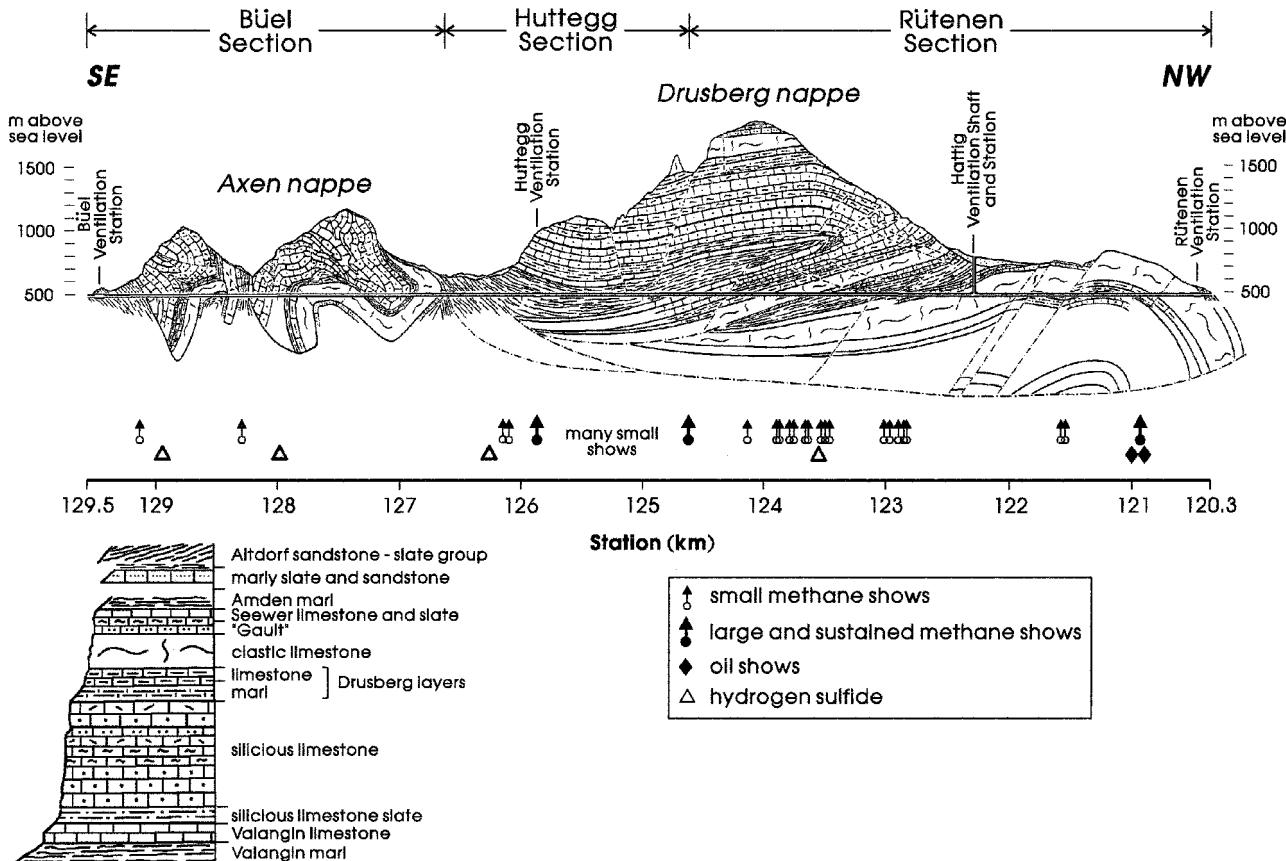


Figure 8-26. Discrete gas inflows observed during construction of Seelisberg highway tunnel, High Calcareous Alps, central Switzerland. (Adapted from Schneider 1976.)

mented fracture a few centimeters wide. The discharge was attributed to a conventional reservoir in the Valangin limestone, which was sealed by overlying Valangin marl. Many small discharges were observed in the north part of the Hüttegg section, bubbling through water in the invert. A discharge of 2 to 3 L s⁻¹ from the center of the Hüttegg section remained steady 5 years after being exposed. A few small discharges were noted in the south part of the Hüttegg section and in the Büel section. The limited gas discharge from the Büel section was attributed to the low cover and high degree of fracturing. In addition to these discrete discharges, slow but widespread discharges of methane occurred in all sections, from hairline fractures and matrix pores. These widespread discharges raised methane concentrations in the tunnel atmosphere to as high as 0.2%. Groundwater inflows to the tunnel were unexpectedly low, generally less than 1 L s⁻¹ km⁻¹, so solution phase inflow was low.

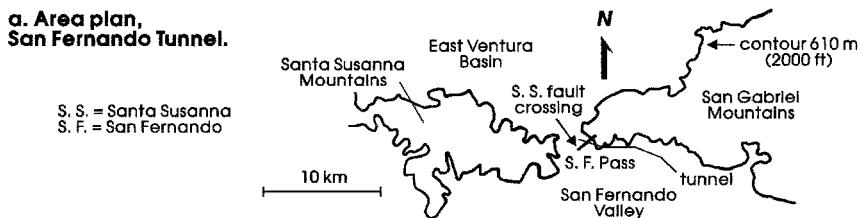
Low concentrations of hydrogen sulfide were noted in all sections, though occurrences were sparse. This gas may have been generated by sulfate reducers utilizing the waste products of aerobic bacteria decomposing higher hydrocarbons.

San Fernando Tunnel

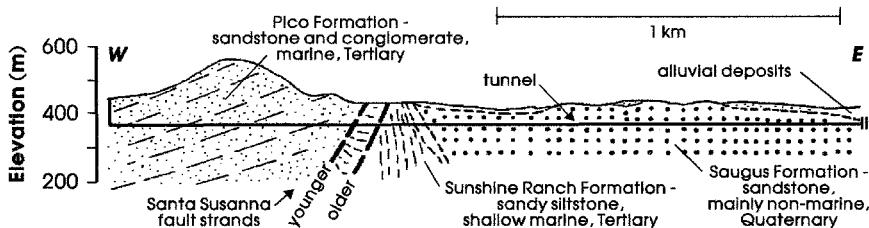
The San Fernando Tunnel is a water conveyance tunnel located about 40 km northwest of the center of Los Angeles, California. The alignment extends from the northern San Fernando Valley into the San Gabriel Mountains, terminating in a shaft near the south end of the San Fernando Pass, as shown in Figure 8-27a. The tunnel is about 9 km long, and has an excavated diameter of 6.6 m (Jacobs 1975). Excavation was proceeding westerly into the mountains when the face reached the faulted margin of the east Ventura basin, a petroleum-producing sedimentary basin north of the mountains. Within three days of encountering this margin, a gas explosion killed 17 workers.

A subsurface profile of the western 2.2 km of the alignment is shown in Figure 8-27b. The west end of the alignment penetrates the Sunshine Ranch and Pico Formations of the Ventura basin, a rift basin that formed during Miocene time (Yeats, Huftile, and Stitt 1994). The basin was compressed during the Quaternary, which thrust its sediments up and over Saugus Formation shelf sediments to form the Santa Susanna Mountains. The south margin of the mountains is marked by the Santa Susanna reverse fault. In the tunnel area this fault bifurcates into two strands. Dip separation along the older strand is at least 2 km; displacement along the younger strand is considerably less (Yeats 1986).

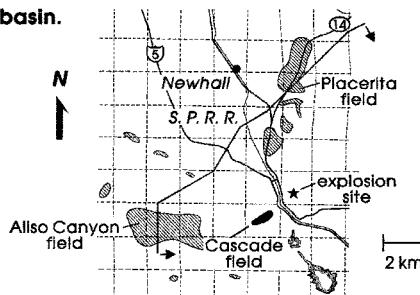
The east Ventura basin contains a number of commercial oil fields; some are shown in Figure 8-27c. Most production is from sandstones overlying Miocene source rocks (Yeats, Huftile, and Stitt 1994). Producing sandstones include the Pico and Sunshine Ranch Formations. The basin contains few dry gas reservoirs; most gas is associated with oil (Dryden et al. 1968). Area basin stratigraphy



b. Profile, west 2.2 km of San Fernando Tunnel.



c. Oil fields of east Ventura basin.



d. Eastern end of east Ventura basin. Oil-producing strata shaded.

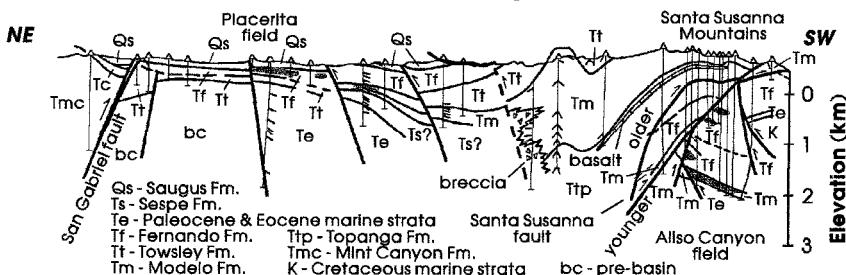


Figure 8-27. Conditions on west end of San Fernando Tunnel. Sunshine Ranch Fm. in (b) a transition between Pico and Saugus. Pico Fm. is upper part of Fernando Fm. in (d). (Adapted from Proctor et al. 1972; Ingram 1963; and Yeats, Huftile, and Stitt 1994.)

is shown in a profile through the Aliso Canyon oil field, west of the tunnel, in Figure 8-27d. The Cascade oil field is nearest the tunnel, about 1.2 km southwest (Ingram 1963). The Cascade field produces from the Sunshine Ranch Formation at a depth of about 760 m. The oil is trapped in an anticline, the trap bounded on three sides by faults, including the Santa Susanna fault on the north. Fluid circulation has been temporarily lost in some wells drilled through the faulted zone into the Cascade field, indicating some fault permeability.

Gas and oil had been encountered during construction of two tunnels nearby, the Newhall water tunnel in 1912, and the Balboa Inlet Tunnel in 1967. The Balboa Inlet Tunnel connects to the west end of the San Fernando Tunnel. The Santa Susanna fault was encountered in the Balboa Inlet Tunnel, marked by numerous layers of gouge 5 to 10 cm thick, and bounded by brecciated sandstone (Proctor et al. 1972). Oil seeps are also known in the area.

When the San Fernando Tunnel heading was still in the valley, the San Fernando earthquake of February 9, 1971, occurred (Proctor et al. 1972). This was a 6.6 M quake. Lateral displacement of 30 cm was measured on the older branch of the Santa Susanna fault, and 11 cm on the younger branch, in separate locations in the area. The east portal of the tunnel was lifted 2.3 m, with uplift diminishing to the north (Proctor 1998).

The San Fernando Tunnel had been free of gas until the heading entered the Sunshine Ranch Formation. At the time, the tunnel was being excavated with a digger shield and lined with precast concrete segments. On June 22, 1971, workers began to sense a strong odor described as kerosine or diesel fuel, and to suffer burning eyes, nausea, and headaches. Air monitoring initially detected no methane, but later readings showed 1% to 19% LEL. Work was halted 10 times to allow fumes to dissipate (Proctor 1980). On June 23 the work was halted 35 times. One worker refused to enter the tunnel because the smell made him ill. In one incident, muck on the conveyor belt ignited behind the face, and flames ran up the belt into the shield in a “whoosh,” injuring four workers (Jacobs 1975). When the second shift entered the tunnel in mid-afternoon of the 23rd, the crew detected no methane. But as excavation resumed 2 hours later, workers began to suffer burning eyes and throat, nausea, headaches, and dizziness. Air monitoring showed methane concentrations of 20% to 60% in the tunnel atmosphere, and up to 100% LEL in the proximity of excavated material. The ventilation system was blowing air into the heading at a rate to produce an average airflow velocity of 28 m min^{-1} . The ventilation duct reportedly terminated where the muck was loaded into rail cars, well behind the face. Electrical equipment was not approved for use in hazardous atmospheres, and there were no controls on welding or smoking. The heading exploded at about 1:00 AM on June 24, killing 17 of 18 workers, and severely damaging the tunneling equipment. A few days later only traces of gas were detected in the heading.

Excavation resumed 2 years later, with an improved ventilation system that produced an average airflow velocity of about 56 m min^{-1} in the tunnel. After advancing a hundred meters or so, the face entered the Pico Formation. This formation proved too hard for machine digging, so the excavation was completed by drill and blast methods. Gas concentrations in the tunnel atmosphere were seldom high enough to measure on gas detectors (Jacobs 1975).

The following is an interpretation of this incident.

The intense odor in the heading indicated the presence of volatile hydrocarbons, the lightest constituents of crude oil. Volatile hydrocarbons are often removed from the near-surface underground by water washing and biodegradation, but these processes were likely inhibited by the lack of infiltrating water in this semi-arid environment. Also, the basin is geologically young, and petroleum may be actively migrating up the margins of the basin. Volatile hydrocarbons, or gasoline-range hydrocarbons, produce toxic effects at low concentrations, which may explain why methane was not detected when odors first became apparent.

The Cascade oil field may have had little direct influence on conditions encountered. Gas and vapors entering the tunnel could have migrated from more proximate areas of the basin, either directly from source strata or from smaller, noncommercial accumulations in leaking traps. The Cascade field does serve as evidence that petroleum generated in the basin has migrated into the area.

The decline in gas and vapor concentrations during work stoppages suggests that diffuse fractures or open pores in the sandstone produced brief inflows when initially exposed. The tunnel did not experience a rapid discharge of gas from a fault acting as an open migration pathway. Tectonic stress in the area is compressive, and faults in such areas usually do not allow unobstructed fluid migration.

Experiences in the earlier tunnels indicate that gas was present on the alignment prior to construction, but this condition may have been made more severe by the San Fernando earthquake. Ground movements may have increased permeability of the sandstone in the faulted zone and may have tilted traps or carrier beds in the basin, causing them to spill additional gas or oil toward the basin margin.

Very little gas was measured in the tunnel atmosphere while completing the work, following the explosion. It seems likely that gas inflow rates from the Sunshine Ranch and Pico formations remaining to be excavated would have been comparable to those encountered earlier. The low gas concentrations observed were a consequence of a more efficient ventilation system. The capacity of the original ventilation system may have been sufficient to handle the gas inflow rate, but positioning the end of the ventilation duct well behind the face allowed gas to accumulate in the heading.

Dallas Area Rapid Transit Tunnel

The Dallas Area Rapid Transit (or DART) system is a light rail mass transit system in Dallas, Texas. The tunnelled section NC-1B extends north 4.8 km from the center of Dallas. It includes twin tubes, each 6.6 m in excavated diameter (Rogstad 1995). Most of the tunnel is located in chalk. The tubes were excavated using a TBM, a continuous conveyor for muck removal, and rock bolts for initial support. The southbound tube was driven first, from the north portal. Excavation of the southbound tube was proceeding normally until progress was interrupted by methane inflows to the heading. Methane had not been encountered in previous tunnel construction in Dallas. An investigation into the cause of the problem and subsequent modifications to the tunneling system resulted in a delay of 79 days and cost \$3 million.

Dallas is located on the updip (northwestern) edge of the Gulf Coastal Plain, a passive continental margin (Allen and Flanigan 1986). Regional stratigraphy is shown in Figure 8-28. Upper strata deposited during a Cretaceous marine transgression dip southeast toward the Gulf of Mexico at about 10 m km^{-1} . Cretaceous strata overlie Pennsylvanian and older strata of the Ouachita fold belt, which trends north by northeast through the region.

Strata encountered within the depth of tunnel construction include alluvium, residual soil, and Austin Chalk (Mohtashemi 1991). Most of the tunnel is located in the lower part of the chalk unit. Maximum depth to invert is about 38 m. Depth to rock ranges from about 4 m at the north portal to 14 m at the south portal. Depth to the groundwater table ranges from 2 to 10 m. The Austin Chalk consists of interbedded chalk and marl, with individual beds ranging in thickness

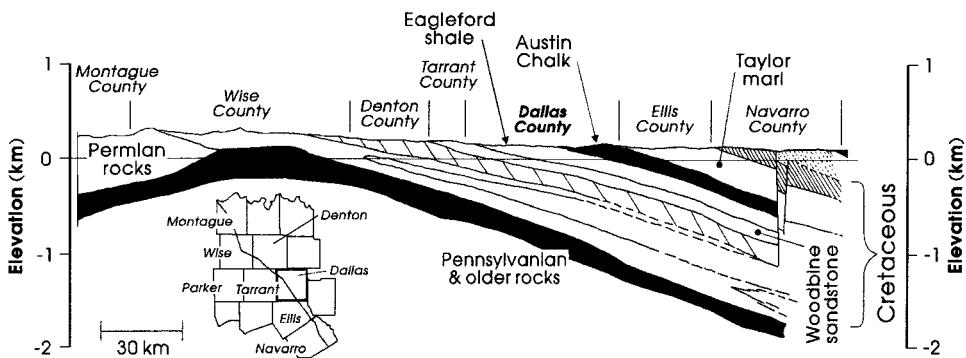


Figure 8-28. Regional stratigraphy of Dallas area. (Adapted from Allen and Flanigan 1986.)

from about 0.3 to 1.5 m (Allen and Flanigan 1986). The top of rock is weathered up to 5 m deep. A consistent bentonite layer ranging from 8 to 46 cm thick was found in most borings penetrating the chalk, a few meters above the crown of the deepest portions of the tunnel. The Austin Chalk is frequently faulted with small offsets. The majority of faults are small, discontinuous, and tight. Porosity of the chalk ranges up to about 3%.

Control systems on the TBM were set to shut down excavation when methane levels in the heading reached 20% LEL. About 3 km into the southbound drive, a shutdown occurred in a tightly fractured section with minimal groundwater inflow. Methane dissipated after excavation stopped. This cycle of excavation, shutdown, and dissipation of methane occurred several more times over a few meters of advance. The gas inflows appeared to correspond to excavation through fractured rock. A transient gas concentration of 33% LEL was also noted at a conveyor booster drive station about 1.5 km behind the heading.

These incidents initiated an investigation to determine the source of the methane (Flanigan 1993). Gas samples were obtained from the tunnel atmosphere throughout its length, from rock of various lithologies cored near the heading, and from holes drilled into the tunnel wall along its length. Samples were analyzed using a gas chromatograph. Samples of the tunnel atmosphere contained consistent hydrocarbon gas concentrations of about 5 to 6 ppmv, indicating that gas outflow from rock exposed behind the heading was insignificant. Gas was extracted from rock cores by crushing a portion of the core, sealing it in a container, and dissolving the solid particles with hydrochloric acid to release entrained gas. Tests showed the rock contained low concentrations of gas, with no trends associated with lithology. Holes in the tunnel wall were drilled to intersect fractures. The holes were about 20 cm deep and 1.3 cm in diameter. Each hole was plugged with a rubber stopper, and after 24 hours a hypodermic syringe was used to extract a sample through the stopper. Analysis showed hydrocarbon concentrations of up to 1.8%. The gas was analyzed for methane, ethane, ethene, propane, propene, isobutane, *n*-butane, and the sum of pentane through heptane. It consisted of 85% to 97% methane, with ethane making up most of the remainder. Investigators concluded that the mixture of hydrocarbon components was typical of a petroleum source.

At the time of the investigation, the main ventilation duct terminated near the end of the trailing gear, and discharged air at a rate to produce a minimum average airflow velocity of 34 m min^{-1} behind the outlet. Distance from the outlet of the main ventilation duct to the face was about 60 m. A scrubber system consisting of two fans and ducts was mounted on the trailing gear; each fan had a capacity to produce an average airflow velocity of 2.5 m min^{-1} . These fans exhausted air from the wheelhead and discharged it to a point about 6 m behind the outlet of the main ventilation duct.

The following is an interpretation of this incident.

The source of the gas is not readily apparent. No producing oil wells have been drilled in Dallas County (Allen and Flanigan 1986). The area is not known for oil or gas seeps (Link 1952), or near-surface shows (Ball Associates 1967). The most likely possibility is that gas migrated from source rocks incorporated into the Ouachita fold belt from the Fort Worth basin. The Fort Worth basin is a foreland basin formed during Ouachita orogeny, and borders on the west margin of the fold belt (Arbenz 1989). The Fort Worth basin contains numerous gas fields in northwest Denton, Wise, and Parker Counties (GSA 1987). A large field in Wise County produces from below elevation –1500 m (Blanchard, Denman, and Knight 1968). A less likely possibility is that gas migrated from the East Texas Embayment, updip through Woodbine sandstones. The Embayment contains numerous oil and gas fields that produce from the Woodbine sandstone (Curtis 1991). Fields closest to the center of Dallas are about 40 km to the south-east (GSA 1987).

There are a number of possible reasons why gas was not known to occur in tunnels in Dallas, prior to DART. Gas may have been observed during previous construction but was unreported. Previous tunnels may have been better ventilated, so any gas inflows were unnoticed. Tunnels constructed previously are nearer to the surface, which may be significant. Shallower rock may be less porous due to weathering or lithologic characteristics, and less able to retain gas. Bentonite layers in the middle of the chalk unit may prevent gas from migrating upward. Aerobic bacteria inhabiting shallower depths may consume methane migrating from below.

Regarding the gas testing, the maximum hydrocarbon gas concentration found in stoppered drill holes was 1.8%. Petroleum gas typically consists of 90% or more hydrocarbons, which suggests that at the time of sampling, the gas mixture in the holes was not yet in equilibrium with that in deeper fractures. Data from gas samples extracted from drill holes showed $C_1/(C_2 + C_3)$ ratios ranging from about 8 to 41, consistent with investigators' conclusion of a petroleum source. As noted in Chapter 4, thermogenic gas typically exhibits $C_1/(C_2 + C_3)$ ratios less than 50. Rock samples for gas analysis were not sealed until after they were crushed, consequently much of the gas they initially retained probably escaped to the atmosphere. The results of analyzing these samples for gas appear reliable as to composition but provide no information on amount of gas retained per unit volume of undisturbed rock.

Gas entry to the tunnel appears to be closely associated with fractures. Entry to the heading may have been through a combination of gaseous phase bulk flow through fractures, and release from rock pores during excavation, with porous rock nearest the fractures containing the most gas. The dissipation of gas in the tunnel atmosphere soon after excavation ceased is consistent with a low rate of gas flow from low-permeability, organic-poor rock. The absence of significant groundwater inflow eliminates this mechanism as significant to gas inflow. The

observation of gas at the belt transfer station, well behind the heading, is difficult to explain. Possibly this gas was released from muck disturbed in passing through the transfer station. Or this gas may have been released in a brief discharge from an exposed fracture in the vicinity. Gaseous phase migration through fractures is typically intermittent. The presence of additional equipment in the area may have deflected the normal flow of ventilation air, preventing this gas from being rapidly swept away.

The original ventilation system may have been inefficient in removing gas from the heading. The airflow velocity produced along the length of the trailing gear by the two scrubber fans, working together, would have been 5 m min^{-1} , about half the normal minimum required velocity. Low air velocities in the heading may have allowed methane to layer in the crown, a possibility made more likely where exhausting in the absence of blower fans. In addition, the scrubber ventilation system overlapped the main ventilation duct by only 6 m, or about one tunnel diameter. In an overlapping ventilation system, an overlap of at least two tunnel diameters is necessary to prevent air recirculation forward of the main ventilation duct (Kissell 1989).

THERMOGENIC GASES IN IGNEOUS ROCKS, METAMORPHIC ROCKS, AND SOILS

Igneous rocks, metamorphic rocks, and soils cannot generate hazardous concentrations of thermogenic gas, but they can retain coal and petroleum gas that has migrated from contiguous thermally mature sedimentary rock. This section provides a few examples of such occurrences.

Coal gas is present within the Columbia River Basalt Group of the Columbia basin, Washington State (Hammer 1934; Johnson, Graham, and Reidel 1993). The Columbia basin is bounded on the east by the Rocky Mountains and on the west by the Cascade Range. The Columbia River Basalt Group is a sequence of Miocene flood-basalt flows. Individual flows are up to 100 m thick, and the sequence is over 3.5 km thick. The Basalt Group overlies Paleogene sediments including Eocene Roslyn Formation coals, the source of thermogenic methane. Studies suggest that methane migrates in solution in groundwater rising vertically from the center of the basin, through cooling joints and thrust faults. Solution phase methane is retained in aquifers formed along the tops and bottoms of basalt flows. In the Rattlesnake Hills gas field, gaseous phase methane is retained above the water table in porous basalt overlain by residual clays. The gas is under very low pressure; some is presumably lost to the atmosphere through fractures. Gas pressure within wells in the Rattlesnake Hills has been observed to increase during periods of heavy rainfall or snowmelt, and to decrease during periods of drought.

Seeps of thermogenic gas and crude oil have been reported from fractured igneous rocks on the orogenic margin of foreland basins. The igneous rocks have been thrust basinward over sedimentary rocks which generated the gas and oil. Examples include the southeastern edge of the Front Range, Colorado, U.S. (Jacob and Fisher 1985), and the northwest edge of the Venezuelan Andes (Hunt 1996, p. 450).

Petroleum gas has been reported in glacial soils in the Michigan basin (Newcombe 1935). This occurs usually in areas where petroleum source rocks and reservoir rocks subcrop beneath the glacial drift. Gas may be retained within the drift or along the soil/rock contact. In some places a gaseous phase is retained in volumes exceeding $5 \times 10^4 \text{ m}^3$.

GEOTHERMAL GAS ENVIRONMENTS

Carbon dioxide can be introduced into the near-surface underground in convecting groundwater associated with liquid-dominated, high- and low-temperature geothermal systems. These types of systems occur in areas of Quaternary volcanism and Cenozoic tectonism. Often both of these geologic processes influence the geothermal environment, with one or the other playing a dominant role. The global distribution of geothermal carbon dioxide discharges is shown in Figure 8-29. Most discharges are associated with volcanism along plate margins and over intracratonic mantle plumes. Discharges not associated with volcanism are distributed along orogenic belts, and in regions of tensional tectonics. Carbon dioxide originates mainly from thermal metamorphism of carbonate rocks, or from magma degassing.

Areas of Quaternary Volcanism

Volcanoes occur along lithospheric plate subduction zones and spreading centers, and over intracratonic mantle plumes. A few occur on transform plate margins. Magma is intruded into the upper crust in volcanic areas. Heat from large plutons in the upper 10 km of the crust can drive convecting groundwater flow systems for tens of thousands to a few million years. Plutons older than the Quaternary have usually cooled to temperatures no longer capable of driving convection (McNitt 1970). This text does not address gas discharge associated with individual active volcanoes.

Volcanic arcs develop along the continental side of lithospheric plate subduction zones, a result of partial melting of the subducting plate as it is forced down into the mantle. The subducting plate is usually oceanic crust, which is denser than continental crust. The volcanic arcs are generally located within 50 to 200 km inland of the oceanic trench (Wright 1988). Crustal melt forms silicic magma, which rises buoyantly into the upper crust. Silicic magma is relatively

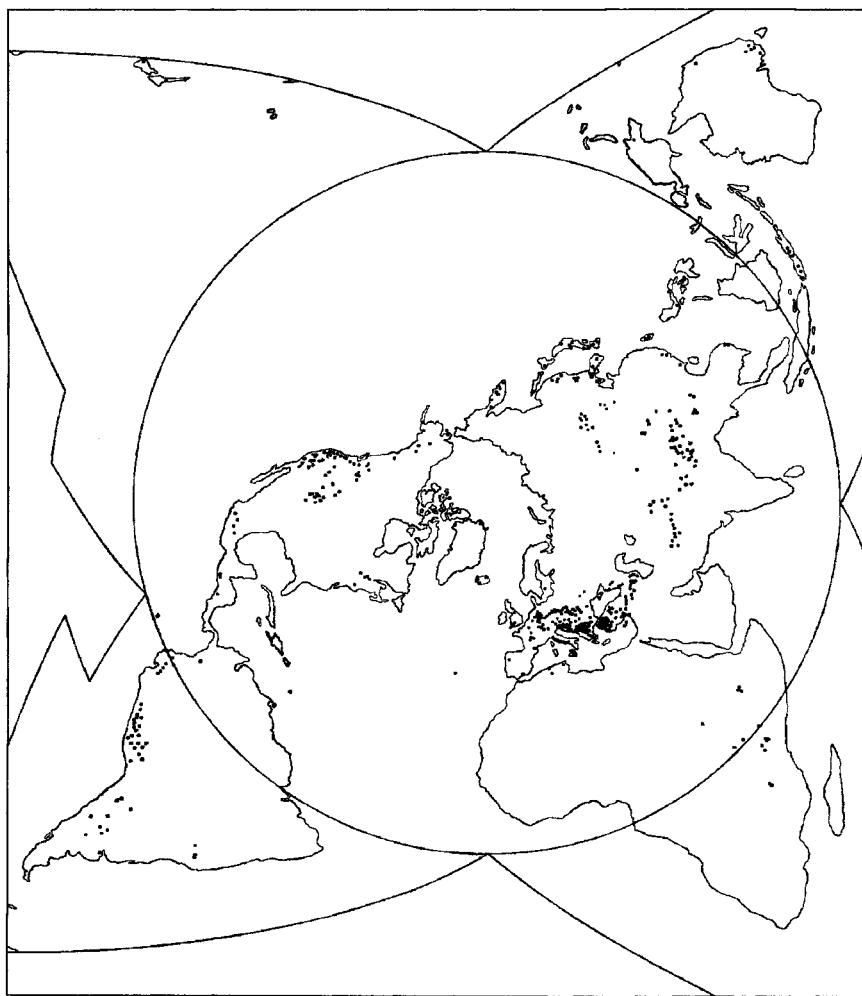


Figure 8-29. World distribution of carbon dioxide charges. (Adapted from Irwin and Barnes 1980; Barnes, Irwin, and White 1984.)

viscous, so tends to form large intrusive bodies. The upper crust may be deeply fractured by caldera and dome formation over the apex of large intrusive bodies, and by other tectonic activity (Heiken 1982). Deep fractures and buried layers of pyroclastics nearer the surface provide permeable pathways for groundwater convection. Carbon dioxide along subduction zones originates mainly from thermal metamorphism of marine carbonates, and from magma degassing.

Volcanic belts develop along lithospheric plate spreading centers and rifts. Spreading centers are located mainly beneath the sea, but in a few locations extend onto continental lithosphere, as in Iceland and east Africa. Spreading rates and geothermal activity at rifts is more moderate than at spreading centers (Rybäck 1981). Basaltic magma is derived from the mantle, from depths greater than 50 km (Wohletz and Heiken 1992, p. 12). Because of its low viscosity, basaltic magma tends to rise directly to the surface in thin dikes and pipes, without forming large shallow intrusive bodies. Thin intrusives cool quickly. Basaltic dikes can provide a heat source for geothermal systems if abundant and frequently intruded. In continental areas, long periods of basaltic magma flux from the mantle can promote melting of crustal rocks to form silicic magma, which rises to form large shallow intrusions. The upper crust may be deeply fractured by fault block and graben formation. Much of the carbon dioxide discharged along tension zones may originate from magma degassing.

Linear or arcuate sequences of volcanoes develop as crustal plates move over intracratonic mantle plumes. The youngest volcanics are closest to the plume. Basaltic magma provides a source of heat for formation of large silicic intrusions in the upper crust. Caldera and dome formation over the apex of intrusive bodies provides deep fractures for convecting groundwater flow systems. Carbon dioxide may originate from the magma degassing, or from thermal metamorphism of carbonate rocks in the overlying crust penetrated by magma or convecting groundwater.

Areas of Cenozoic Tectonism

Cenozoic tectonism as a principal influence on geothermal environment accounts for a great deal fewer geothermal systems than Quaternary volcanism, due to low reservoir temperatures. But Cenozoic tectonism covers a much larger geographic area (McNitt 1970). Tectonism produces fracture systems that allow circulation of groundwater to depths of several kilometers. Heat at these depths can be sufficient to drive convecting groundwater flow systems in areas of normal or elevated geothermal gradients. Recurring tectonic activity maintains fracture permeability. Geothermal systems associated mainly with non-volcanic tectonism occur in young orogenic belts, in cratonal areas undergoing extensional tectonics, and along transform plate margins. Carbon dioxide in geothermal discharges associated with Cenozoic tectonism may originate from magma degassing from great depth, or from thermal metamorphism of carbonate rocks along the groundwater convection route (D'Amore et al. 1989).

Many geothermal systems associated with Cenozoic tectonism occur in young mountain belts such as the Alps, the Rocky Mountains, and the Himalayas (Henley and Ellis 1983; Rybach 1995). Elevated geothermal gradients in these belts may be due to rapid uplift of crustal rocks. A Swiss study showed close

association between geothermal areas and seismic activity (Jaffè, Rybach, and Vuataz 1978). In young orogenic belts the highest geothermal gradients tend to occur in the hinterland, or convex side of the orogenic front, opposite the peripheral foreland (Wunderlich 1970). Geothermal systems in older orogenic belts are associated with recent tectonic activity unrelated to formation of the belt, as in the Appalachian Mountains of the United States (Irwin and Barnes 1980).

Sporadic geothermal systems are associated with extensional tectonics in cratonic areas. Extension is associated with crustal thinning and elevated geothermal gradients, and in some cases igneous intrusions absent volcanic activity. An example is the Basin and Range Province of the United States, bordered by the Colorado Plateau on the east and the Sierra Nevada Mountains on the west (Renner, White, and Williams 1975).

Case Histories of Tunnels in Geothermal Environments

Mono Craters Tunnel

The Mono Craters Tunnel is located in east central California, east of Yosemite National Park and about 40 km southwest of the Nevada border. It was constructed from 1934 to 1938, to convey water from the Mono Basin watershed southeast to the Owens River watershed. The tunnel is 18.2 km long and was excavated to a diameter of about 3.8 m (Jacques 1940). The alignment crosses the Mono Craters, an arcuate chain of small volcanic craters, domes, and coulees. A zone of fractured rock beneath the chain discharged heavy inflows of warmed groundwater containing carbon dioxide in solution. Gas overwhelmed the ventilation system and necessitated construction of an additional ventilation shaft near the heading. The tunnel was completed without injury due to gas.

A location map of the Mono Craters Tunnel is shown in Figure 8-30a. The site lies on the eastern front of the Sierra Nevada Mountains. The Mono Craters align along a series of volcanic dikes associated with range front faulting (Bursik and Sieh 1989). Volcanism along the chain occurred from 35 to 0.6 ka B.P. (Bailey, Miller, and Sieh 1989). Domes and coulees that formed in the final stage of individual eruptions rise 600 m above the surrounding topography. A coulee is an obsidian dome that has expanded beyond the limits of its tuff ring. The tunnel crosses beneath the South Coulee, its flows issued from several outlets now marked by prominent spines (Putnam 1938).

A profile along the western 7.5 km of alignment is shown in Figure 8-30b. Basement rocks consist of pre-Tertiary sandstone, shale, and limestone metamorphosed to hornfels by plutonic intrusions (Putnam 1949). Basement rocks are overlain by gravelly till left by Pleistocene valley glaciers that advanced from the Sierra Nevada Mountains. Till is overlain by Bishop Tuff, a welded rhyolitic ash, jointed to resemble closely fitted masonry. The eruption that deposited the

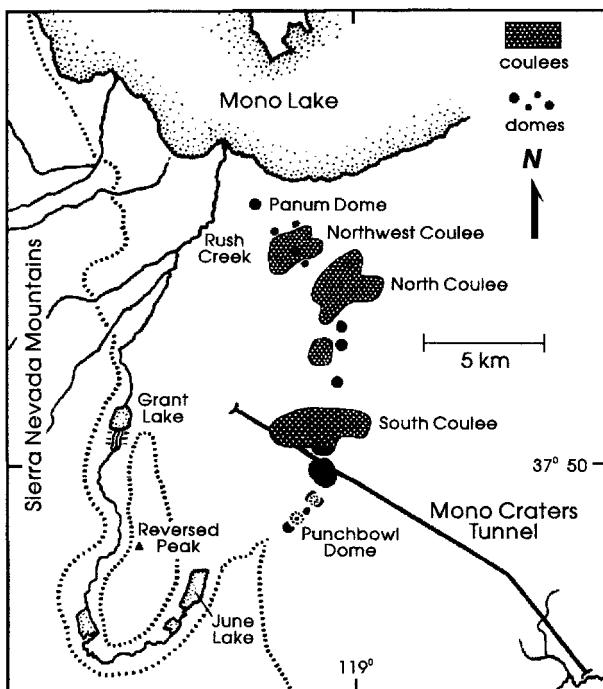


Figure 8-30a. Location map of Mono Craters Tunnel, California. (Adapted from Putnam 1938. © 1938 American Geographical Society.)

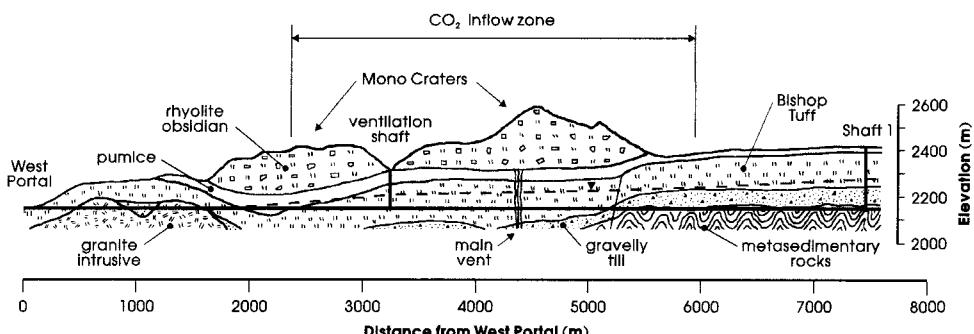


Figure 8-30b. Geologic section through west 7.5 km of Mono Craters tunnel. (Adapted from Putnam 1949 and Jacques 1940.)

Bishop Tuff 700,000 years ago led to collapse of the Long Valley caldera, 50 km to the south (Bailey, Miller, and Sieh 1989).

The tunnel was driven from six headings. Carbon dioxide was encountered only in Heading 1, driven down-gradient from the West Portal nearly the full distance to Shaft 1. Small quantities of carbon dioxide began entering the heading 2380 m in from the West Portal (Jacques 1940). Inflows of groundwater and gas increased as the face advanced. At 3960 m the ventilation system was overwhelmed by carbon dioxide inflows of about $5.5 \text{ m}^3 \text{ min}^{-1}$ (Putnam 1949). Work was halted temporarily to sink a ventilation shaft behind the heading. The upgraded ventilation system, operated in blow mode, produced an average airflow velocity in the tunnel of about 58 m min^{-1} (Wyckoff 1938).

The rock became badly fractured at 4390 m. Discharge of groundwater and gas increased as the face advanced through the fractured zone, which continued for a few hundred meters (Jacques 1940). Groundwater temperatures rose from 2°C where first encountered on the edge of the craters, to 36°C (Putnam 1949).

At a point almost directly beneath the arcuate crater chain, the heading collapsed under a mass of ash, brecciated obsidian, and shattered tuff (Putnam 1949). The rock contained a swarm of closely spaced obsidian dikes, most of which were under 15 cm wide. Fragments of granite and limestone were found in the vent (Jacques 1940). Large crevices were intercepted at about 4640 m, and groundwater inflows increased considerably, flooding the tunnel. Pumping capacity was increased to regain the heading. Excavation continued by drilling and grouting 12 m ahead of the face, and by drilling the walls and crown to relieve hydrostatic pressure in soft strata.

Within the fractured zone, carbon dioxide was released into the tunnel at rates that varied from 24 to $34 \text{ m}^3 \text{ min}^{-1}$ and averaged about $28 \text{ m}^3 \text{ min}^{-1}$. Gas inflows reportedly fluctuated with changes in barometric pressure, with increased inflows during periods of falling pressure (Wyckoff 1938). Carbon dioxide entering the tunnel atmosphere represented 60% of gas in solution in groundwater outside the tunnel (Jacques 1940). Carbon dioxide concentrations occasionally reached 15% to 20% during periods of rapid groundwater inflow, forcing the crew to evacuate. Reports do not indicate where or how often this occurred, or groundwater inflow rates and ventilation rates when this occurred. The ventilation system was apparently generally successful in maintaining carbon dioxide concentrations below 2% in the heading (Wyckoff 1938).

Groundwater inflows over the drive from Heading 1 peaked at about $35 \text{ m}^3 \text{ min}^{-1}$ (Gresswell 1940). Efforts were made to capture water in the pumping system as soon as it entered the tunnel, to limit the time that carbon dioxide could exsolve. Sump pumps were uniformly spaced at intervals of 300 m, with additional sumps at points of heavy inflow of groundwater and gas (Jacques 1940). It was necessary to use pumps made of bronze to prevent corrosion from carbon dioxide.

The heading passed through a transition zone at 5270 m into a sedimentary series of thinly bedded quartzites, sandstones, shales, and slates. This series was greatly distorted and fractured. Bedding planes dipped from vertical to 70° toward the north. Permeability was high. For 900 m the sandstones were calcareous, and quartzites and shales contained carbonates in joints. Investigators were of the opinion that these carbonates were the source of carbon dioxide (Jacques 1940). The heading passed out of the carbon dioxide zone at 5940 m.

Carbon dioxide inflow to this tunnel continues to require prodigious ventilation during maintenance inspections (Proctor 1998).

The following interpretation of this incident is somewhat speculative, due to lack of detailed information.

A carbon dioxide release rate of 28 m³ min⁻¹ into the tunnel atmosphere combined with an average airflow velocity of 58 m min⁻¹ would produce a carbon dioxide concentration of about 4%, above the 2% concentration reportedly maintained in the heading. It is possible that sustained groundwater inflows caused carbon dioxide concentrations to increase behind the heading. Respiration rate increases perceptibly at carbon dioxide concentrations of 5%. Perhaps concentrations of 4% were not debilitating to workers merely traveling back and forth between the West Portal and the heading. Further improvements made in the ventilation system after Heading 1 holed through (Wyckoff 1938) probably improved air quality such that it did not affect subsequent concrete lining operations.

The solution concentration of carbon dioxide in groundwater outside the tunnel can be estimated using Equation 7-4, dividing the gas inflow rate by the groundwater inflow rate:

$$L_{gw} = \left(\frac{28 \text{ m}^3 \text{ CO}_2}{\text{min}} \right) \left(\frac{1}{0.6} \right) \left(\frac{\text{min}}{35 \text{ m}^3 \text{ H}_2\text{O}} \right) \left(\frac{1000 \text{ ml}}{\text{L}} \right) = 1330 \frac{\text{ml CO}_2}{\text{L H}_2\text{O}}$$

where the second term accounts for only 60% of gas coming out of solution. This is a gross estimate of solution concentration. Local solution concentrations may have varied considerably, due to environmental effects such as temperature, degree of exposure of geothermal waters to calcareous rock below the tunnel, and degree of mixing between geothermal waters and meteoric waters.

The saturation concentration of carbon dioxide is about 7000 ml L⁻¹, at 8 atm pressure (1 atm barometric pressure plus an estimated 70 m water head at tunnel depth) and 20°C. This is well above the average solution concentration, suggesting that gaseous phase carbon dioxide was not present in the ground at tunnel depth prior to tunneling. It is possible that higher local solution concentrations supported gaseous phase exsolution from rising geothermal waters. A gaseous phase likely would have escaped to the atmosphere through fractured and porous rock, rather than become trapped in conventional reservoirs.

Barometric pressure fluctuations were reported to effect total gas inflow rates by 15% to 20%, though details of these observations were not published. The influence of barometric pressure fluctuations would depend in part on the surface area of water exposed to the tunnel atmosphere. This surface area would have been large. It would comprise water moving through the invert as well as water held in fractures exposed in tunnel walls, over a length of 3600 m.

Calcareous sandstones and calcareous joint fillings encountered in the sedimentary series beyond the transition zone were probably not the source of carbon dioxide, as original investigators believed. It seems more likely that matrix cements and joint fillings were calcite precipitated by carbon dioxide escaping from geothermal waters. Limestone found in the vent is evidence of a more likely, deeper source of gas.

Capo Calavà Tunnel

The Capo Calavà Tunnel lies on the Messina-Palermo motorway along the north coast of Sicily (Restelli 1978). The tunnel penetrates the Capo Calavà massif near the seaside town of Gioiosa Marea. This is a twin-tube tunnel, about 3 km long; it was excavated by drilling and blasting. Carbon dioxide was encountered unexpectedly in the middle of the alignment, necessitating an extensive grouting program to cut off gas inflows.

A profile along the alignment is shown in Figure 8-31. Carbon dioxide first entered a heading from the Palermo side, 1226 m in from the portal. Excavation in all four headings was suspended pending investigation. Four horizontal borings were drilled to investigate the intervening rock between opposing headings, over a distance of 236 m on one side and 283 m on the other.

The results of the investigation were as follows. Geologic study led investigators to conclude that the gas was associated with volcanism in the Aeolia Is-

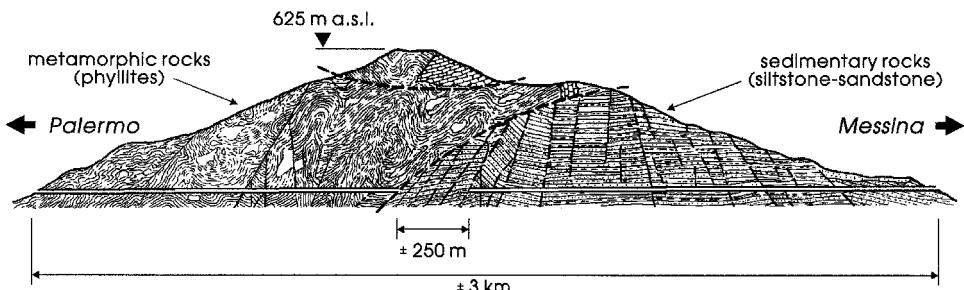


Figure 8-31. Capo Calavà Tunnel on Palermo-Messina motorway, Sicily. Warm geothermal gas encountered in sedimentary rocks in center section. (Adapted from Restelli 1978.)

lands (Isole Eolie), about 30 km north in the Tyrrhenian Sea. Details of this study were not provided. The gas was trapped in a sandstone-shale series, along a faulted contact with overlying metamorphics. Gas consisted of 98.07% CO₂ (vol.), 0.61% CH₄, 0.08% H₂S, and 1.2% O₂ plus N₂. Gas pressure varied from a few tenths to 1.8 atm above atmospheric, "due to the dimensions and geometry of the fissures encountered." Gaseous phase discharges from borings ranged from a few to more than 6 m³ min⁻¹. Gas temperature was consistent at about 35°C. Rock was very finely fractured. Shale beds were relatively impervious to gas; sandstones discharged large amounts.

Excavation resumed after an in-tunnel grouting program had been developed to cut off gas inflows. The program included three concentric sets of closely spaced perimeter holes, with cement grout in the inner and outer sets and acrylic grout in the center set. An additional pattern of holes in the face was used to grout a plug directly in advance of excavation. These efforts were successful in cutting off gas inflows, and the project was completed without injury due to gas.

The following is an interpretation of this incident.

The direct source of the gas is not apparent from the information provided. Sicily lies on the boundary between the African and Eurasian plates. The African plate is being subducted beneath the Eurasian plate, under the Ionian Sea to the southeast. Active volcanism in the southern Tyrrhenian Sea, and at Mount Etna about 40 km south of the site, is associated with this plate subduction (Fridleifsson 1978; Allard 1983). Carbon dioxide discharges have been reported in this area of Sicily (Barnes, Irwin, and White 1984).

Reported gas temperature is relatively high, suggesting that the gassy zone is an active seep or very leaky trap. Gas held in a more static accumulation would have cooled to the temperature of surrounding rock. Gas seeps are probably present on the surface of the massif, aligned along exposed fractures and tectonic contacts, though the seeps may be difficult to locate above the water table.

The report of this incident seemed to imply that gas pressures were lower in low-permeability strata, and higher in high-permeability strata. It seems unlikely that a gaseous phase accumulation would exhibit a wide range in excess pressures over the short distance between headings. Assuming these pressure variations occurred throughout the strata penetrated, they may be the result of testing procedures too short in duration to allow pressures to equilibrate in low-permeability strata.

Hydrogen sulfide in this gas mixture poses an interesting problem with respect to tunnel ventilation. Hydrogen sulfide is a common, usually minor constituent of geothermal gas. Diluting an inflow of this gas mixture to achieve a carbon dioxide concentration of 0.5% (TLV-TWA for CO₂; see Table 1-2) would reduce the hydrogen sulfide concentration to a safe level of about 4 ppmv (TLV-TWA for H₂S is 10 ppmv). However, diluting an inflow of this gas mixture to a carbon dioxide concentration of 3.0% (TLV-STEL for CO₂) would reduce the

hydrogen sulfide concentration to about 24 ppmv, an unsafe level (TLV-STEL for H₂S is 15 ppmv). Consequently, it would be appropriate to monitor both carbon dioxide and hydrogen sulfide concentrations in the tunnel atmosphere to ensure that safe conditions were maintained.

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9

Gasoline Vapor Inflow to Excavations

INTRODUCTION

Some areas of the underground environment within a few tens of meters of the surface are contaminated with gasoline, particularly in urban centers. Gasoline may leak from underground storage tanks, associated piping, and from distribution pipelines. The most prevalent sources are automotive service stations. Underground releases may sustain liquid gasoline migration for considerable distances through permeable pathways above or along the water table. Gasoline can reside for decades underground; in some cases, long after the source has been abandoned, removed, or converted to other uses. Liquid gasoline is highly volatile, and its vapors are toxic and combustible. A small amount of gasoline introduced into an underground excavation can quickly generate a hazardous atmosphere.

In addition to gasoline, numerous other volatile contaminants from man-made sources can generate hazardous atmospheres in excavations. Chlorinated solvents associated with dry cleaning facilities are one example. The principles presented here for gasoline may provide some insight into dealing with other contaminants. Contaminated soil, rock, or groundwater may also pose toxic hazards through dermal exposure or environmental hazards relating to their disposal. These issues are not addressed here.

HYDROCARBON COMPOUNDS

Hydrocarbons are the principal constituents of gasoline and other refined petroleum fuels. Properties of bulk fuels derive from their constituent compounds. This section is an introduction to the chemistry of hydrocarbon compounds.

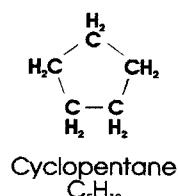
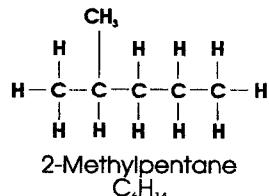
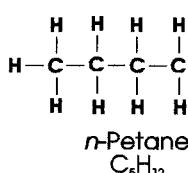
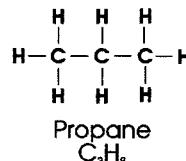
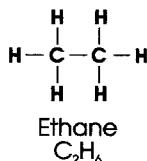
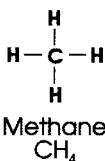
Hydrocarbons consist exclusively of hydrogen and carbon, hence their collective name. The carbon atoms bond together into a network of straight or branched chains, or closed rings of five or six carbons. Carbon-carbon bonds may be single or double. All non-carbon-carbon bonds are satisfied by hydrogen atoms. Hydrocarbon compounds above C₃ (more than three carbons in chain) that have the same number of carbon and hydrogen atoms can assume different structural configurations, and these are called isomers. The number of possible configurations increases exponentially with increasing number of carbon atoms. Isomers exhibit different chemical properties, occasioning the need to distinguish them. Straight-chain isomers are called “normal” isomers, and branched-chain isomers are called “iso” isomers.

Hydrocarbon compounds number in the hundreds but can be differentiated into a few characteristic groups by how the carbon atoms in the network bond together. Hydrocarbon groups found in petroleum include the *alkanes*, the *alkenes*, and the *aromatics*. Example structural formulas of group members are shown in Figure 9-1.

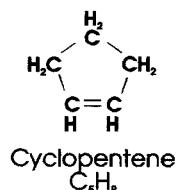
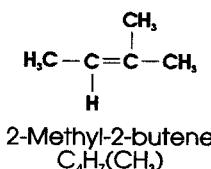
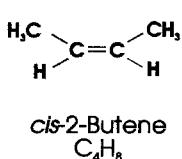
Hydrocarbons of the alkanes group are based on singly bonded carbon atoms in a chain or ring. The group includes straight-chain alkanes (normal alkanes), branched-chain alkanes (isoalkanes), and cyclic alkanes (cycloalkanes). Alkane group hydrocarbons include the maximum possible number of hydrogen atoms, so are called saturated hydrocarbons. Normal alkanes and isoalkanes are generally referred to simply as alkanes, or paraffins. Cyclic alkanes are also known as naphthenes.

Hydrocarbons of the alkenes group include double carbon–carbon bonds among the carbon chain or ring. They include straight, branched, and cyclic configurations. Alkenes are unsaturated hydrocarbons. Normal alkenes and isoalkenes are chemically unstable relative to other hydrocarbons, so are not prominent among hydrocarbon groups. Normal alkenes and isoalkenes are generally referred to simply as alkenes, or olefins.

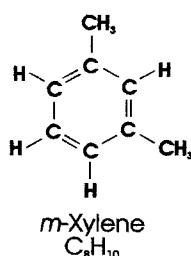
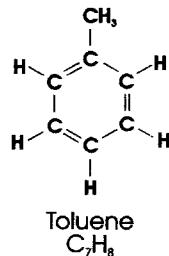
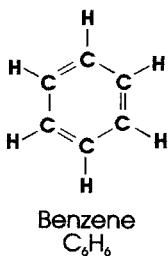
Hydrocarbons of the aromatic group are based on a ring of six carbon atoms bonded by what is commonly depicted in structural formulas as alternating single and double bonds. Actually these bonds are not static but resonate between single and double bonds, a characteristic that gives the ring unusual stability. The simplest aromatic compound is benzene, which consists of a ring of six carbons surrounded only by hydrogens. An important subgroup of aromatic hydrocarbons, the alkylbenzenes, include alkyl groups (CH₃) bonded to carbons in the parent



Alkanes



Alkenes



Aromatics

Figure 9-1. Structural formulas of simple hydrocarbons.

ring, as in toluene and the xylenes. Aromatic rings commonly bond together in polycyclic structures to form high-molecular-weight hydrocarbons.

The basic carbon structures described above may combine to form heavier hydrocarbon compounds. Cyclic and polycyclic structures commonly bear straight or branched chains. By convention, a saturated molecule containing at least one ring is identified as a cycloalkane. A molecule containing at least one aromatic ring among several saturated chains or rings is identified as an aromatic. An important aromatic subgroup, the naphthenoaromatics, consists of one or more aromatic rings bonded to one or more naphthalenes (cyclic alkanes).

Some aromatic compounds have distinctive odors, a property that inspired their group name. Non-aromatic hydrocarbon groups, the alkanes and alkenes, are collectively referred to as aliphatic hydrocarbons. Organic chemistry nomenclature originates from a combination of historical usage and a more recently developed systematic naming method, a topic described in more detail in basic texts on organic chemistry (for example, McMurry 1994).

GASOLINES AND OTHER REFINED PETROLEUM PRODUCTS

Distillation products of crude oil include straight-run gasoline (C_5 to C_{10}), kerosene (C_{11} to C_{13}), diesel fuel (C_{14} to C_{18}), heavy gas oil (C_{19} to C_{25}), lubricating oil (C_{26} to C_{40}), and waxes and asphalt (C_{40+}). These successive fractions contain increasingly heavier hydrocarbon compounds, as indicated by the carbon number subscripts. Liquid petroleum distillation products are normally processed further to enhance their combustion properties as fuels. Bulk properties of some of these fuels are summarized in Table 9-1.

Commercial gasolines are generally composed of from 50 to 150 hydrocarbon compounds, ranging from C_4 to C_{12} but predominantly C_5 to C_9 (Cole 1994, p. 57; Riser-Roberts 1992, p.28). Gasolines are a blend of the lightest condensates of crude oil distillation (straight-run gasoline), with gasoline-range hydrocarbons produced by cracking heavier hydrocarbon fractions, and non-hydrocarbon additives. Gasoline is the most volatile of common liquid petroleum fuels, as is apparent from its high vapor pressure and low flashpoint temperature range. Flashpoint is the lowest temperature at which a liquid is capable of generating a combustible concentration of vapors. Normal ground temperatures are well above the flashpoint temperature range for gasoline, so gasoline underground vaporizes readily. Its vapors constitute both a toxic and an explosion hazard. Vapor pressures as a function of temperature for two gasolines are shown in Table B-7, in Appendix B. The blends are identified by Reid vapor pressure, a measure of motor fuel volatility (ASTM D 323). Miscellaneous properties of bulk gasoline and gasoline vapors are shown in Table 9-2. Liquid gasoline is sometimes referred to as *LNAPL* (a light, non-aqueous-phase liquid) because it is less dense than, and immiscible in, water.

Table 9-1 Properties of Common Liquid Petroleum Fuels

Fuel	Vapor pressure ^a (mb)	Flashpoint (°C)	Flammability limits (% vol.)		Solubility in water ^a (mg L ⁻¹)	Kinematic viscosity ^a (mm ² s ⁻¹)
			LEL	UEL		
Gasoline ^b	275–550	−30–−43	1.4	7.6	50–100	0.5–0.6
JP-4	110	−10–35	1.3*	8.2*	<1	0.8–1.2
Kerosene	0.76	40–75	1.4	6.0	<1	1.5–2
Diesel	0.6	40–65	1.3	6.0	<1	2–4
#1, #2 oil	<0.07	40–100	rnf ^c	rnf ^c	<1	1.4–3.6
#4–#6 oil	<0.07	65–130	1.0	5.0	<1	6–194

^a At 20°C±.^b Values vary slightly depending on grade.^c Relatively nonflammable.

Sources: Adapted from Cole 1994, Tbls. 3-3 & 3-4, except as noted. *From Kuchta 1985.

JP-4 jet fuel also constitutes a toxic and an explosion hazard underground, though to lesser extent than gasoline. JP-4 is used principally in military aircraft; it is the most volatile of widely used jet fuels (Riser-Roberts 1992, p. 29). JP-4 is not considered further in this text because it is not a widely distributed contaminant underground. However, the same principles of vapor generation described here for gasoline can be applied to jet fuels.

Kerosene, diesel fuels, and fuel oils are not capable of generating combustible concentrations of vapors at normal underground temperatures, though they can constitute a fire hazard if exposed in an excavation.

Table 9-2 Miscellaneous Properties of Gasoline

Liquid density ^a	0.72–0.78	g ml ⁻¹
Apparent molar mass ^b	95	g mol ⁻¹ (est.; fresh)
	111	g mol ⁻¹ (est.; weathered)
Surface tension ^a	20	dyn cm ⁻¹
Vapor specific gravity ^c	3–4	
Vapor pressure ^b	50	mb (est.; weathered)
Vapor diffusion coefficient in air ^d	0.05	cm ² s ⁻¹ (est.)

Sources: ^aSchiegg and Schwille 1989. ^bJohnson et al. 1990. ^cSax and Lewis 1989. ^dJury, Spencer, and Farmer 1984.

PROPERTIES OF GASOLINE

Chemical Composition

Gasoline released into the underground environment behaves not as a simple bulk liquid but as a complex solution of chemical constituents. Each constituent is unique in its volatility, solubility in water, tendency to adsorb to organic matter, susceptibility to bacterial decomposition, and toxicity. These properties influence the environmental significance of each constituent in geologic media. Major constituents of gasoline are shown in Table 9-3. Commercial gasoline blends vary somewhat in composition, but from an environmental point of view they generally behave in a similar manner (Cole 1994, p. 56).

Liquid gasoline consists of about 30% to 90% alkanes, 6% to 9% alkenes, and 10% to 50% aromatics (Weaver 1992). Among these major hydrocarbon groups, alkanes are the most volatile and are relatively insoluble in water. Alkenes are moderately soluble in water and more toxic than alkanes (Cole 1994, p. 47). Aromatics are less volatile, relatively highly soluble in water, and the most toxic. Properties of some alkanes and aromatics found in gasoline are compared in Table 9-4. Constituent solubility is approximately inversely proportional to molecular weight, for all groups. The most soluble gasoline hydrocarbons are the aromatic compounds benzene, toluene, ethylbenzene, and the xylenes, often referred to collectively as "BTEX." They are of considerable interest in environmental investigations of gasoline contamination in groundwater.

In addition to hydrocarbon compounds, gasoline fuels contain a number of non-hydrocarbon additives that improve their performance in internal combustion engines. These include antiknock compounds, oxygenates, antioxidants, antirust agents, anti-icing agents, detergents, lubricants, and dyes. With one exception they are present in low concentrations and have little environmental significance. Methyl tertiary butyl ether, or "MTBE," is an oxygenated compound used to promote burning. It is usually blended with gasoline in concentrations from 2% to 7% by volume, with the highest proportions used in unleaded premium (Garrett, Moreau, and Lowrey 1986). MTBE is 24 times more soluble in water than benzene, has low volatility, has little tendency to adsorb to organic surfaces, and is very resistant to bacterial decomposition. In groundwater plumes contaminated with gasoline, MTBE tends to spread farther and faster than hydrocarbons (Landmeyer et al. 1998).

Vapor, Solution, and Adsorbed Phase Partitioning

Liquid gasoline released into the underground environment gradually loses constituents via chemical equilibration with geologic media. Gasoline constituents follow various pathways to equilibration, in a process called *partitioning*. The

Table 9-3 Major Hydrocarbon Constituents of Gasoline

Hydrocarbon group	Compound	Number of carbons	Concentration (% wt.)
Straight-chain alkanes	<i>n</i> -butane	4	3.93–4.70
	<i>n</i> -pentane	5	5.75–10.92
	<i>n</i> -hexane	6	0.24–3.50
	<i>n</i> -heptane	7	0.31–1.96
	<i>n</i> -octane	8	0.36–1.43
Branched alkanes	2,3-dimethylbutane	6	0.59–1.55
	Isopentane	5	6.07–10.17
	2-methylpentane	6	2.91–3.85
	2,3-dimethylpentane	7	0.32–4.17
	2,4-dimethylpentane	7	0.23–1.71
	2,2,4-trimethylpentane	8	0.32–4.58
	2,3,3-trimethylpentane	8	0.05–2.28
	2,3,4-trimethylpentane	8	0.11–2.80
	2-methylhexane	7	0.36–1.48
	3-methylhexane	7	0.30–1.77
	2,2,5-trimethylhexane	9	0.17–5.89
	2,3,5-trimethylhexane	9	0.05–1.09
	2-methylheptane	8	0.48–1.05
	3-methylheptane	8	0.63–1.54
	2,2,4-trimethylheptane	10	0.12–1.70
Cyclic alkanes	cyclopentane	5	0.19–0.58
Straight-chain alkenes	<i>trans</i> -2-pentene	5	0.52–0.90
Branched alkenes	2-methyl-2-butene	5	0.96–1.28
Aromatics	benzene	6	0.12–3.50
	toluene	7	2.73–21.80
	ethylbenzene	8	0.36–2.86
	<i>o</i> -xylene	8	0.68–2.86
	<i>m</i> -xylene	8	1.77–3.87
	<i>p</i> -xylene	8	0.77–1.58
	1-methyl-4-ethylbenzene	9	0.18–1.00
	1-methyl-3-ethylbenzene	9	0.31–2.86
	1,2,4-trimethylbenzene	9	0.66–3.30
	1,3,5-trimethylbenzene	9	0.13–1.15
	1,2,3,5-tetramethylbenzene	10	0.14–1.06

Source: Adapted from Riser-Roberts 1992, Tbl. A.2–4.

Table 9-4 Properties of Pure Gasoline-Range Hydrocarbon Compounds

Hydrocarbon	Molar mass ¹ (g mol ⁻¹)	Vapor pressure ^{1,a} (mb)	Solubility in water ^{1,a} (mg L ⁻¹)	Henry's Constant ^{1,a}		TLV-TWA in air ^{2,b} (ppmv)
				(mb L mg ⁻¹)	(atm)	
<i>Alkanes</i>						
<i>n</i> -pentane	72.15	684	39	17.3	68500	600
<i>n</i> -hexane	86.17	202	10	19.7	93200	50
<i>n</i> -heptane	100.21	61.1	2.7	23.0	126000	400
<i>n</i> -octane	114.23	18.8	0.72	26.3	164000	300
isopentane	72.15	926	48	19.1	75700	
2-methylpentane	86.17	282	14	19.7	93200	
2,3-dimethylpentane	100.21	91.8	5.3	17.5	96000	
2,4-dimethylpentane	100.21	131	4.4	29.9	164000	
2,2,4-trimethylpentane	114.23	65.6	2.3	28.9	181000	
2,3,4-trimethylpentane	114.23	36.0	2.2	16.6	104000	
2-methylhexane	100.21	87.8	2.5	34.5	190000	
3-methylhexane	100.21	82.1	3.4	23.9	132000	
2,2,5-trimethylhexane	128.26	22.1	0.81	27.3	192000	
3-methylheptane	114.23	26	0.79	32.9	206000	
cyclopentane	70.14	424	161	2.64	10100	600
<i>Aromatics</i>						
benzene	78.11	127	1800	0.070	302	10
toluene	92.13	38.0	523	0.073	367	50
ethylbenzene	106.2	12.7	169	0.075	439	100
<i>o</i> -xylene	106.2	8.82	187	0.047	274	100
<i>m</i> -xylene	106.2	11.0	167	0.066	384	100
<i>p</i> -xylene	106.2	11.7	175	0.067	389	100

^a At 25°C.^b ACGIH recommended limits.Sources: ¹ Mackay and Shiu 1981. ² Plog, Niland, and Quinlan 1996, Appendix B.

more volatile compounds vaporize into pore gases in the unsaturated zone, the more soluble compounds dissolve into groundwater, and the least soluble compounds adsorb to organic matter and mineral surfaces. Liquid gasoline becomes less volatile as it loses lighter constituents to vapor and solution phases. Partitioning is in part a function of constituent vapor pressure and solubility, factors that vary with temperature. Temperature effects can generally be ignored within the normal range of underground temperatures, about 0° to 35°C (Ellerd and Brown 1997).

The gradual change in composition of liquid gasoline from loss of compounds into vapor, solution, and adsorbed phases, with additional losses to bacterial decomposition, is called *weathering*. The weathering process is complex. There are no reliable methods of predicting the chemical composition of weathered gasoline or its vapor, solution, or adsorbed phases (Potter 1989), though general trends can be discerned.

Hydrocarbon concentrations in geologic media are measured from tests on soil, rock, groundwater, and pore gas samples. Hydrocarbon concentrations in soils and rocks are commonly expressed as mass fractions based on dry mass of bulk sample, using the equivalent units $\mu\text{g g}^{-1}$, mg kg^{-1} , or ppm (Denahan et al. 1993). The ppm mass unit is not used in this text. Solution concentrations in groundwater are commonly expressed as mass concentrations, in units of mg L^{-1} . Vapor concentrations are commonly expressed as volume fractions, such as $\text{cm}^3 \text{cm}^{-3}$, or ppmv.

Vapor Phase Partitioning

Liquid phase gasoline hydrocarbons tend to partition into vapor phase according to Raoult's law, Equation C-41. Alkanes are the most volatile (exhibit highest vapor pressures) of the major groups of hydrocarbons, so make up a higher proportion of the vapor phase relative to the liquid phase. Aromatics are the least volatile, so make up a smaller proportion of the vapor. The difference in composition between fresh liquid gasoline and its equilibrium vapor phase is shown in Figure 9-2.

Raoult's law can be combined with the ideal gas law to develop an equation for estimating mass concentration of vapor over liquid gasoline (Johnson et al. 1990):

$$\rho_v \approx \sum_i^n \frac{M_i x_i p_{vi}}{R T} \quad (9-1)$$

where ρ_v is mass concentration (mg L^{-1}), M_i is molar mass of constituent i (g mol^{-1}), x_i is mole fraction of the constituent in the liquid phase, p_{vi} is vapor pressure of the constituent, R is the universal gas constant, T is absolute temperature, and n is number of constituents. This equation provides an upper bound

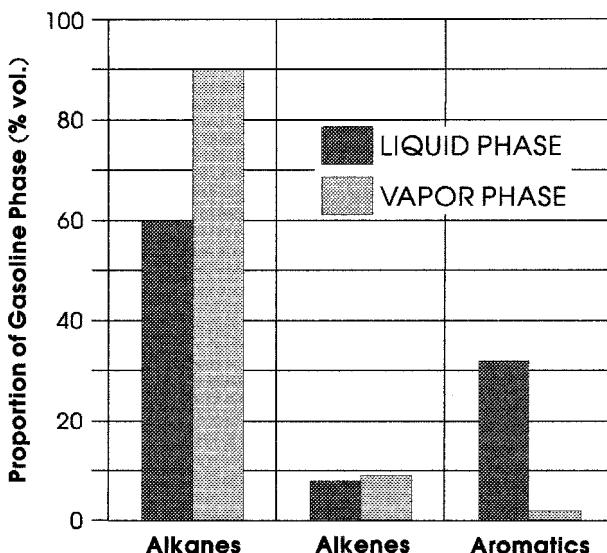


Figure 9-2. Compositions of liquid and vapor phases of gasoline. (Adapted from Weaver 1992.)

vapor concentration and is valid for total hydrocarbon concentrations in excess of 500 mg kg^{-1} , which is typical of spill sites. Vapor concentration can be limited by low contaminant concentration.

Solution Phase Partitioning

Solution concentrations of hydrocarbons in water in contact with liquid gasoline are typically well below the solubility concentrations for pure compounds shown in Table 9-4. Solution concentrations in water are limited by the low proportion of each constituent in the fuel. Hydrocarbon partitioning between liquid gasoline and a solution phase in water is described by:

$$K_{fw} = \frac{\rho_i(f)}{\rho_i(aq)} \quad (9-2)$$

where K_{fw} is the *fuel-water partition coefficient*, $\rho_i(f)$ is mass concentration of the constituent in the fuel (mg L^{-1}), and $\rho_i(aq)$ is mass concentration of the constituent in water (mg L^{-1}). This equation is valid where individual hydrocarbon constituents make up less than 10% (wt.) of the fuel (Bruce, Miller, and Hockman 1991).

The solubility of hydrocarbons in gasoline is so much higher than in water that the fuel–water partition coefficient is mainly a function of water solubility. Partition coefficients for hydrocarbons can be estimated from (Bruce, Miller, and Hockman 1991):

$$\log K_{fw} \approx 5.95 - 1.05 \log S \quad (9-3)$$

where S is solubility of the constituent in water, in units of mg L^{-1} .

Aromatics typically constitute about 87% to 95% (wt.) of hydrocarbons in solution in water in contact with liquid gasoline (Wilson and Rees 1985). The results of a laboratory investigation to determine fuel–water partition coefficients for BTEX compounds are summarized in Table 9-5. Note that total BTEX solution concentrations in water compare with the range of solubility concentrations for bulk gasoline in water shown in Table 9-1. In field situations, dissolved hydrocarbon concentrations in water seldom exceed 0.2 times the solution concentrations shown in Table 9-5, unless liquid phase gasoline is inadvertently taken up with the water sample. Solution concentrations tend to decrease with distance from the source due to dilution in moving groundwater, volatilization into pore gas, adsorption to organic matter and mineral surfaces, and bacterial decomposition (Bruce 1993).

Hydrocarbon partitioning between vapor phase and solution phase in water is described by Henry's law, Equation C-25. Henry's constants for some gasoline-range hydrocarbons are included in Table 9-4. Vapor concentrations over solution phase hydrocarbons are as much as two to three orders of magnitude lower than vapor concentrations over liquid gasoline (Thompson and Marrin 1987). Partitioning from solution phase is relatively slow.

Table 9-5 Fuel-Water Partition Coefficients for BTEX Compounds in Gasoline

Hydrocarbon	Concentration in gasoline		Solution conc. in water (mg L^{-1})	Partition coefficient* K_{fw}
	(% wt.)	(mg L^{-1})		
Benzene	1.9–3.2	14250–24000	32.4–51.2	420 ± 50
Toluene	8.5–12.7	63750–90000	34.3–53.4	1950 ± 380
Ethylbenzene	1.0–1.7	7125–12750	1.5–3.2	4990 ± 1000
Total Xylene	3.5–9.2	27000–69000	5.0–12.9	4850 ± 780

From laboratory tests using five gasolines. No agitation of fluids. Results after 10 days. Fuel density 0.75 g ml^{-1} .

* Average and standard deviation.

Source: Adapted from Bruce et al. 1991.

Adsorbed Phase Partitioning

Hydrocarbons partition into an adsorbed phase by adsorbing onto organic and mineral surfaces (Jury 1986). Adsorption onto organic matter can be significant in organic-rich soils. Adsorption onto mineral surfaces is relatively insignificant unless the soils are extremely dry. Mineral surfaces are electrically charged, so have a much stronger affinity for water molecules, which are polar, than for hydrocarbons, which are nonpolar (Chiou and Shoup 1985).

Partitioning of solution phase hydrocarbons into an adsorbed phase on organic matter is described by (Devitt et al. 1987, p. 101):

$$K_{oc} = \frac{C_a}{f_{oc} C_s} \quad (9-4)$$

where K_{oc} is the organic carbon partition coefficient, C_a is the adsorbed hydrocarbon concentration (mg g^{-1} ; dry soil basis), C_s is the solution phase hydrocarbon concentration (mg g^{-1}), and f_{oc} is the soil organic carbon fraction. The relationship is generally valid for organic carbon contents ranging from about 0.1% to nearly 20% (Lyman 1982).

The organic carbon partition coefficient is inversely proportional to the compound's solubility in water; it can be estimated using:

$$\log K_{oc} \approx 3.64 - 0.55 \log C_s \quad (9-5)$$

where C_s is in units of mg kg^{-1} . Other relationships have also been developed (Lyman 1982). Estimated partition coefficients are generally considered accurate within one order of magnitude. Values measured from tests on the soil or rock of interest are preferred.

MIGRATION AND RETENTION OF GASOLINE IN GEOLOGIC MEDIA

Liquid gasoline released into the unsaturated zone seeps downward through permeable features, under the influence of gravity and capillary forces. A gasoline release may eventually reach the saturated zone, where it spreads laterally across the capillary fringe. Liquid gasoline provides a lasting source for vapor phase partitioning into pore gases, and solution phase partitioning into pore waters. These three phases combined constitute the gasoline contaminant plume. This section describes forces that control migration and retention of liquid, vapor, and solution phase gasoline, and biochemical consumption mechanisms that affect all phases.

Liquid Phase Migration and Retention

Liquid phase gasoline migration through geologic media is complicated by the influence of pore water. Liquid gasoline and water are immiscible fluids: they maintain a distinct fluid–fluid interface between them. The limited ability of gasoline constituents to dissolve in water does not change this immiscible behavior. Water and gasoline migrate independently through porous media. Water molecules, being polar, have a high affinity for mineral surfaces. Water is generally the wetting fluid in porous soil and rock, relative to liquid gasoline and pore gases, which are nonwetting fluids. A wetting fluid is difficult to displace from small pores, which leaves only larger pores available to nonwetting fluids. Degree of water saturation strongly influences gasoline migration and retention.

Water in porous media above the water table is held by capillary forces. Pore water distribution above the water table, absent recent infiltration induced by meteoric recharge, is shown in Figure 9-3. In the pendular zone, water is held in isolated rings around the contact points of adjacent grains, as shown in Figure 9-4a. Lacking continuous connections between pores, pendular water cannot flow. The pendular zone is at or below the irreducible water content, or field capacity, of the media. In the funicular zone, pendular rings coalesce into a par-

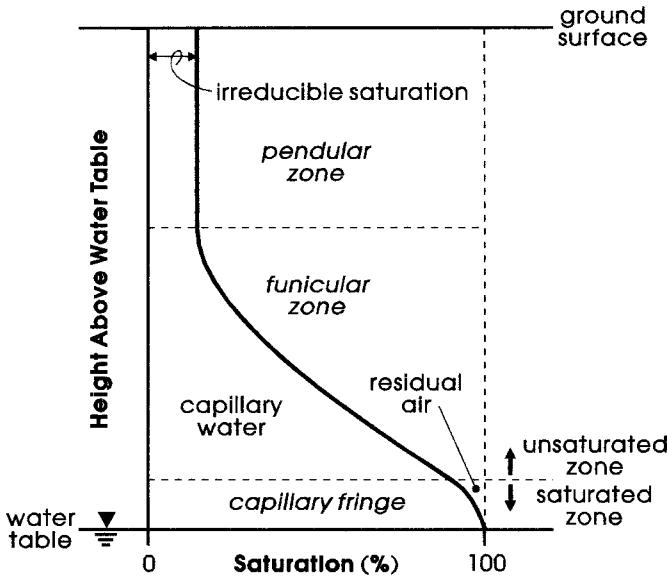


Figure 9-3. Porewater distribution above the water table. No vertical scale. (Adapted from Abdul 1988. © 1988 *Ground Water Monitoring & Remediation* [formerly *Ground Water Monitoring Review*].)

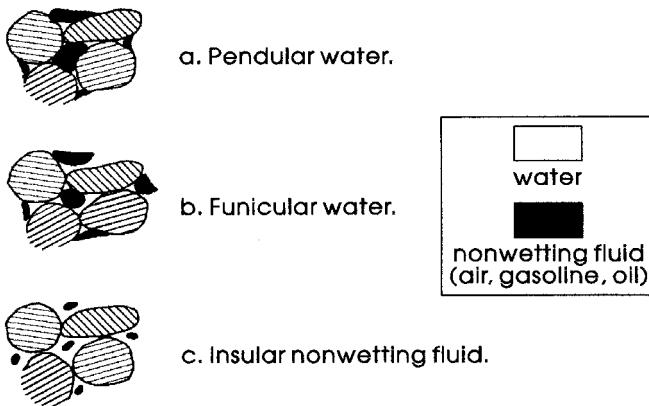


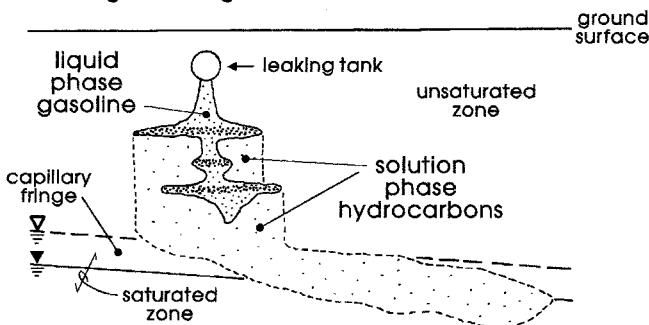
Figure 9-4. Possible fluid saturation states in water-wet sand. (Adapted from Bear 1972, Fig. 9.2.3.)

tially continuous wetting fluid, as shown in Figure 9-4b. Capillary flow of water becomes possible in this zone. The height of the funicular zone above the water table is a function of pore size, and may range from less than 10 cm in gravels to over 2 m in clays (Stephens 1996, p. 1). The capillary fringe approaches complete saturation. It may contain a residual nonwetting fluid isolated in larger pores, as shown in Figure 9-4c.

Liquid gasoline migrates by both gravity-driven bulk flow and capillary flow. Liquid gasoline in sufficient concentration to form a continuous phase, capable of supporting bulk or capillary flow, is termed *free product*. Liquid gasoline migrates through the pendular and funicular zones by displacing pore gases from the largest interconnected pores. Bulk flow through homogeneous unsaturated soil produces a narrow vertical plume. In heterogeneous ground the plume configuration can be complex. Impermeable strata in the flowpath can block bulk flow to form a perched accumulation of gasoline or can deflect flow laterally through more permeable matrix (Kramer and Keller 1995). Bulk flow above the water table occurs preferentially along high-permeability pathways, such as coarse granular seams, rock fractures (Willhite, Garner, and Stanley 1986), and leaky conduits (Collins 1985). Liquid gasoline has migrated for several kilometers through utility trench backfill (Cole 1994, p. 89). Capillary flow can occur in any direction. It contributes to lateral spreading of the plume, tending to shape the plume into an inverted cone. The spatial character of an underground gasoline release in permeable soil is shown in Figure 9-5.

Some liquid gasoline migrating through porous media is held by capillary forces, as residual gasoline. Liquid gasoline can migrate below the funicular zone

a. Migration Through Heterogeneous Ground.



b. Migration Through Homogeneous Ground.

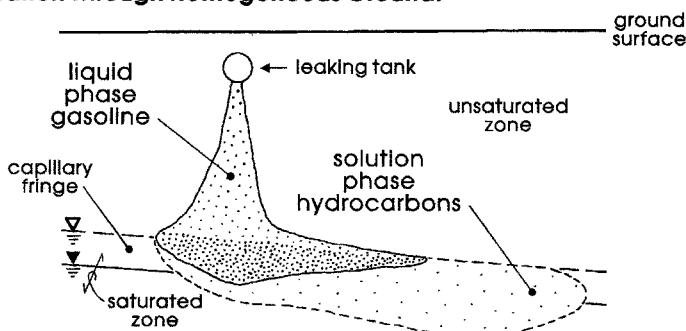


Figure 9-5. Gasoline migration pattern in permeable soils. Vapor phase not shown. Volume of spill in "b" exceeds residual saturation demand. (Adapted from Schwille 1984.)

only as long as the volume released from the source exceeds the total residual saturation demand of ground within the vertical plume. Residual saturation depends on pore size distribution and water content. Higher residual saturations occur in finer-grained soils. Residual gasoline saturation in the pendular and funicular zones may range from 0.5% to 4% in porous granular soils (Bruce 1993). Liquid gasoline within the plume continues to migrate after flow from the source is terminated, until residual saturation is established throughout (Collins 1985). Residual liquid gasoline held in the unsaturated zone or capillary fringe provides a lasting source for vapor and solution phase partitioning. Vapor and solution phase hydrocarbons may continue to migrate long after the liquid phase has become immobile.

Liquid gasoline that penetrates the funicular zone may develop enough pressure head to displace funicular water from larger pores, spread laterally over

the capillary fringe, and depress the top of the capillary fringe to the proximity of the water table. Free product thicknesses of a meter or more on the capillary fringe are not uncommon. Gasoline on the capillary fringe migrates mainly by bulk flow. Some gasoline migrating through the saturated zone is retained as residual saturation, in larger pores in an insular state. This retention reduces the volume of gasoline available for lateral spreading across the capillary fringe. Residual gasoline saturation in the saturated zone may range from about 10% to 60% (Mercer and Cohen 1990).

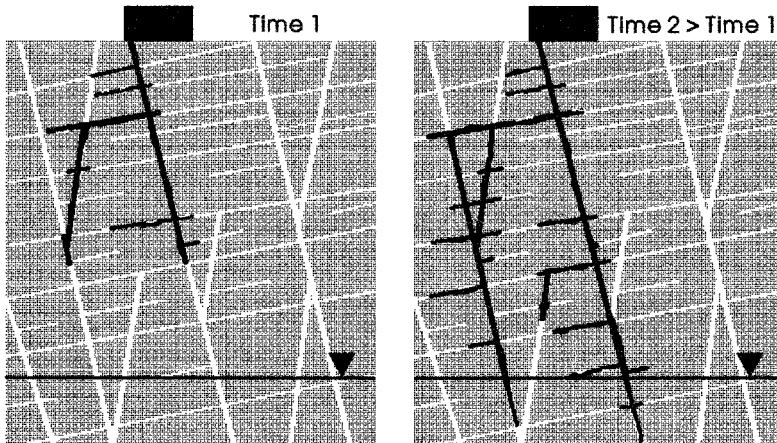
Groundwater movement affects the distribution of liquid gasoline on the capillary fringe. Water table fluctuations tend to distribute liquid gasoline over porous media, increasing the volume of gasoline held in residual saturation, and limiting lateral spreading. Significant rise or fall of the water table can periodically connect free product to high-permeability pathways normally positioned above or below the capillary fringe, resulting in a pulsed bulk flow (Collins 1985; Davis, Jasmer, and Ore 1987). Water table fluctuations can trap liquid gasoline below the water table, as residual gasoline, and as free product under confining layers (Vroblesky, Robertson, and Rhodes 1995). Lateral migration of groundwater below the water table may distort the areal distribution of the floating plume.

Some gasoline spills in permeable ground are remediated by extracting free product through wells. A water pump positioned in the bottom of the well is used to depress the water table slightly, causing gasoline on the capillary fringe to flow toward the well under the influence of gravity (Dunlap 1985). A liquid hydrocarbon pump positioned near the top of the water column skims gasoline from the well. This method is generally effective in recovering no more than about 50% (vol.) of the original gasoline release; a 30% recovery is more typical (Beckett and Lundegard 1997). The remainder is retained in the ground as residual saturation, stranded free product, and vapor, solution, and adsorbed phases. Site characteristics that limit free product recovery include fine-grained porous media, fractured media, heterogeneous ground, and a fluctuating water table.

Gasoline released into fractured rock is subject to the same forces that control migration and retention in porous soil, but the influence of fracture permeability over matrix permeability accounts for some differences in contaminant distribution. Liquid gasoline migrates through rock mainly by bulk flow, driven by pressure head developed in gasoline-filled fractures. Migration occurs predominantly through vertical to subvertical fractures, in which the highest pressure heads develop. Groundwater capillary pressures oppose gasoline migration by blocking access to fractures; these capillary pressures are insignificant in fractures more than 1 cm wide (Hardisty et al. 1994).

Liquid gasoline migration through fractured rock is shown in Figure 9-6a. Gasoline becomes increasingly capable of penetrating finer fractures with depth, as pressure head on the migration front increases with vertical extension of the gasoline-filled portion of the fracture. Bulk flow through horizontal to subhoriz-

a. Gasoline Migration Through the Unsaturated Zone.



b. Gasoline Entrapment by Fluctuating Water Table.

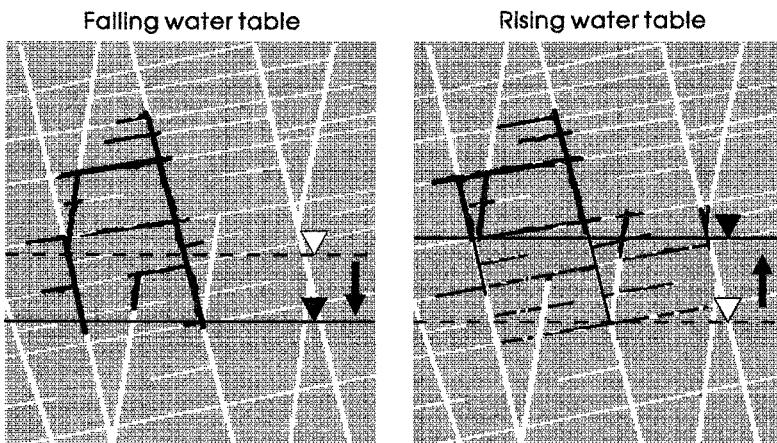


Figure 9-6. Liquid gasoline migration through fractured sedimentary rock. (Adapted from Hardisty et al. 1994. © 1994 National Ground Water Association.)

horizontal fractures is driven by pressure head at the intersecting vertical fracture, which may remain constant in cases of a continuous leak. Liquid gasoline reaching the water table will tend to spread laterally, as in porous soil. If matrix permeability is low, little of the gasoline will be retained in residual saturation. Pressure head may develop on the gasoline front sufficient to overcome hydrostatic pressure in fracture water, and drive liquid gasoline well below the water table.

Groundwater table fluctuations may cause liquid gasoline to become trapped in horizontal to subhorizontal fractures and may contribute to lateral spreading, as shown in Figure 9-6b.

Vapor Phase Migration and Retention

Portions of the contaminant plume exposed to the unsaturated zone are enveloped in gasoline vapors. Vapors migrate through the unsaturated zone mainly by diffusion. Vapor diffusion through unsaturated porous media follows Fick's first law, as shown in Equation 6-16. The effective diffusion coefficient for vapors in partially saturated porous media can be estimated using the Millington equation, Equation 6-18. The diffusion coefficient D for hydrocarbons of intermediate molar mass, in air, is shown in Table 9-2. Vapor concentrations decline with distance from the source according to Fick's second law, shown in general form in Equation 6-15.

Environmental factors cause vapor concentrations in the unsaturated zone to vary with location and time. Infiltrating meteoric water may carry vapor phase hydrocarbons in solution to the water table (Silka 1986). Clay lenses overlying a contaminant plume may impede vapor diffusion (Walther, Pitchford, and Olhoeft 1986). Vapor concentration may be attenuated by adsorption on organic matter and by bacterial decomposition. High vapor concentrations are commonly observed in the vicinity of liquid gasoline migration through highly permeable pathways, such as utility trenches.

Solution Phase Migration and Retention

Groundwater acquires solution phase hydrocarbons through contact with liquid or vapor phases. This can occur where groundwater infiltrates through residual liquid gasoline or gasoline vapors in the unsaturated zone, or flows laterally beneath a floating plume of liquid gasoline. A plume of liquid gasoline spread over the capillary fringe is pervious to water. The globular distribution of gasoline in pores presents a large surface area to infiltrating groundwater, which can become saturated with hydrocarbons within a travel distance of a few tens of centimeters (Devitt et al. 1987, p. 105). A fluctuating water table promotes hydrocarbon solutioning by increasing the volume of liquid gasoline held in residual saturation, which increases the surface area available for volatilization or dissolution.

Solution phase hydrocarbons migrate through porous media mainly by groundwater bulk flow. Hydraulic head gradients and aquifer permeability control groundwater flow, and hence the shape of the contaminated plume. Solution phase hydrocarbons are dispersed on a local scale by mechanical mixing induced by water movement through pore constrictions, and by diffusion along chemical concentration gradients. Solution phase hydrocarbon concentration is attenuated by numerous factors such as dispersion, diffusion, dilution by recharge, volatiza-

tion, adsorption to organic matter, and bacterial decomposition (Buscheck, Wickland, and Kuehne 1996). As a result of attenuation, groundwater plumes contaminated with hydrocarbons rarely extend farther than about 80 m from the source.

Biochemical Consumption of Gasoline

Bacteria underground are capable of decomposing gasoline hydrocarbons; the process is controlled by environmental conditions. Hydrocarbon decomposition via aerobic processes is most efficient. Anaerobic decomposition is much less efficient but can account for some hydrocarbon loss. Susceptibility to bacterial decomposition varies among hydrocarbon groups, generally declining in the following order: straight-chain alkanes > branched-chain alkanes > light aromatics > cyclic alkanes. High concentrations of hydrocarbons inhibit bacterial decomposition. They support a high oxygen demand, which can turn the environment anoxic, and their lighter constituents are toxic to bacteria (Leahy and Colwell 1990).

Aerobic decomposition is limited principally by availability of oxygen, but it may also be limited by nitrogen and phosphorous, which are not abundant in natural environments (Leahy and Colwell 1990). Aerobic decomposition tends to lower concentrations of vapor and solution phase hydrocarbons in the vicinity of a gasoline spill (Silka 1988). The unsaturated zone is generally a favorable environment for aerobic bacteria. Oxygen and carbon dioxide concentrations in unsaturated zone pore gases may exhibit an inverse relationship, very similar to that shown in Figure 3–3 (Marrin 1991; McLinn and Rehm 1997).

Anoxic conditions commonly develop in areas heavily contaminated with gasoline hydrocarbons. BTEX compounds are more water soluble than oxygen, and in groundwater near a plume of liquid gasoline they commonly support an oxygen demand in excess of supply. Benzene, toluene, and the xylenes can be at least partially degraded anaerobically via methanogenesis and sulfate reduction (Leahy and Colwell 1990; Coates, Anderson, and Lovley 1996). Bacterial methane, presumably generated by anaerobic decomposition of hydrocarbons, has been found in pore gases over liquid phase gasoline plumes, in concentrations up to about 4% (Marrin 1991). Because anaerobic bacteria have very limited ability to decompose hydrocarbons, gasoline in anoxic environments may persist for very long periods of time.

HAZARDOUS CONCENTRATIONS OF GASOLINE IN THE GROUND

For the purposes of this text, gasoline in the ground will be considered a hazard where it can move from the ground to form concentrations in an excavation atmosphere that exceed the toxic exposure limit of 300 ppmv, from Table 1-2 (partial

pressure 3×10^{-4} atm, at 1 atm total pressure; or volume fraction 3×10^{-4}). Gasoline vapors are combustible in concentrations from 1.4% to 7.6% (14,000 to 76,000 ppmv), so may also pose an explosion hazard. Hazardous properties of gasoline vapors are described further in Chapter 1. Relationships between concentrations of gases in the ground, their ability to move into an excavation, hazardous atmospheres in the excavation, and ventilation capacity are described in Chapter 7. These concepts are applicable to gasoline, and will not be reiterated here.

Liquid Phase Gasoline

Volatization of very small amounts of liquid gasoline can generate hazardous concentrations of vapors. The relationship between volatized mass of liquid and vapor concentration can be shown using a modification of Equation C-23:

$$\rho_v = \frac{M_b p_v}{R T} \quad (9-6)$$

where ρ_v is mass concentration of gasoline vapors, M_b is apparent molar mass of gasoline, p_v is partial pressure of gasoline vapors, R is the universal gas constant, and T is absolute temperature. The mass of gasoline in a unit volume of atmosphere containing the toxic exposure limit of vapors, at 20°C, is:

$$\begin{aligned} \rho_v &= \left(\frac{95 \text{ g}}{\text{mol}} \right) \frac{(3 \times 10^{-4} \text{ atm})}{(293 \text{ K})} \left(\frac{\text{mol K}}{8.206 \times 10^{-2} \text{ L atm}} \right) \left(\frac{1000 \text{ L}}{\text{m}^3} \right) \\ &= 1.2 \text{ g m}^{-3} \end{aligned}$$

where apparent molar mass of bulk gasoline is from Table 9-2. In other words, volatization of 1.2 g (about 1.6 ml) of fresh liquid gasoline per 1 m³ of atmosphere could generate the toxic exposure limit of vapors. Volatization of an amount of liquid gasoline equal to 14,000/300 times the result above, or 56 g (about 74 ml) per 1 m³ of atmosphere, could generate an explosive concentration of vapors.

Vapor Phase Gasoline

Gasoline vapors occupying unsaturated pores could generate equal concentrations of vapors in unventilated areas of an excavation. Fresh gasoline can generate vapor pressures up to about 550 mb (from Table 9-1), equal to a partial pressure of 0.5 atm, or a concentration of 500,000 ppmv. Weathered gasoline may generate vapor pressures of about 50 mb (from Table 9-2), equal to a concentration of 50,000 ppmv. Both of these vapor concentrations are far in excess of explosive concentrations.

Solution Phase Gasoline

The equilibrium vapor concentration generated by gasoline hydrocarbons in solution in groundwater can be determined using Henry's law, from Appendix C:

$$x_i(\text{aq}) = \frac{p_{vi}}{H_i} \quad (\text{C-25})$$

where $x_i(\text{aq})$ is concentration of gasoline hydrocarbon i in solution, in terms of mole fraction; p_{vi} is partial pressure of gasoline hydrocarbon i in the vapor phase; and H_i is Henry's constant for hydrocarbon i at a specific temperature.

Gasoline hydrocarbons in solution in groundwater consist mainly of BTEX compounds, and the most soluble of these is benzene. The toxic exposure limit of benzene is considerably lower than for bulk gasoline vapors; the ACGIH TLV-TWA is 10 ppmv (1×10^{-5} atm), from Table 1-2. The solution concentration of benzene capable of equilibrating to a vapor concentration of 10 ppmv can be calculated from Equation C-25, and Henry's constant for benzene from Table 9-4:

$$x_i(\text{aq}) = \frac{1 \times 10^{-5} \text{ atm}}{302 \text{ atm}} = 3.31 \times 10^{-8}$$

where $x_i(\text{aq})$ is solution concentration of benzene in water (mole fraction). Converting this result to mass concentration of benzene in solution yields:

$$\begin{aligned} \rho_i &= \left(\frac{3.31 \times 10^{-8} \text{ mol C}_6\text{H}_6}{\text{mol H}_2\text{O}} \right) \left(\frac{78 \text{ g C}_6\text{H}_6}{\text{mol C}_6\text{H}_6} \right) \left(\frac{\text{mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) \\ &\times \left(\frac{1000 \text{ g H}_2\text{O}}{\text{L H}_2\text{O}} \right) \left(\frac{1000 \text{ mg}}{\text{g}} \right) \\ &= 0.14 \frac{\text{mg C}_6\text{H}_6}{\text{L H}_2\text{O}} \end{aligned}$$

As was noted in the section above on solution phase partitioning, benzene concentrations in groundwater seldom exceed 0.2 times the solution concentrations shown in Table 9-5, or about 6 to 10 mg L⁻¹. This analysis shows that benzene in solution in groundwater could generate vapor concentrations well above the toxic exposure limit.

Henry's law can also be used to calculate the solution concentration of gasoline hydrocarbons capable of equilibrating to an explosive concentration of vapors. An approximate Henry's constant for fresh gasoline can be calculated from the general definition of Henry's constant (Appendix C), and gasoline vapor pressure and solubility from Table 9-1 (Peterson 1997):

$$H = \frac{\text{vapor concentration}}{\text{equilibrium solution concentration}} = \frac{P_v}{\rho_g(\text{aq})}$$

$$= \left[\frac{550 \text{ mb}}{\left(\frac{100 \text{ mg}}{\text{L}} \right)} \right] \left(\frac{\text{atm}}{1013.25 \text{ mb}} \right) = 5.43 \times 10^{-3} \frac{\text{atm}}{\left(\frac{\text{mg}}{\text{L}} \right)}$$

(In this case it is convenient to express Henry's constant in units other than atm, as is normally done in this text. The result above can be converted to 28,700 atm, using the apparent molar mass of fresh gasoline and molar mass of water to convert the mg L^{-1} unit to mole fraction.) Most solution phase hydrocarbons are BTEX compounds, which have a lower explosive limit (LEL) slightly below that for bulk gasoline vapors, about 1.2% from Table B-9. Applying the general form of Henry's law above, the solution concentration of gasoline hydrocarbons capable of equilibrating to a vapor concentration of 1.2% (0.012 atm) is

$$\rho_g(\text{aq}) = (0.012 \text{ atm}) \left(\frac{\text{mg}}{5.43 \times 10^{-3} \text{ atm L}} \right) = 2.2 \text{ mg L}^{-1}$$

This result is well within the solubility range of fresh gasoline (50 to 100 mg L^{-1} from Table 9-1), indicating that gasoline in solution can generate an explosive concentration of vapors.

GASOLINE INFLOW TO EXCAVATIONS

There are several mechanisms of gasoline entry to excavations: 1) in liquid phase, via free product bulk flow, or via bulk excavation in ground containing residual liquid; 2) in vapor phase, via bulk excavation in unsaturated porous ground; and 3) in solution phase, via groundwater inflow. These inflow mechanisms are analyzed separately in this section, though often two or more may apply concurrently. Each of these mechanisms is capable of generating toxic or explosive concentrations of gasoline vapors in the excavation atmosphere.

Liquid Phase Inflow

Liquid gasoline can enter the tunnel by free product bulk flow, or by bulk excavation in porous ground containing residual liquid gasoline. In this evaluation it is assumed that liquid gasoline entering the tunnel volatizes completely into vapor before it can be removed from the excavation.

The mass inflow rate of liquid gasoline that the ventilation system in a tunnel can control can be estimated from a modification of Equation 7-1:

$$q_m = q_{ta} \rho_v = v_a A \rho_v \quad (9-7)$$

where q_m is mass inflow rate of liquid gasoline (g min^{-1}), q_{ta} is volumetric airflow rate at the face ($\text{m}^3 \text{ min}^{-1}$), ρ_v is mass density of the maximum allowable concentration of gasoline vapors in tunnel air (g m^{-3}), v_a is average effective airflow velocity (m min^{-1}), and A is area of the excavation face (m^2). The mass density of fresh gasoline vapors at the toxic exposure limit, determined previously using Equation 9-6, is about 1.2 g m^{-3} . Assuming an average airflow velocity of 9 m min^{-1} (the normal minimum), and a tunnel diameter of 3 m , the maximum mass inflow rate of fresh gasoline that the ventilation system could control is:

$$q_m = \left(\frac{9 \text{ m}}{\text{min}} \right) \left(\frac{\pi}{4} \right) (3 \text{ m})^2 \left(\frac{1.2 \text{ g}}{\text{m}^3} \right) = 76 \text{ g min}^{-1}$$

This result converts to a volumetric inflow rate of:

$$q_l = \left(\frac{76 \text{ g}}{\text{min}} \right) \left(\frac{\text{ml}}{0.75 \text{ g}} \right) = 100 \text{ ml min}^{-1}$$

Free product bulk flow is potentially the most rapid of gasoline inflow mechanisms. Bulk flow occurs along hydrostatic head gradients that develop around the excavation perimeter. In excavations above the water table, free product can migrate from accumulations perched on impermeable layers that transect the contaminant plume. In excavations that straddle or lie slightly below the water table, free product can migrate from accumulations on the capillary fringe, following the depression formed by groundwater inflow to the excavation, as shown in Figure 9-7. Free product can also enter an excavation well below the water table, in ground characterized by a low-permeability matrix and high-permeability pathways. As groundwater drains from permeable pathways, they open to bulk flow of free product. Bulk flow of gasoline is most likely to be concentrated at the excavation face but could occur anywhere on the perimeter.

The mass inflow rate of residual liquid gasoline with bulk excavation in porous media can be estimated using a modification of Equation 7-25:

$$q_m = c_{\text{bulk}} E_r A \quad (9-8)$$

where c_{bulk} is bulk mass concentration of residual liquid gasoline (g m^{-3}), E_r is bulk excavation rate (TBM advance rate during excavation, m min^{-1}), and A is area of the excavation face (m^2). Solving for c_{bulk} using the maximum allowable mass inflow rate calculated above, a TBM advance rate of 1 m per 10 min , and inside tunnel diameter of 3 m :

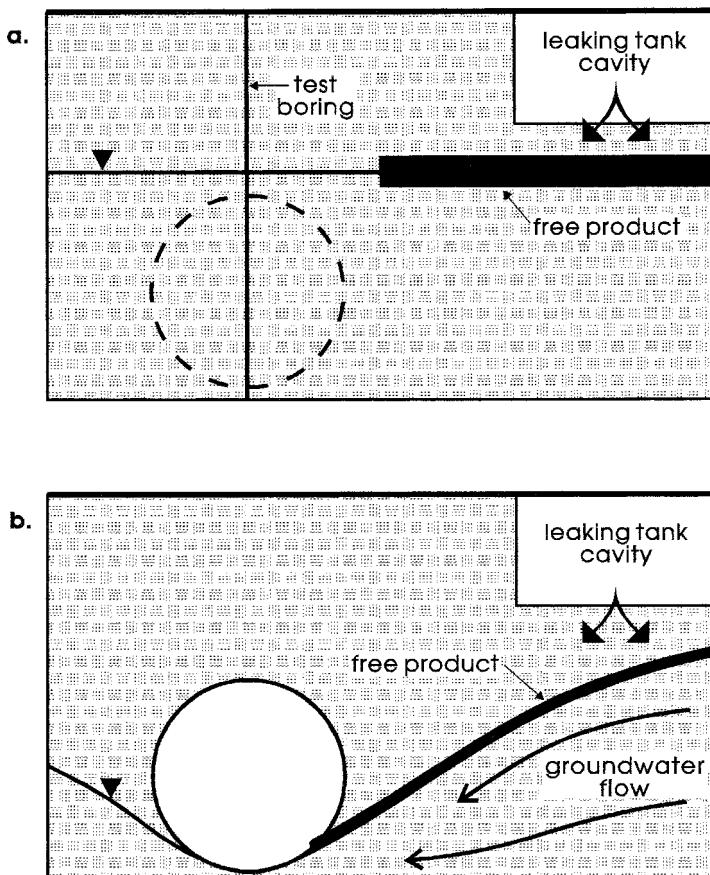


Figure 9-7. Possible mechanism of liquid phase gasoline flow into tunnel below water table. In “a”, plume lies off alignment. Little or no contaminant is apparent in borehole on centerline, prior to tunneling. In “b”, tunnel excavation depresses water table, drawing liquid gasoline into heading. Vapor and solution phase gasoline not shown.

$$c_{\text{bulk}} = \left(\frac{76 \text{ g}}{\text{min}} \right) \left(\frac{10 \text{ min}}{1 \text{ m}} \right) \left(\frac{4}{\pi} \right) \left(\frac{1}{3 \text{ m}} \right)^2 = 108 \text{ g m}^{-3}$$

This converts to a bulk volume concentration of:

$$c_{\text{bulk}} = \left(\frac{108 \text{ g}}{\text{m}^3} \right) \left(\frac{\text{ml}}{0.75 \text{ g}} \right) = 144 \text{ ml m}^{-3}$$

Assuming sand and gravel with a void ratio of 0.30, bulk volume concentration converts to residual gasoline saturation of:

$$S_r = \left(\frac{144 \text{ cm}^3}{\text{m}^3} \right) \left(\frac{1}{0.30} \right) \left(\frac{\text{m}^3}{1 \times 10^6 \text{ cm}^3} \right) (100) = 0.05\%$$

This is the maximum average residual saturation of liquid gasoline that the ventilation system could safely dilute and remove under the assumed conditions.

The rate at which liquid phase gasoline entering an excavation volatizes into vapor is unknown. Vapor flux rate from contaminated ground (flux measured in $\text{g cm}^{-2} \text{ s}^{-1}$) is a complex function of composition and concentration of liquid gasoline, air diffusion coefficient and vapor pressure of each hydrocarbon constituent, vapor concentration in the atmosphere, and temperature (Johnson, Hertz, and Byers 1993). Liquid gasoline entering a TBM muck chamber during an excavation cycle would present a very large surface area to the atmosphere, given the degree of ground breakage and churning that takes place. Measurements of hydrocarbon flux rates from contaminated soil piles (Johnson, Hertz, and Byers 1993), and tunneling experience in contaminated ground (Doyle, Hunt, and Kettler 1997), suggest that volatilization rate is very rapid. In the absence of definitive studies, it seems reasonable to assume that all liquid gasoline entering an excavation will volatize into vapor before the contaminated ground can be removed.

Vapor Phase Inflow

Gasoline retained in vapor phase in the unsaturated zone can be released into an excavation from ground broken up at the face. This inflow mechanism is likely most significant in TBM-mined tunnels in porous soil or rock.

The rate of gasoline vapor inflow with bulk excavation can be estimated using a modification of Equation 7-25:

$$q_v = c_{\text{bulk}} E_r A \quad (9-9)$$

where q_v is vapor phase inflow rate ($\text{m}^3 \text{ min}^{-1}$), c_{bulk} is bulk vapor concentration ($\text{cm}^3 \text{ vapor per cm}^3 \text{ soil or rock}$), E_r is bulk excavation rate (m min^{-1}), and A is area of the excavation face (m^2). In inorganic porous media partially saturated with water, $c_{\text{bulk}} \approx \phi_e c_{\text{fluid}}$, where ϕ_e is effective porosity to a vapor phase, and c_{fluid} in this case is vapor concentration (volume fraction). Effective porosity to vapor is:

$$\phi_e = \phi \left(1 - \frac{S}{100} \right) \quad (6-3)$$

where ϕ is total porosity, and S is water saturation (%). Vapor phase inflow rate is then:

$$q_v = \phi \left(1 - \frac{S}{100} \right) c_{fluid} E_r A \quad (9-10)$$

The vapor inflow rate that the ventilation system can control can be estimated from a modification of Equation 7-1:

$$q_v = q_{ta} \phi_a = v_a A \phi_a \quad (9-11)$$

where q_{ta} is volumetric airflow rate at the face ($m^3 \text{ min}^{-1}$), ϕ_a is allowable vapor concentration in the excavation atmosphere (volume fraction), v_a is average effective airflow velocity ($m \text{ min}^{-1}$), and A is area of the excavation face (m^2). Equating terms for q_v from Equations 9-10 and 9-11, and solving for c_{fluid} :

$$c_{fluid} = \frac{v_a \phi_a}{\phi \left(1 - \frac{S}{100} \right) E_r} \quad (9-12)$$

This equation will be solved assuming the ventilation system produces an average effective airflow velocity of 9 m min^{-1} , vapor concentration in the tunnel atmosphere is equal to the toxic exposure limit, the excavation is in sand and gravel with a total porosity of 0.30, water saturation is 20%, and TBM advance rate is $1 \text{ m per } 10 \text{ min}$. Inserting these parameters into the equation above:

$$c_{fluid} = \frac{\left(\frac{9 \text{ m}}{\text{min}} \right) (3 \times 10^{-4})}{(0.3) \left(1 - \frac{20}{100} \right) \left(\frac{1 \text{ m}}{10 \text{ min}} \right)} = 0.1125 = 112,500 \text{ ppmv}$$

This is the maximum average pore vapor concentration that the ventilation system could safely dilute and remove under the assumed conditions. It is within the range of pore vapor concentrations that could be generated by fresh liquid gasoline line.

Solution Phase Inflow

The most immediate risk posed by inflow of groundwater contaminated with gasoline appears to be from benzene vapors. The following example shows the maximum groundwater inflow that could be tolerated in a 3 m diameter tunnel or shaft, where the average effective airflow velocity is 9 m min^{-1} and the concen-

tration of benzene in groundwater outside the excavation is 10 mg L^{-1} . The AC-GIH TLV-TWA for benzene is 10 ppmv ($1 \times 10^{-5} \text{ atm}$).

Equation 7-16, the relationship between solution gas inflow and gas concentration in the excavation atmosphere, can be rearranged to:

$$q_{gw} = \frac{\rho_{gta}}{\rho_{ggw}} q_{ta} = \frac{\rho_{gta}}{\rho_{ggw}} v_a A$$

where q_{gw} is groundwater inflow rate to the excavation, ρ_{gta} is mass concentration of gas (or vapor) in the excavation atmosphere, ρ_{ggw} is mass concentration of gas (or vapor) in groundwater outside the excavation, q_{ta} is volumetric airflow rate in the excavation, v_a is average effective airflow velocity in the excavation, and A is area of the excavation face.

The mass concentration of benzene in the excavation atmosphere at the toxic exposure limit, from Equation C-23, is:

$$\begin{aligned} \rho_{bia} &= \frac{M_b p_b}{R T} \\ &= \left(\frac{78 \text{ g C}_6\text{H}_6}{\text{mol C}_6\text{H}_6} \right) \left(\frac{1 \times 10^{-5} \text{ atm}}{293 \text{ K}} \right) \left(\frac{\text{mol K}}{8.206 \times 10^{-2} \text{ L atm}} \right) \left(\frac{1000 \text{ mg}}{\text{g}} \right) \\ &= 3.24 \times 10^{-2} \text{ mg L}^{-1} \end{aligned}$$

Using this result to solve the previous equation yields:

$$\begin{aligned} q_{gw} &= \left(\frac{3.24 \times 10^{-2} \text{ mg}}{\text{L}} \right) \left(\frac{\text{L}}{10 \text{ mg}} \right) \left(\frac{9 \text{ m}}{\text{min}} \right) \left(\frac{\pi}{4} \right) (3 \text{ m})^2 \left(\frac{1000 \text{ L}}{\text{m}^3} \right) \\ &= 206 \text{ L min}^{-1} \end{aligned}$$

This is the maximum groundwater inflow that could be tolerated under the assumed conditions.

Gasoline Inflow with Barometric Pressure Fluctuation

Vapor phase gasoline could be drawn into an excavation following a sustained reduction in barometric pressure in the excavation atmosphere. This mechanism may be significant in shafts excavated through highly porous ground in an area of low water table. Gas inflow with barometric pressure fluctuation is described in Chapter 7.

Case Histories of Tunnels in Gasoline-Bearing Strata

East Lansing Sewer Tunnel

This tunnel was part of a combined sewer overflow abatement project constructed in East Lansing, Michigan, from 1995 to 1997. The tunnel is 1.6 mi (2.5 km)

long, 13.7 ft (4.2 m) in excavated diameter, and was excavated in glacial soils. The alignment runs through an urban commercial area, mainly beneath city streets, and passes a property formerly occupied by an automotive service station. Liquid gasoline had leaked from the service station's underground storage system, and some was drawn into the tunnel. Vapors in the TBM muck chamber exploded, injuring four workers in the heading.

A site plan and subsurface profile in the vicinity of the explosion are shown in Figure 9-8. The soil profile consists of two layers of till, separated by a layer of glaciofluvial deposits from an interglacial period. The upper till is predominantly clayey, with layers of sandy and silty soils. The glaciofluvial layer consists of uniformly graded coarse to fine sand, to silty fine sand. The lower till is predominantly clayey, but more granular than the upper till. Several of the borings drilled to rock show sand and gravel along the soil–rock contact. At the time of tunneling, existing piezometric head at the soil–rock contact ranged from tunnel springline to crown. Granular soils above held perched groundwater.

Gasoline was discovered to have leaked into soils on the service station property in 1985. The leaks were repaired, but in 1993 the underground storage system was removed and the property converted to a convenience store. A remediation investigation unrelated to tunnel construction was performed on the property in 1994, to determine the extent of contaminated ground (BLDI 1994). Boring locations are shown on the site plan (r1 to r7). Soil samples were screened for vapors using a headspace technique and photoionization detector (PID). Selected soil samples were analyzed for BTEX compounds using a gas chromatograph (GC). Groundwater samples from four monitoring wells were analyzed using the GC. Results of these tests are summarized in Figure 9-9. Soils contaminated with gasoline were found to a maximum depth of about 30 ft (9 m). Soil layering appeared to have contributed to significant lateral spreading of contamination. High concentrations of gasoline hydrocarbons in borings on property boundaries led these investigators to conclude that gasoline had probably migrated off the site to the north, west, and southwest. No free product was observed in the ground during the 1993 tank removal or the subsequent remedial investigation.

An environmental investigation was performed along the tunnel alignment in 1995 to determine the extent of gasoline contaminants and to evaluate their effects on health and safety during tunneling (borings e1 to e6). Gasoline contaminants were found in borings e1 to e5. Highest concentrations were found in boring e3, where PID readings from sand near crown depth ranged up to 8000 ppmv, and total BTEX concentrations reached $156,000 \mu\text{g kg}^{-1}$. Investigators recommended that groundwater entering the tunnel from the contaminated zone be treated prior to disposal into sewers, that contaminated soils be disposed of in an appropriately classified landfill, and that tunnel workers be trained in handling hazardous waste. No specific recommendations were made regarding control of gasoline vapor concentrations in the tunnel atmosphere.

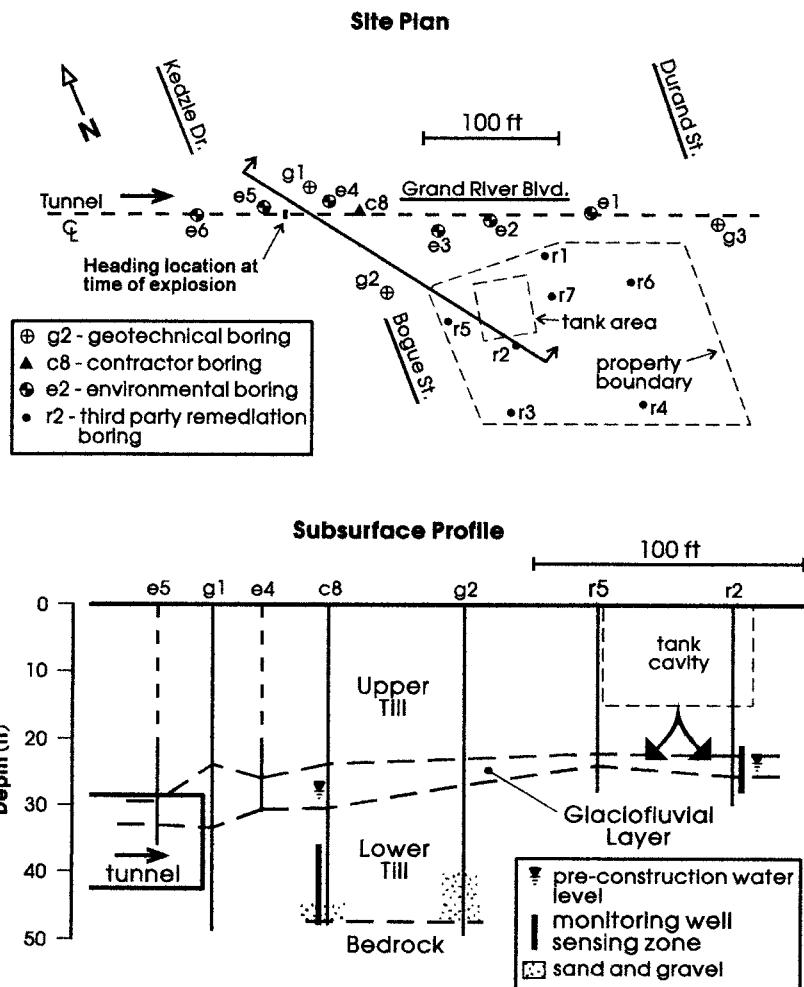


Figure 9-8. Subsurface conditions in vicinity of East Lansing sewer tunnel explosion. Fill not shown. Till layers predominantly clayey with granular inclusions. Glaciofluvial layer predominantly fine sand. Lower till contains sand and gravel near top of rock. (Adapted from Doyle, Hunt, and Kettler 1997.)

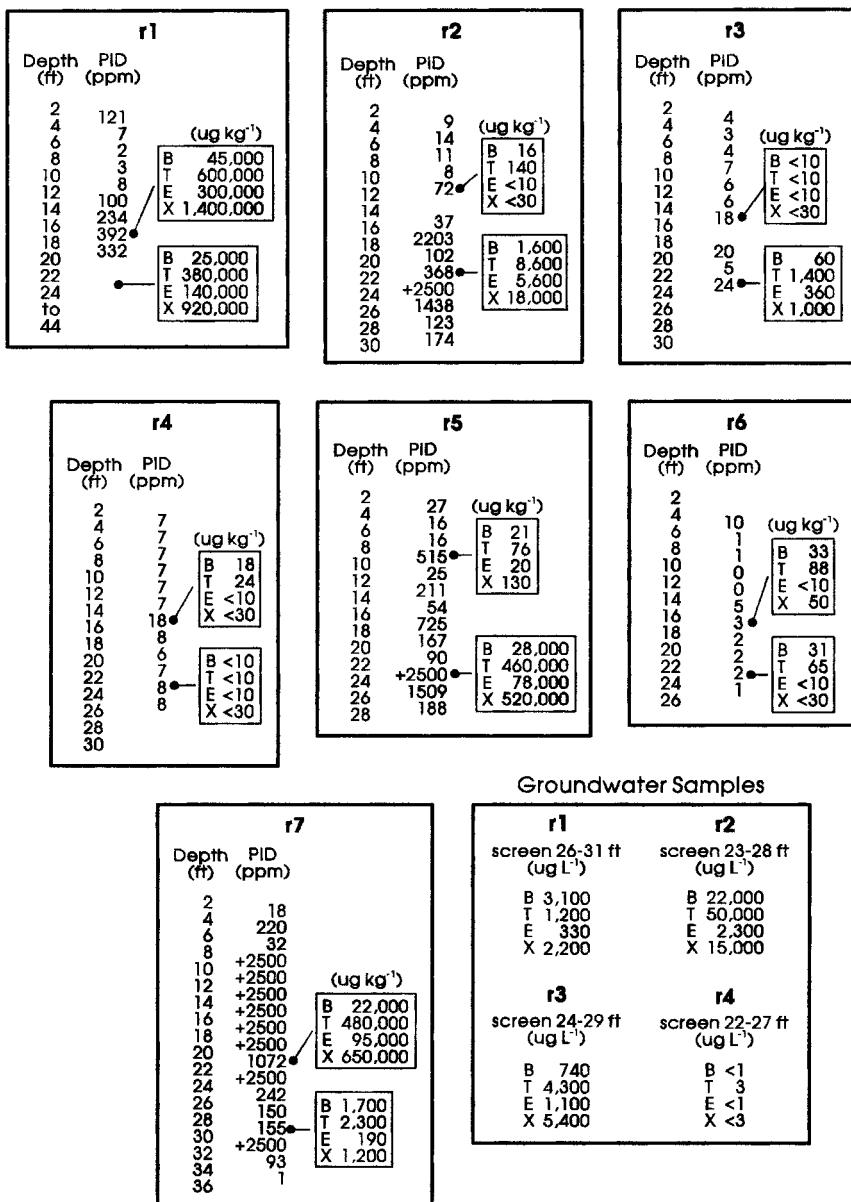


Figure 9-9. Results of field screening and laboratory analyses of soil and groundwater samples contaminated with gasoline, from automotive service station site adjacent East Lansing sewer tunnel alignment. (Data from BLDI 1994.)

The TBM used to excavate the tunnel featured movable flood doors that allowed muck entry through the cutter head into a muck chamber. Muck was discharged onto a conveyor through an open muck door in an inner bulkhead. Steel ribs and wood lagging were used for initial support.

When the tunnel face was about 18 ft (5.5 m) short of where heaviest contaminant concentrations were expected, strong gasoline fumes rapidly filled the heading. Excavation continued for another 13 ft, over a period of 11 hours spanning two shifts. Vapors subsided during prolonged periods of inactivity. During periods of excavation, workers in the heading reported intense odor, watering and burning eyes, throat irritation, and a foul taste. Workers monitored the tunnel atmosphere using handheld methane detectors (inappropriate for monitoring gasoline vapors), and reported combustible vapor concentrations of up to about 5% LEL in the heading and inside the TBM wheel chamber.

During an excavation cycle the cutterhead struck a granitic boulder embedded in the till, apparently initiating a friction spark. Vapors inside the wheel chamber exploded, venting through the open muck door in the inner bulkhead. All six of the workers in or near the TBM were knocked down by the force of the explosion. Two workers standing on catwalks used to erect the initial support system were blown into the invert, and one of these suffered a serious head injury. Four suffered burns and other injuries requiring treatment. The explosion started a small fire in the heading, apparently fueled by foam plastic packing rods and leaked hydraulic oil. Three workers extinguished the fire prior to evacuating the tunnel with the rest of the crew.

Workers reentering the tunnel hours after the explosion observed a rainbow sheen on water in the tunnel invert. A detailed investigation was conducted 20 days later (STS 1995). The face was visible through an open flood door, from the crown to about 2 ft above invert. Soil consisted of moist clayey till; the glaciofluvial layer was not apparent. Very little groundwater seepage was visible at the face. Total seepage into the heading was about 5 gpm (20 L min^{-1}). No petroleum products were visible in the tunnel or the wheel chamber. The wheel chamber was about 25% full of muck, which left a remaining void volume of about 250 ft³ (7 m³). The muck door opening measured about 2.3 ft (0.7 m) square.

The explosion was attributed to entry of a small amount of liquid gasoline into the wheel chamber, possibly through a thin granular seam or a fracture in the till. Liquid gasoline may have been drawn to the heading by drawdown of the water table around the excavation, as shown in Figure 9-7. Calculations show that an inflow of 1 pint (0.5 L) of fresh, liquid gasoline could have generated an explosive concentration of vapors in the wheel chamber at the time of the explosion.

After the explosion, the remaining tunnel drive was completed by hand mining. During shaft excavation to retrieve the TBM, gasoline odors were noted

in the glaciofluvial deposits (Doyle, Hunt, and Kettler 1997). Odors dissipated as the excavation advanced into the lower till. When the shaft bottom approached tunnel invert elevation, groundwater and liquid gasoline began flowing from the granular till. The amount of liquid gasoline pumped from the shaft is unknown, but an estimated 180 gallons (680 L) was pumped from the tunnel invert.

Subsequent to tunnel construction, a remediation was performed on the former service station property to remove free product. Workers involved attributed the absence of free product in the 1994 investigative borings to a concurrent drought. The water table was depressed at that time, and much of the liquid gasoline was apparently retained in the unsaturated zone as residual saturation. Recovered free product was relatively unweathered, evidence that it had been retained in an anoxic environment.

Baltimore Metro Tunnel

The Baltimore Metro Northeast Extension consists of twin tubes, each 2.4 km in length, and was constructed from 1990 to 1993. The tunnels are mainly in dense sands and gravels below the water table. They were excavated using two open-faced digger shields, with initial support provided by an ungasketed, unbolted precast concrete segmented liner. Groundwater control was provided by a combination of deep wells and compressed air. Encounters with gasoline in several areas along the alignment caused numerous problems.

Early in the tunnel drives, while operating under free-air, gasoline vapors entered both headings (Edwards and Merrill 1995). One minor ignition was reported. Investigation revealed that a fast-food restaurant directly above the tunnel had at one time been a gasoline service station. A ground penetrating radar study showed the underground storage tanks had been removed. High vapor concentrations eventually prompted a 9-month suspension of tunneling, during which time measures were developed to improve vapor control measures. Upon resuming tunneling, gasoline vapors forced several evacuations. Further improvements were made in the ventilation system, and with the use of respirators, workers completed the drive through this contaminated area.

A subsequent length of tunnel was excavated under compressed air, with air pressures limited to 0.8 atm above ambient pressure. A substantial amount of air was being lost through the face and ungasketed lining. Within a month of commencing compressed air work, there were reports of gasoline vapors in dwellings 5 blocks away from the alignment. An investigation revealed that lost air was traveling through a sand layer capped by a thick layer of clay. This air passed through an area contaminated with gasoline, and was carrying vapors into dwellings through utility connections. This situation was addressed by suspending tunneling until the final lining was installed, to reduce the amount of lost air.

In another incident, 1500 office workers were temporarily evacuated from their building following reports of gasoline vapors in the lower floors. An investi-

gation revealed that the building had been constructed over an old parking facility, which had included a fueling station and underground storage tanks. Lost air from the tunnel traveled through the tank area, and carried gasoline vapors into the building through openings in the bottom floor slab. This situation was addressed by installing vapor extraction wells around the building.

In the most serious incident, gasoline vapors were reported in commercial buildings 150 m from the alignment. An investigation revealed 13 underground storage tanks in the area. These tanks were eventually removed. This situation was addressed by installing over 150 vapor extraction wells, upgrading ventilation systems in several buildings, and placing hundreds of portable fans and air filters in buildings throughout the area.

This project demonstrates that numerous concealed sources of gasoline contaminants may be present in metropolitan areas. Chlorinated solvents from dry cleaning facilities were also encountered during tunneling; this issue is addressed elsewhere (Smith, Eisold, and Schrad 1993; Edwards and Merrill 1995).

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10

Site Investigation and Hazard Assessment for Gas

INTRODUCTION

A hazard assessment for gas is a comprehensive description of the nature of gas in the ground at a particular site, and how it may move into a tunnel or shaft. The assessment is important to design of atmosphere control measures for construction. It should be performed prior to excavation, and should be based on the nature of gas in the ground as ascertained from quantitative data. Assessments based mainly on indications of gas in previous excavations in the area, or in an advancing excavation, are prone to error. An inaccurate assessment may delay installation of appropriate atmosphere control measures, and raise the risk of a serious accident in the interim.

Hazard assessments are applied in hazard analysis, a process of identifying potential hazards (such as a combustible atmosphere), and initiating factors (such as sources of ignition) that can turn a potential hazard into a loss. Hazard analysis is the basis of system safety engineering, a design approach to eliminating hazards associated with operation of a system. Hazards are eliminated from a system by removing potential hazards or initiating factors. In this context, the system refers to the means and methods of tunnel and shaft construction in a particular geologic environment. This chapter describes how to perform a hazard assessment for natural gases and gasoline hydrocarbons prior to excavation, and how to apply the assessment in hazard analysis for design of atmosphere control measures.

Efforts to characterize hazardous gas during design of tunnels and shafts are not uncommon in the underground construction industry. However, there currently is no sound standard of practice for performing this work. Consequently, the results are often less than satisfactory; the nature of the gas is inadequately described, and atmosphere control measures applied during construction show an unreasoned relationship to conditions encountered. The approach described here for hazard assessment and its application in hazard analysis is proposed as a basis for developing a standard of practice. Although this approach incorporates technology generally accepted within various disciplines, it is largely a product of the author's opinions. Designers are encouraged to apply their own skill and ingenuity toward advancing the standard of practice.

ELEMENTS OF A HAZARD ASSESSMENT FOR GAS

A hazard assessment for gas is a comprehensive description of the nature of gas in undisturbed ground, how this gas may enter the proposed excavation, and the effects this gas may produce when mixed with air in the excavation. Describing, rather than merely identifying, the geologic hazard provides the contractor with a basis for developing efficient means and methods of excavation that can preclude losses resulting from gas inflows. The assessment would generally involve a moderate expansion in scope of the geotechnical exploration program, which normally considers only soil, rock, and groundwater. Elements of a hazard assessment may include:

- Principal hazardous gases present
- Chemical properties of hazardous gases
- Apparent sources of gas
- Gas migration mechanisms from the source to the site
- Strata within the zone of influence of excavation that retain gas
- Phases of gas in the ground (gaseous, solution, adsorbed)
- Composition of gas mixtures
- Concentrations of solution and adsorbed phase hazardous gas
- Mechanisms of gas inflow to the excavation
- Potential gas inflow rates to the excavation, for each phase identified

In addition to these elements, it may be appropriate to include:

- Mechanisms of gas inflow to the completed underground structure
- Potential gas inflow rates to the completed underground structure

Performing a hazard assessment for gas might be divided into three major tasks: 1) a study of regional and area geology—to identify geological factors that control gas occurrence, retention, and movement, 2) site exploration, gas sampling, and testing—to develop a quantitative understanding of the nature of

gas on a particular site, and 3) characterization of gas inflows to excavations—to identify potentially significant sources and manners of inflow. Approaches for performing these tasks are described in following sections.

GEOLOGICAL INVESTIGATION FOR GAS

The objective of the geological investigation is to explain the general nature of gas on a particular site, that is, how and where it is generated, how it migrated to the site if generated elsewhere, how it is distributed and retained on site, and how accumulations of gas may respond to excavation. This investigation is an ongoing effort toward refining a geological model, incorporating information from regional and area geological studies, from site investigation, and from observations made in the excavation during construction. The regional geology may reveal sources of thermogenic or geothermal gas located several kilometers below or tens of kilometers laterally from the site, and extensive permeability networks through which this gas can migrate. The area geology may reveal sources of bacterial gas. Existing geological information on the nature of gas can be used to optimize drilling and gas sampling programs for site investigation.

The area geology can indicate where a gas sampling program should, and need not, be focused. Factors of interest in area geology include:

Geologic and hydrogeologic setting, and interconnected hydrostratigraphic units

Nature and distribution of fractures and permeable strata, which control gaseous and solution phase migration

Nature and distribution of groundwater flow zones, which influence aerobic and anaerobic bacterial activity

Availability of substrates for bacterial gas generation, including organic matter, sulfide minerals, and sulfates

Distribution of porous ground, which controls gaseous and solution phase retention

Distribution of carbonaceous rock, which controls adsorbed phase gas retention

Hydrostatic pressure at depth of excavation, which controls gas retention, and movement into excavations

Location of oxic/anoxic boundary, along which methane and hydrogen sulfide are consumed in biochemical and geochemical reactions

Strata capable of discharging gas into excavations at significant flow rates are of main interest. Gas sampling can be dispensed with if it can be shown that a particular stratum is incapable of rapidly discharging the gas it contains. In some cases it may be sufficient to identify the stratum as a potential hazard, and ensure that routine atmosphere control measures are employed in excavating

through it. For example, pore gases in the unsaturated zone, and solution phase gases retained in low-yield aquifers or aquiclude, are generally not capable of entering excavations at high flow rates.

SITE INVESTIGATION FOR GAS

Site investigation for gas refers to efforts undertaken in a subsurface exploration program to characterize the occurrence and distribution of gas. This is in addition to those efforts normally performed to characterize soil, rock, and groundwater. The objective is to define gas distribution, and quantify gas concentration and mixture composition, through sampling and analysis. A considerable body of experience has been developed in sampling gas in the near-surface underground, mainly by investigators in the environmental field, but also by explorationists in the energy fields (petroleum, coal, and geothermal). No standard methodologies have evolved, however, owing to the wide range of geologic environments investigated, differing applications of data obtained, and rapidly developing technology for sampling and analysis. A detailed description of sampling and analytical methods is beyond the scope of this text. This section describes general aspects of gas sampling programs and sampling procedures for natural gases and gasoline hydrocarbons. Numerous examples of gas sampling efforts are cited, although these should not be considered inclusive. It is recommended that gas sampling and analysis be performed by personnel experienced in this type of work.

In developing sampling and analytical procedures, economy can be achieved and reliability maintained if some consideration is given to allowable error and to appropriate detection levels for gas. It is desirable to limit sampling error to within that of analytical error—say, within about $\pm 20\%$ (Barcelona, Helfrich, and Garske 1988). Analytical detection levels should at least meet minimum potentially hazardous concentrations of gas, as shown in Table 7-1 for natural gases, and as identified in Chapter 9 for gasoline hydrocarbons. Quality control and quality assurance are important aspects of gas sampling and analysis. Records should be sufficiently detailed to demonstrate that an appropriate level of care was taken.

Accuracy in this work is more important than precision. Expenditures to achieve a high degree of precision would be difficult to justify, considering that the results are employed in making gas inflow estimates, which are subject to considerable error and that inflow estimates are used to design atmosphere control measures, which by their nature must incorporate a factor of safety. Accuracy may best be achieved by carefully considering the nature and variability of geologic conditions, and selecting sampling locations and collecting sufficient numbers of samples to define the range of gas inflows likely to occur during excavation.

Gas Sampling Program

A gas sampling program can be designed in stages, in conjunction with design of the exploration program for soil, rock, and groundwater. Design stages of a gas sampling program are shown in Table 10-1. Stage 1, the initial geologic investigation, may reveal potential sources of gas that could influence the site, or evidence of gas in previous boreholes or excavations in the area. Stage 2, the preliminary design, includes an initial assessment of the gas hazard, and development of a scope of work for gas sampling and analysis. Stage 3, the working design, is a detailed plan for obtaining and analyzing gas samples during a Phase 1 drilling program. Stage 4, refined design, is an opportunity to improve sampling and analytical procedures, and to perform additional investigation in subsequent phases of the boring program. It is possible that initial procedures will prove adequate, such that they can be applied unchanged in further investigative efforts on the site.

Indications of gas in geologic media (gas shows) are often subtle and widely dispersed. Every opportunity should be taken to collect evidence of gas as it becomes available, hence the suggestion to incorporate a gas sampling program into the Phase 1 drilling investigation. Where regional or area geology is complex or poorly understood, lack of conspicuous evidence of gas should not be interpreted as absence of gas. In these cases, limited sampling or at least monitoring for gas during drilling should be considered. Important data can be lost if investigators are not looking for gas, or are unprepared to collect evidence of gas shows.

Field sampling offers greater potential for introducing error into the results than does analysis. Errors can be minimized by developing simple, practical sampling procedures, documenting them, applying them in a consistent manner, and evaluating the results as they become available (Barcelona, Helfrich, and Garske 1988). Companion analytical procedures should be considered in selecting sample containers, sample volumes, methods of preservation, and allowable storage periods, to ensure compatibility. It should not be assumed that sampling procedures proven successful in similar investigations elsewhere will be applicable, as site conditions may justify some modification (Lee and Jones 1983).

Gases in the Unsaturated Zone

In some cases it may be of interest to sample pore gases in the unsaturated zone. In environmental remediation and petroleum exploration work, this is generally referred to as soil gas sampling. A common method of soil gas sampling is to install a sampling tube to the depth of interest, attach a vacuum pump, and draw pore gas to the surface, into a container or analyzer. The method is most applicable in dry, coarse-grained soils (Marrin 1988). The unsaturated zone can be a complex and dynamic environment, considering its physical geology, hydrogeology, geochemistry, and active bacterial population. Periodic sampling from multi-

Table 10-1 Design Stages in a Gas Sampling Program

Stage	Activity
1. Initial geologic investigation	Site characterization Regional and area geology Hydrogeology Geochemistry Environmental contamination
2. Preliminary design	Preliminary hazard assessment Gas or gases of interest Potential gas reservoirs Potential gas migration mechanisms Potential gas retention mechanisms Relevant gas inflow mechanisms Sampling locations Drilling locations and depths Drilling procedures Well placement and construction Well development and performance evaluation Sampling program Geochemical constituents of interest Sampling methods Analytical methods Quality control considerations
3. Working design	Sampling protocol Well materials and installation Sampling mechanism Well purging procedure Sample collection procedure Sample preservation method Sample storage/transport procedure Quality control procedure Analytical procedures Initial phase sampling and analysis Ongoing evaluation of procedures Adaptation to conditions encountered
4. Refined design	Data analysis and interpretation Sampling protocol modification Second phase sampling

Source: Based on Barcelona and Gibb 1988, Tbl. 1.

ple sampling points may be necessary to develop a reliable assessment of pore gas conditions, as they can vary over time and distance, particularly near the water table (Tillman, Ranlet, and Meyer 1989).

Deep soil gas sampling tubes are commonly installed in cased boreholes, in essentially the same manner as groundwater monitoring wells or piezometers (Stephens 1996, p. 235). Numerous configurations for single- and multi-port sampling installations have been developed; three examples are shown in Figure 10-1. The borehole should be drilled in a manner that will limit the introduction of foreign materials to the sampling zone, as this could alter pore gas composition. Air rotary drilling methods may charge the pores with oxygen, and drilling fluid additives may introduce organic matter or sulfates. Any of these chemicals may stimulate bacterial activity.

Sampling tubes have been constructed of flexible vinyl tubing (Gole and Butt 1985), polyvinyl chloride (PVC) pipe (Proctor and Monsees 1985), and stainless steel (SS) tubing (Hubbell et al. 1998). The bottom of the tube is usually screened to avoid plugging with soil. The top of the tube should be valved to prevent atmospheric air from migrating into the vadose zone and contaminating the pore space. Use of small-diameter tubing reduces purge volumes required prior to sampling. Many polymeric tubing materials are permeable to gas, which can introduce errors into the results. The effects of gas diffusion through tubing

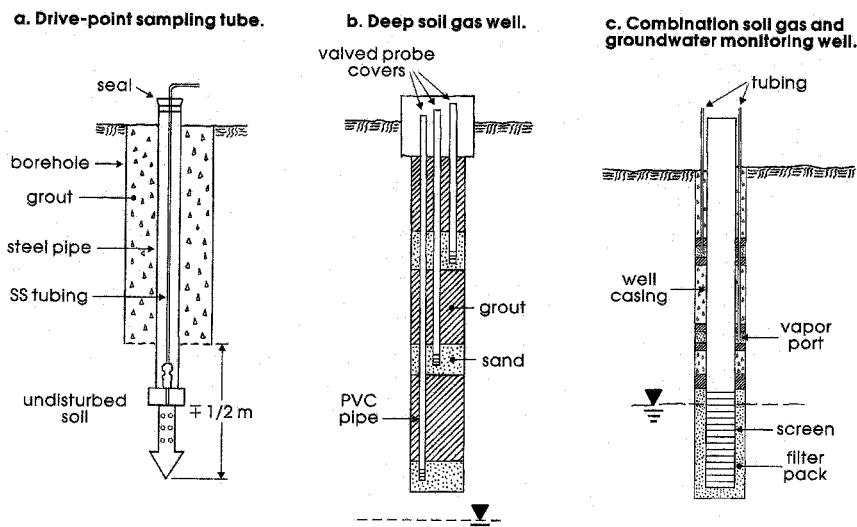


Figure 10-1. Examples of soil gas monitoring installations. (Adapted from: (a) Ullom 1995, (b) McLinn and Rehm 1997, (c) Hubbell et al. 1998.)

walls can be reduced by minimizing tubing length, maximizing flow rate, and maximizing tubing wall thickness (Holm, George, and Barcelona 1988).

Prior to sampling, the installation should be checked for leaks and purged of air. A purge criterion of three tubing volumes has been used in some studies (Stephens 1996, p. 238; Hubbell et al. 1998). Continuous pumping should be avoided, as it may draw in well bore gases or gases from other strata, or induce vertical movement between multiple sampling ports (Tillman, Ranlet, and Meyer 1989; Hubbell et al. 1998).

Samples for laboratory analysis can be captured in glass or stainless steel containers, inert flexible bags (Jarke 1998), or hypodermic syringes. Sample containers or bags can be evacuated or purged with inert gas prior to sampling, to minimize atmospheric contamination. Rigid containers are positioned in the sampling stream between the top of the sampling tube and the vacuum pump; after filling, the taps are closed and the container removed (Bishop et al. 1990). Flexible bags are best filled by enclosing the deflated bag in a sealed container such as a desiccator, and applying a vacuum to the container; filling the bag from vacuum pump discharge is not recommended (Jarke 1998). Hypodermic syringes are filled through a tap or septum fitted in the sampling tube (Gole and Butt 1985). As an alternative to laboratory analysis, pore gas can be directed from the sampling tube into a properly calibrated field analyzer (Amundson and Davidson 1990; Nicholson 1993, p. 217; Stephens 1996, pp. 238–239). Field analyses can guide the investigative effort while underway. About 10% of the samples should be analyzed in the laboratory to verify composition.

Gases in Solution in Groundwater

Most gas in the near-surface underground is retained in solution in groundwater. For excavations below the water table, hazard assessment for gas should include hydrogeological evaluation, groundwater sampling, and analysis of solution gas concentrations. Hydrogeologic evaluation is necessary to estimate rate and duration of groundwater inflows to excavations, and can help explain variations in gas concentration. Groundwater samples for gas concentration analysis are usually obtained from groundwater monitoring wells, constructed and sampled in accordance with methods developed mainly in the environmental science field.

Sampling Locations

Any aquifer within the zone of hydrostatic pressure reduction surrounding an excavation can contribute inflows of solution phase gas to the excavation. The significance of an aquifer with respect to gas inflow depends on the rate and duration of groundwater it can produce, and on its solution gas concentration. Aquifers of interest may lie above, below, or laterally off the alignment—particularly in rock, where open fractures can provide extensive and highly permeable

pathways for groundwater flow. Some low-yield aquifers may also be capable of discharging significant amounts of solution phase gas into excavations, especially if their pore waters contain hydrogen sulfide, which is hazardous at very low concentrations compared to methane or carbon dioxide. Surface bodies of stagnant water (such as ponds or small lakes) may retain solution phase gas, and can produce sustained inflows if hydraulically connected to the excavation. Seasonal overturn of the water body, which can affect gas concentration in bottom waters, should be considered in scheduling a sampling program.

Gas concentrations may vary among aquifers, and over short distances within an aquifer. Concentration is a function of charge rate of gas into solution from source strata or gaseous bodies, hydrostatic pressure, groundwater flow rate, biochemical and geochemical consumption mechanisms, and other factors. Of interest is the average gas concentration in groundwater discharge to an excavation. A groundwater sample from a well is a composite of inflows over the length of the screen, a function of inflow rate and chemical composition of the groundwater (Gibs et al. 1993). A well screened over the part of the aquifer likely to produce inflows should produce a representative sample. A well screened over a very short length, or one spanning multiple aquifers, may yield misleading results. Hydrogeologic complexity should be considered in determining the number of sampling wells and screen locations needed to characterize solution gas inflows.

Well Construction

Groundwater monitoring wells should be constructed to ensure compatibility with the sampling device, and to yield a representative sample. Well construction disturbs the underground environment, and can change groundwater chemistry in the vicinity of the well.

Drilling fluids used in constructing the well can introduce foreign chemicals to the underground environment. Fresh water contains dissolved oxygen. Some drilling additives used in rotary wash drilling contain organic matter, as do some foaming agents used in air rotary drilling. Bentonites may contain 4% to 6% organic matter (Herzog, Pennino, and Nielsen 1991), and sulfates in concentrations of 7 to 12 mg g⁻¹ (Remenda and van der Kamp 1997). Air rotary drilling can drive air several meters from the borehole, through permeable pathways in the formation. Any of these chemicals can stimulate bacterial activity, which can alter solution gas concentrations. Drilling fluid invasion into the formation can necessitate extensive well development to remove foreign chemicals (Keely and Boateng 1987).

Sealing materials used to backfill well casings can also alter groundwater chemistry. Bentonite pellets can elevate sulfate concentrations (Remenda and van der Kamp 1997). Cement grouts that fail to harden—due, for example, to placement through standing water—can increase groundwater pH (Barcelona and Hel-

frich 1986). In low-yield formations the effects of sealing agents on groundwater chemistry can persist for a year or more. Contamination from sealing materials can be minimized by sampling from a small-diameter drive-point well.

Casing materials can affect the chemistry of stagnant groundwater in the casing. Casing is commonly constructed of polyvinyl chloride (PVC) or stainless steel (SS). In particularly harsh environments, poly-tetrafluoroethylene (PTFE, or Teflon) or other materials have also been used (Barcelona, Helfrich, and Garske 1988). Steel and stainless steel can leach iron, which reacts with hydrogen sulfide to precipitate iron sulfides (Barcelona and Helfrich 1986; Lee and Jones 1983).

Purging

Purging the well is critical to obtaining a representative groundwater sample. Purging removes groundwater that has been chemically altered by extended contact with sealing and casing materials, and with atmospheric gases in well headspace. Proper purging may be more important to obtaining a representative sample than are well construction materials and sampling mechanisms (Wilson 1995, p. 114).

Numerous methods and devices have been used for purging monitoring wells, but not all are appropriate where solution gases are chemical parameters of interest. Devices that develop strong negative pressure, utilize driving gases that come into contact with water being purged, cause high turbulence, or introduce atmospheric gases into the well can cause gases to come out of solution and should be avoided; these include suction-lift pumps (centrifugal and peristaltic), gas-lift pumps, some electric-drive submersible pumps, and bailers. Gas-operated bladder pumps have been proven effective for collecting groundwater samples for solution gas analysis, under a wide range of sampling conditions. They operate within the well, can pump at variable rates, generate positive pressure, and prevent contact between the driving gas and water being purged (Nielsen and Yeates 1985; Herzog, Pennino, and Nielsen 1991).

The most common problem with purging is over-pumping the formation (Herzog, Pennino, and Nielsen 1991). Over-pumping can cause water to move vertically toward the well screen, mixing chemically different waters in stratified deposits. It can lower the groundwater table, aerating previously saturated ground. Dewatering the well can aerate the filter pack, thus altering its chemistry, and can cause water to cascade down the sides of the screen, liberating solution gases.

Purging the minimum amount of water necessary to acquire a fresh sample is preferred. Drawdown can be minimized by placing the purge pump just below the water surface (Wilson 1995, p. 132). Purge volumes can be reduced by placing the pump in the screened interval, or by using packers to isolate the well screen from standing water in the well. A traditional approach is to purge a specified

number of well volumes, defined as the volume of water in the casing, screen, and filter pack. A purge criterion of at least three well volumes appears reasonably reliable (Wilson 1995, p. 116). Another generally accepted purge criterion, used to reduce purge volumes, is to monitor the discharge for certain field parameters such as temperature, pH, dissolved oxygen, and specific conductance, and to initiate sampling after these field parameters have stabilized (Barcelona, Wehrmann, and Varljen 1994).

Sampling

Groundwater samples can be collected at ground surface, from discharge of a pump positioned at the screen, or at the depth of the screen, using a sampling device lowered into the well. In sampling groundwater to determine solution gas concentrations, it is important to prevent contact between the sample and the atmosphere, abrupt changes in pressure that may allow gas to come out of solution, and chemical changes in the sample during the period of time between sampling and analysis.

Sampling pumps are subject to requirements similar to those of purge pumps, with the exception that sampling is usually conducted at lower flow rates. Ideally, a single, variable-speed pump is used for purging and sampling (Herzog, Pennino, and Nielsen 1991). A purge rate of about 1 L min^{-1} and a sampling rate of 100 ml min^{-1} have been recommended as a general guide (Wilson 1995, p. 122; Barcelona, Wehrmann, and Varljen 1994). The sampling pump discharge rate should be controlled through the driving mechanism, not by constricting the discharge orifice or delivery line, as this exerts abrupt pressure changes that may alter the chemical composition of the water (Nielsen and Yeates 1985; Herzog, Pennino, and Nielsen 1991). Wells containing large volumes of water may require a separate, high-capacity purge pump and a low-capacity sampling pump.

A number of methods have been used for sampling from pump discharge at the surface. A simple method is to insert the discharge tube to the bottom of a narrow-mouth bottle, overfilling by at least 1/2 to 1 sample volume, and quickly capping (Nacht 1983; Barker and Dickhout 1988). This method would fail to capture bubbles of gas discharged with the water. Methane or carbon dioxide in solution in groundwater, in excess of saturation concentration at atmospheric pressure, would be lost by ebullition during pumping. The method would be adequate for sampling hydrogen sulfide, which in natural waters does not reach concentrations sufficient to generate a gaseous phase at atmospheric pressure.

A gaseous phase generated by ebullition during pumping can be captured with the groundwater sample by directing the pump discharge into a deflated, flexible bag. The sampling tube should be arranged to prevent internal trapping of the gaseous phase. The bag could be purged with an inert gas prior to sampling, to remove traces of atmospheric gases. The concentration of solution gas at sampling depth can be calculated from (Andrews and Wilson 1987):

$$\rho_i(\text{aq}) = \rho'_i(\text{aq}) + \rho'_i(\text{g}) \quad (10-1)$$

where $\rho_i(\text{aq})$ is mass concentration of gas i in solution in groundwater, $\rho'_i(\text{aq})$ is mass concentration of gas remaining in solution in the sample, and $\rho'_i(\text{g})$ is mass concentration of gas in gaseous phase in the sample.

Some samplers are designed to be filled at screen depth. These include a syringe device, which is lowered into the screened interval on a flexible tube. The upper end of the tube is connected to a pump that is used to apply gas pressure or vacuum to activate the sampler. The syringe can be sealed at the surface, or the sample can be transferred into another container (Nielsen and Yeates 1985; Gillham 1982).

Low-yield formations are not conducive to recovery of representative groundwater samples from monitoring wells. Their low recovery rate makes it difficult to purge groundwater that has been chemically altered by extended contact with sealing and casing materials, and with the atmosphere (Wassenaar and Hendry 1999).

Numerous methods have been developed for sampling sediment pore waters beneath lakes and seas (for example, Adams 1994; Mudrock and Azcue 1995). One method is to retrieve a core sample of sediment and extract pore waters by squeezing in a closed system (Martens 1974; Jahnke 1988). Sediment samples have also been analyzed for solution gases using an inert headspace technique (Fendinger and Adams 1986). Core samples taken in highly gas-charged sediment under high hydrostatic pressure may expand or burst during retrieval, and lose much of their gas to the atmosphere. Procedures to overcome this problem have been developed (Christian and Cranston 1997).

Groundwater samples to be analyzed in a laboratory should be preserved to minimize chemical changes in the interim between sampling and analysis. Preservation commonly involves protecting the sample from light and holding on ice (at about 4°C; Herzog, Pennino, and Nielsen 1991). A bactericide is sometimes added to the sample to preserve hydrogen sulfide (Barker and Dickhout 1988; Clesceri, Greenberg, and Eaton 1998, pp. 4–162). Holding times should be limited to minimize changes due to diffusion through container walls, leakage through container seals, and chemical reactions within the sample.

Gases in Conventional and Unconventional Reservoirs

Conventional gas reservoirs hold gas in gaseous phase, in highly permeable ground below the water table. Unconventional gas reservoirs hold gas in porous, low-permeability ground below the water table; inorganic reservoirs hold a gaseous phase, and organic reservoirs such as coal beds hold gaseous and adsorbed phases. Any of these reservoirs may discharge a gaseous phase into boreholes or excavations.

Conventional gas reservoirs in the near-surface underground are generally of limited extent. It is likely that of those present along an alignment, few if any would be intercepted by boreholes during a subsurface investigation. The possibility of encountering conventional gas reservoirs during excavation may be best evaluated by examining the site geology for potential traps, and ground-water for solution concentrations of gas approaching saturation concentration. Conventional gas reservoirs off the alignment should be considered, as they may discharge gas laterally or down into excavations following hydrostatic pressure reduction around the excavation perimeter.

Unconventional gas reservoirs tend to be laterally extensive, but their gaseous phase discharges are confined mainly to narrow permeable features, such as fractures and beds. Potential gaseous phase discharges may be best evaluated by conducting packer tests and examining core data, to characterize the nature and distribution of permeable pathways. Gaseous phase discharges from organic rock may originate from adsorbed phase gas. Methods for determining adsorbed gas content are described in Chapter 6, in the section on coal.

Gaseous phase discharges from boreholes in conventional and unconventional gas reservoirs do not directly indicate number, distribution, or size of accumulations actually present, or the magnitude of potential discharges into excavations. Gaseous phase accumulations intercepted during drilling do not always discharge into the borehole, which further obscures their presence. Discharge may be prevented by the weight of drilling fluid in a mud-filled borehole (Selley 1998, p. 436). Rotary drilling can cause a mud filtrate buildup on borehole walls, which can effectively seal off low-pressure gas zones in low-permeability sedimentary rocks (Steece 1989).

The volumetric rate and duration of gaseous phase discharges from boreholes drilled into conventional and unconventional gas reservoirs can give a *qualitative* indication of discharges that may occur in excavations, and should be measured. High volumetric discharge rates can be estimated by multiplying casting area by flow velocity, measured using an anemometer or pitot tube positioned at the top of the borehole casing (EMCON 1980, p. 73; Peters et al. 1985). The flow measuring device should be simple to operate, quick to position, relatively immune to water that may be discharged with the gas, and incapable of igniting combustible gases. Low volumetric discharge rates can be measured by attaching a very light, deflated plastic bag of known volume to the top of the casing, and measuring the time it takes the gas to fill the bag. In either case, a high degree of accuracy is unnecessary. Discharge rate is likely to decrease with time, so measurement should begin as close to the start of discharge as possible. A plot of discharge rate versus time can give some indication of the behavior of the reservoir, as shown in the example in Figure 10-2. Results will vary among reservoirs. Gaseous phase discharges should be allowed to vent as long as possible, to reduce gas inflows to the excavation from that portion of the reservoir.

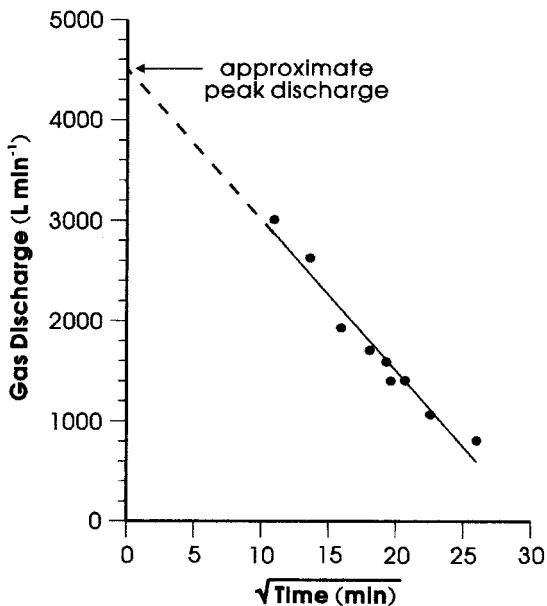


Figure 10-2. Gaseous phase methane discharge from borehole in tightly jointed mudstone. (Data from Peters et al. 1985.)

Safety precautions for gas are warranted during drilling conventional and unconventional gas reservoirs. A rapid discharge of gaseous phase methane can ignite or explode, endangering the drilling crew and rig. The oil and gas drilling industry has developed safety procedures for controlling gaseous phase discharges, called “gas kicks” (Australian Drilling Industry 1997; pp. 524–533). Gas discharges are controlled using blow-out preventers, which redirect the discharge through a hose to a flare pit some distance from the rig. Gas kicks may occur in any of the following situations, and control procedures should be established for each:

- During drilling
- When tripping drill tools in the hole
- When the drill string is out of the hole
- When sampling or other operations are proceeding in the hole

Most gas kicks occur while pulling the drilling string, when pressure on the bottom of the hole is reduced by swabbing of the bit, and by delay in replacing the volume of tools removed with drilling mud. Gas kicks in holes drilled using air rotary methods can be very hazardous, due to rapid transport of gas to the

surface. Essential elements of a safety program for drilling conventional and unconventional gas reservoirs include combustible gas detectors, fire protection equipment, a kill switch on the rig, and a fire watch during welding and cutting operations.

A gaseous phase discharge at the surface can be sampled to determine its composition. A continuous borehole discharge of gas with no water can be directed through a tube to the bottom of a narrow-mouth bottle, allowed to flow for a sufficient period of time to overfill the bottle with gas, and quickly capped (Fritz, Frape, and Miles 1987). The bottle should be inverted if sampling methane. A borehole discharge of gas accompanied by water can be sampled using the arrangement shown in Figure 10-3. The composition of a gaseous phase discharge from a borehole or seep cannot be directly related to solution phase concentrations at depth (Sheppard, Truesdell, and Janik 1992). Because constituents of a gaseous mixture have differing solubilities, they interact differently with groundwaters

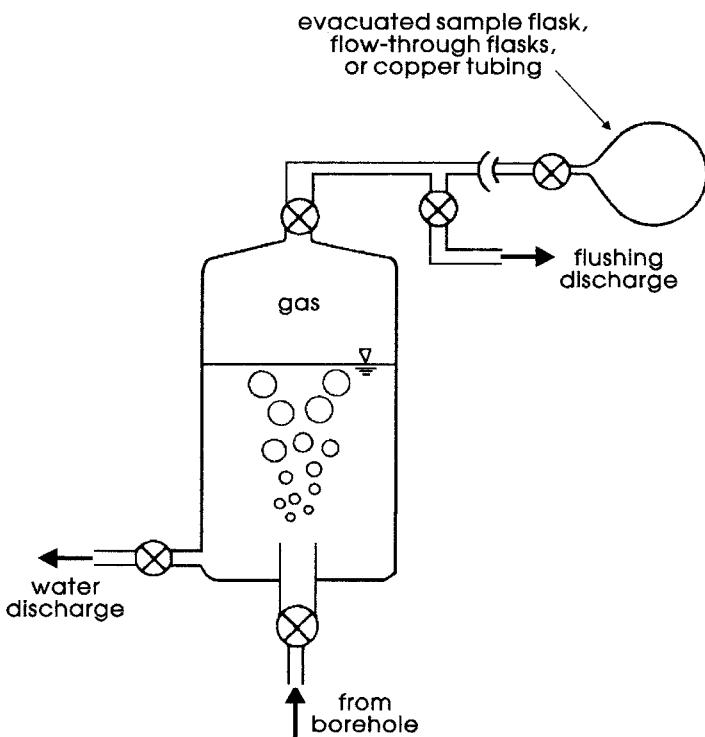


Figure 10-3. Sampling device for collecting gas from flowing boreholes. (From Fritz, Frape, and Miles 1987.)

through which they flow. A gaseous discharge through water may also entrain atmospheric gases dissolved at the surface.

Use of Gas Detectors

Portable gas detectors are sometimes used during drilling investigations to monitor hazardous gases emitted from boreholes. They can warn of unsafe conditions developing in the vicinity of the drilling rig, and can indicate the presence of gas in the ground that may otherwise go undetected in the absence of more sophisticated methods of sampling and analysis. However, gas detector readings taken within or very near boreholes or monitoring wells are subject to gross inaccuracy, and should not be interpreted as quantitative measures of gas concentrations in the ground.

The atmosphere within or very near a borehole during drilling is in a dynamic state, affected by rates of gas discharge from the borehole, dilution with atmospheric gases, geochemical reactions with oxygen in drilling fluids and the atmosphere, and other factors. Even in groundwater monitoring wells capped at the surface, gas concentrations in borehole headspace are unlikely to be in equilibrium with groundwater in the screened portion of the well.

In addition, gas detectors designed for use in normal atmospheres may not respond accurately to gas mixtures likely to occur in boreholes or monitoring wells. Hazardous gas concentrations in boreholes may be far above allowable limits, and out of range of the device. Borehole or monitoring well atmospheres may be oxygen deficient, and thus unable to support combustion necessary for operation of catalytic combustible gas detectors commonly used to monitor for methane. As methane concentrations exceed 5% (100% LEL), catalytic combustible gas detectors respond in a nonlinear manner; and as concentrations increase beyond about 10%, detector response declines to zero. The response of a catalytic gas detector to a full range of methane–air mixtures is shown in Figure 10-4.

Although gas detectors perform an important function in maintaining safe conditions during drilling, and have some value as a screening device for hazardous gases, investigators should avoid overinterpreting the data. Reliability can be improved by ensuring that field personnel understand the capabilities and limitations of each device used.

Gas Shows During Drilling

The top of the borehole should be observed during drilling for indications of gas, or gas shows. These include rapid discharge of a gaseous phase, possibly accompanied by ejection of water or drilling fluid or by gurgling sounds; bubbles rising from drilling fluids; gas detector response over the borehole or fluid circulation tank; ignition of combustible gas; or odor (of hydrogen sulfide).

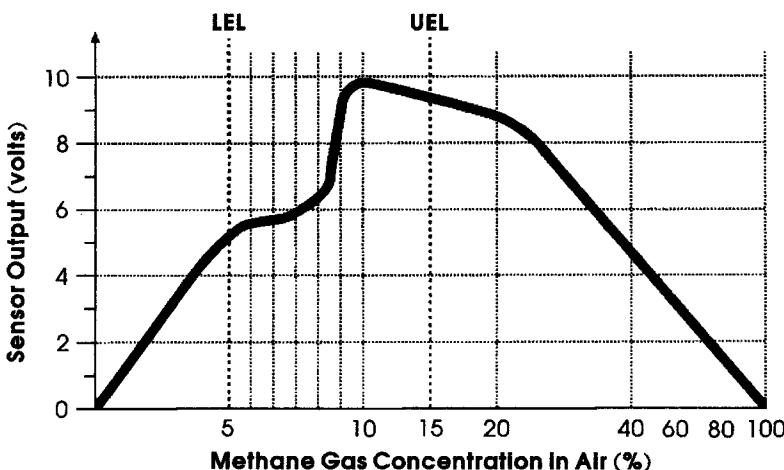


Figure 10-4. Catalytic gas detector response to range of methane concentrations. (From Chou 2000, p. 42.)

Drilling may release a gaseous phase from the formation in several ways (Schowalter and Hess 1982): 1) continuous gaseous phase accumulations in conventional and unconventional gas reservoirs can escape into the borehole following a decrease in hydrostatic pressure (as noted in a previous article); 2) decrease in hydrostatic pressure around the borehole can allow isolated bubbles of residual gas to expand into a local continuous phase, and subsequently flow into the borehole; 3) grinding action of the bit through organic deposits can release adsorbed phase gas; 4) gas can escape solution in formation water rising in the borehole, by ebullition. Only the first mechanism should be capable of producing a sustained gaseous phase discharge from a borehole, with the exception of an artesian discharge of water saturated with gas. In addition, gas in solution in borehole fluids can diffuse into the atmosphere, with agitation of these fluids at the surface.

Hydrogen gas (H_2) has been generated in boreholes drilled below the water table, absent circulating fluids (Bjornstad et al. 1994). In the incident cited, welding at the top of the borehole casing ignited the gas, causing a small explosion. Hydrogen is combustible in concentrations ranging from 4% to 74%. The borehole penetrated an unconsolidated to semiconsolidated fluvial sedimentary sequence of gravel in a sandy matrix. Quartz was the predominant mineral constituent. The hole was advanced by percussion cable-tool method with core barrel. Steel casing was used to maintain the opening. Hydrogen was generated in the borehole 30 m below the water table, at a depth of about 130 m. High concentrations of hydrogen coincided with periods of poor drilling progress, when slurry

stagnated in the casing; low concentrations coincided with borehole bailing, which allowed oxygenated formation water to enter through the bottom of the casing. Laboratory studies led investigators to conclude that hydrogen was generated under anoxic conditions, by geochemical reactions between formation water, steel casing, steel fragments, and rock fragments. There is no evidence that significant amounts of hydrogen would be generated in boreholes drilled using circulating fluids. Seeps of hydrogen-rich gas have been reported in ultramafic rocks, where the gas is apparently generated by low-temperature serpentinization (Neal and Stanger 1983). These natural occurrences of hydrogen appear to be too rare to warrant further consideration here.

Gasoline Hydrocarbons

Numerous methods of investigating gasoline spills have been developed to deal with the variety of geologic environments in which spills have occurred. The objective in these investigations is generally to identify the source of the spill, define the vertical and lateral extent of the contaminant plume, determine the severity of soil and groundwater contamination, and identify appropriate methods of remediation. Some environmental firms have developed a high level of expertise in this work and can provide valuable assistance in performing risk assessments for gasoline. However, it should not be assumed that environmental specialists will anticipate the effects of tunnel or shaft excavation on contaminant migration, or the effects of gasoline on the excavation atmosphere (Doyle, Hunt, and Kettler 1997). Project staff should be involved in the environmental work to ensure that all important issues are understood and addressed.

Dewatering associated with excavation can cause floating plumes of liquid gasoline to migrate for considerable distances toward the water table depression, through coarse-grained soils, utility trench backfill, rock fractures, and other permeable pathways. Borings drilled along the alignment prior to excavation may not intercept free product plumes that pose a threat. A site survey and review of public records may identify potential sources of spilled gasoline that warrant further investigation.

Soil Gas Surveys

Soil gas surveys are often used as a screening technique in gasoline contaminant investigations. Soil gas is sampled over a broad area, and contaminant concentrations used to produce a contour map to locate the source and extent of contamination. The map is then used to plan monitoring well networks and sampling programs (Morgan and Klingler 1987; Marrin and Kerfoot 1988). Soil gas surveys provide qualitative data that is not sufficiently reliable for use in equilibrium calculations to estimate contaminant concentrations in soil or groundwater (Selby 1991; Ullom 1995; Lewis et al. 1996). The technique is used in the unsaturated

zone, and is most applicable in coarse-grained soils, although it has been used in fine-grained soils and rock (Selby 1991; McLinn and Rehm 1997).

Pore gas is extracted through sampling tubes installed to the depth of interest. Often, metal probes are driven from the ground surface, to depths of a meter or so. Deeper probes can be installed in boreholes. A vacuum pump is attached to the probe at ground surface, and samples taken after purging the system of about two volumes of gas. Samples can be collected in glass or metal containers positioned upstream of the sampling pump, in flexible bags sealed inside a desiccator attached to the vacuum pump, or in syringes tapped into the sampling line (Whitmann, Quinn, and Lee 1985; Evans and Thompson 1986; Denahan et al. 1993; McLinn and Rehm 1997).

Vapors can be analyzed on site using a portable gas chromatograph (GC), flame ionization detector (FID), photoionization detector (PID), or infrared gas sensor. GC devices are capable of measuring low to high contaminant concentrations (Morgan and Klingler 1987). FID and PID devices are accurate at low contaminant concentrations, but exhibit nonlinear, declining response at high concentrations (Robbins et al. 1990). FID and PID devices are nonspecific detectors, each responding quantitatively only to the individual compound to which it is calibrated. The FID measures total organic compounds in vapor phase (Denahan et al. 1993). The FID will respond to methane, so it may give misleading indications of gasoline contamination in environments containing methane. Because the FID operates on a combustion principle, it may not respond accurately to gasoline contamination under oxygen deficient conditions (Robbins et al. 1990). The PID measures total ionizable compounds in vapor phase, both organic and inorganic. It will respond to numerous inorganic gases, including hydrogen sulfide. The PID cannot detect methane. PID response may be significantly reduced by high relative humidity (Fitzgerald 1989). The PID is insensitive to oxygen concentrations down to about 4% (Robbins et al. 1990).

Residual Contamination in Soil or Rock

Residual gasoline contamination can be evaluated using a headspace technique on soil or rock samples placed in sealed containers. A significant amount of the most volatile fraction can be lost in transferring the sample to the container. Accuracy can be improved by collecting intact cores, minimizing sample disturbance and contact with the atmosphere during sample transfer, minimizing headspace, preserving samples in methanol, storing samples on ice, limiting storage times, and using containers that can be connected directly to the analytical device (Lewis et al. 1996).

Groundwater Contamination

Gasoline contaminants in solution in groundwater can be evaluated from groundwater samples drawn from monitoring wells. Considerations for monitoring well

installation and sampling are similar to those for natural gases in solution. Where free product is present in monitoring wells screened across the water table, care should be taken to prevent free product from contaminating the sample (Herzog, Pennino, and Nielsen 1991). Purging should be performed using a separate device, preferably after free product has been removed from the well.

BTEX compounds are generally of great interest in analyzing groundwater for gasoline contamination. Groundwater in carbonaceous sedimentary environments may contain low concentrations of BTEX compounds from natural sources. For example, BTEX solution concentrations of 0.5 mg L^{-1} have been reported in shale in southwestern Ontario, Canada (Slaine and Barker 1990).

Free Product Plumes

Free product plumes floating on the water table may be identified in monitoring wells screened across the water table. The thickness of free product in monitoring wells typically exceeds that of the plume outside the well by 2 to 10 times (Mercer and Cohen 1990). The relationship depends on grain size and distribution, product density, and water table fluctuations (Ballesteros, Fiedler, and Kinner 1994). A rudimentary estimate of free product thickness in the formation can be made from:

$$\frac{h_w}{h_f} \approx \frac{\rho_n}{(\rho_w - \rho_n)} \quad (10-2)$$

where h_w is free product thickness in the well, h_f is free product thickness in the formation, ρ_n is density of free product, and ρ_w is density of water. For gasoline, $h_w/h_f \approx 3$. The well screen should be placed to span the entire free product layer, taking into account seasonal water table fluctuations.

Sources of Frictional Ignition

Where methane or gasoline hydrocarbons pose a hazard to excavation, it is of interest to also identify potential sources of frictional ignition. Frictional ignitions are ignitions of combustible gas caused by a spark or very hot surface produced by rubbing or impact during excavation (National Coal Board 1979, p. 81). Statistics show that about 75% of methane ignitions in underground coal mines are caused by frictional ignitions from mining machines, with an additional 4% caused by frictional ignitions from roof bolters and roof falls (Kawenski, Price, and Stephan 1979). While geologic conditions and excavation methods in civil works tunnels and shafts differ from those in coal mining, these statistics indicate that frictional ignition sources are relatively important to the occurrence of gas explosions in excavations.

Incendive temperature potential (ITP) is a qualitative measure of risk of generating friction temperatures capable of igniting a combustible concentration

of gases (National Coal Board 1979, p. 81). The only two common minerals found in coal mines that produce frictional ignitions are quartz and pyrites. ITP increases with increasing strength of the rock and proportion of quartz grains over 0.005 mm. ITP is high for rocks containing over 50% quartz, intermediate for rocks containing 30% to 50% quartz, and low for rocks containing less than 30% quartz. Average quartz composition of some common rocks are: sandstone—70%, granite—30%, shale—30%, and limestone—4% (Duff 1993, Tbl. 4.2). ITP is intermediate for rocks containing pyrite and very high for rocks containing quartz and pyrite.

Coal mining research has shown that cutter speed and bit wear are factors in frictional ignition (Kawenski, Price, and Stephan 1979). Rotational speed affects the energy of impact. Broken or worn cutter bits present a large surface area for generating heat. Coal mining machines operate at higher rotational speeds than do TBM's, but this research is relevant nonetheless. Frictional ignitions have been caused by TBM's in rock (Loehr 1983; Stokes and Stewart 1985), as well as in soil, from cutter bits striking granitic boulders firmly embedded in a soil matrix (Doyle, Hunt, and Kettler 1997).

IDENTIFICATION OF GAS ORIGIN

In developing a comprehensive understanding of gas on a particular site, it is useful to identify its origin. Common origins of hazardous gas found in the near-surface underground are shown in Table 10-2. In most cases a plausible explanation of origin can be derived from gas composition and area geology, by identifying mechanisms of gas generation consistent with both. For example, hydrogen sulfide can be assumed to be bacterial, and to have been generated in recent geologic time. It is likely to originate in anoxic local, intermediate, or regional groundwater flow systems containing organic matter and sulfates. Carbon dioxide in the near-surface underground is usually of bacterial origin. Bacterial carbon dioxide is generated in hazardous concentrations in the unsaturated zone, under

Table 10-2 Common Origins of Natural Hazardous Gases in Near-Surface Underground

Gas	Origin of gas				
	Bacterial	Late-stage bacterial	Ancient bacterial	Thermogenic	Geothermal
CH ₄	×	×	×	×	
H ₂ S	×	×			
CO ₂	×	×			×

oxic conditions. Carbon dioxide found in hazardous concentrations below the water table, in gaseous or solution phases, is likely of geothermal origin. Thermogenic methane is often associated with 2% (vol.) or more ethane and propane, whereas bacterial methane is dry, as described in Chapter 4.

Gas composition and area geology sometimes yield insufficient information to identify the origin of methane, for a number of reasons. Bacterial methane can be generated from substrates derived from ancient organic matter, which is more commonly associated with thermogenic gas. Bacterial methane can persist for millions of years in unconventional reservoirs that no longer support bacterial activity. Thermogenic methane can migrate into the near-surface underground, possibly mixing with bacterial methane generated there. Migrating mixtures of thermogenic gas can be stripped of ethane and propane, yielding a dry gas characteristic of bacterial methane. Where the origin of methane is not apparent, it may be possible to distinguish bacterial and thermogenic methane by their isotopic composition. Isotopic analysis of gases is relatively expensive (Endres, Chilingarian, and Yen 1991). Considerable care in sampling, sophisticated laboratory equipment, and skilled interpretation are necessary to obtain reliable results.

Bacterial and thermogenic methane are distinguished by their proportions of stable carbon isotopes, ^{12}C and ^{13}C . Normal carbon consists of about 98.9% ^{12}C and about 1.02% to 1.13% ^{13}C (Coleman et al. 1977; Fuex 1977). The ^{13}C content of methane is mainly a function of isotopic composition of its source, and preferential bond separation, or fractionation, during generation. The ^{12}C – ^{12}C bond is more easily broken than the ^{12}C – ^{13}C bond. As a result of fractionation, bacterial methane is more depleted in ^{13}C compared to thermogenic methane. The isotopic composition of methane is changed little or not at all by migration (Fuex 1980).

The isotopic composition of a carbonaceous sample is normally expressed as a difference from a given standard:

$$\delta^{13}\text{C}_{\text{sample}} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000 \quad (10-3)$$

where $\delta^{13}\text{C}_{\text{sample}}$ is the difference (delta), expressed in parts per thousand or per mil (‰). Carbon isotope compositions are referenced to the PDB standard, prepared from belemnite of the Peedee formation, a Cretaceous marine carbonate found in South Carolina. Isotopic compositions of selected carbonaceous materials referenced to the PDB standard are shown in Figure 10-5. A negative $\delta^{13}\text{C}$ means that the sample is “light,” or depleted in ^{13}C , relative to the standard. $\delta^{13}\text{C}$ for hydrocarbon gases is often expressed as δC_1 for methane, δC_2 for ethane, and so on.

Bacterial methane generally exhibits δC_1 values ranging from about –90‰ to –55‰; thermogenic methane generally exhibits δC_1 values ranging from about

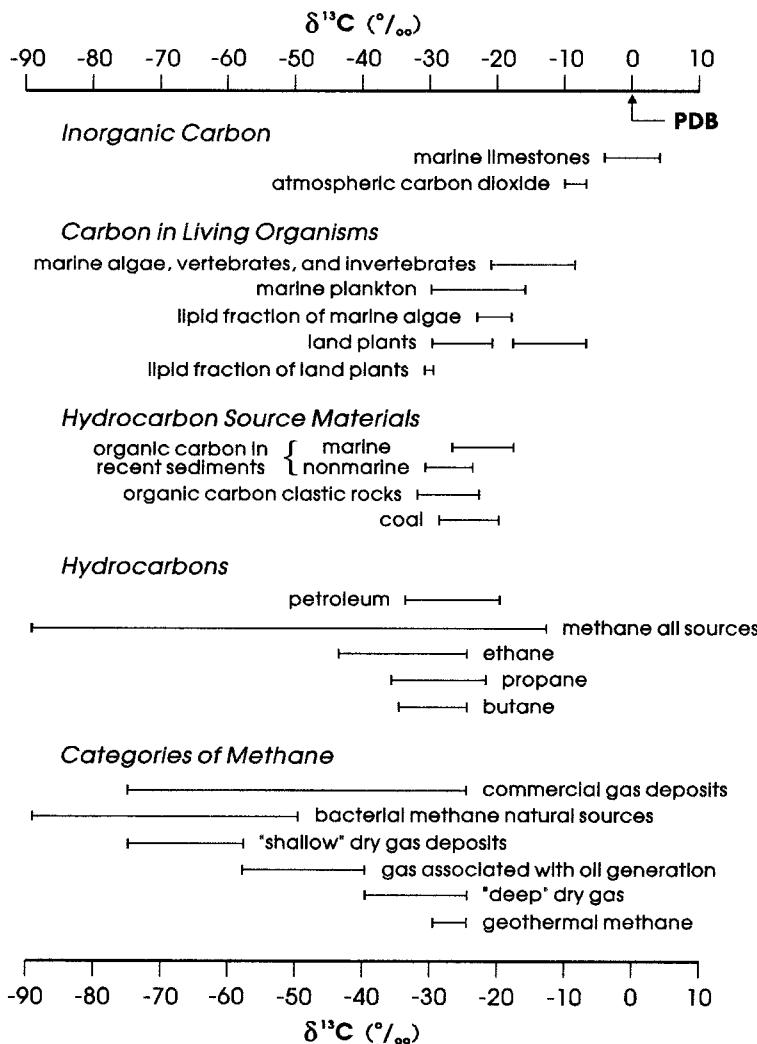


Figure 10-5. Range in isotopic compositions of selected carbonaceous materials, referenced to PDB standard. (Adapted from Fuex 1977. © 1977 Elsevier Science.)

$-50\text{\textperthousand}$ to $-25\text{\textperthousand}$ (Zhang, Grossman, and Ammerman 1998). The origin of methane can be inferred from its isotopic composition and the ethane and propane content of the gas mixture, using Figure 10-6. Among the factors that should be considered in interpreting data plotted on this figure are the following:

δC_1 values between $-60\text{\textperthousand}$ and $-50\text{\textperthousand}$ may indicate a mixture of bacterial and early thermogenic gas (Schoell 1983).

Bacterial oxidation of methane can preferentially diminish ^{12}C to the extent that δC_1 increases by 5\textperthousand to $30\text{\textperthousand}$, giving bacterial gas an isotopic composition characteristic of thermogenic gas (Barker and Fritz 1981; Coleman, Risatti, and Schoell 1981). Methane oxidation can be associated with aerobic bacterial activity or sulfate reduction.

Bacterial methane generated via the carbon dioxide reduction pathway generally yields δC_1 values ranging from about $-110\text{\textperthousand}$ to $-60\text{\textperthousand}$, whereas methane generated via the acetate fermentation pathway exhibits δC_1 values ranging from about $-65\text{\textperthousand}$ to $-50\text{\textperthousand}$, close to that for thermogenic methane (Hornibrook, Longstaffe, and Fyfe 1997). The acetate fermentation pathway is typical of landfills (Coleman, Benson, and Hutchinson 1990).

The isotopic composition of thermogenic methane becomes increasingly positive as its source thermally matures, due to earlier preferential loss of ^{12}C (Stahl et al. 1981).

Thermogenic coal gases exhibit δC_1 's that are $10\text{\textperthousand}$ to $15\text{\textperthousand}$ higher than

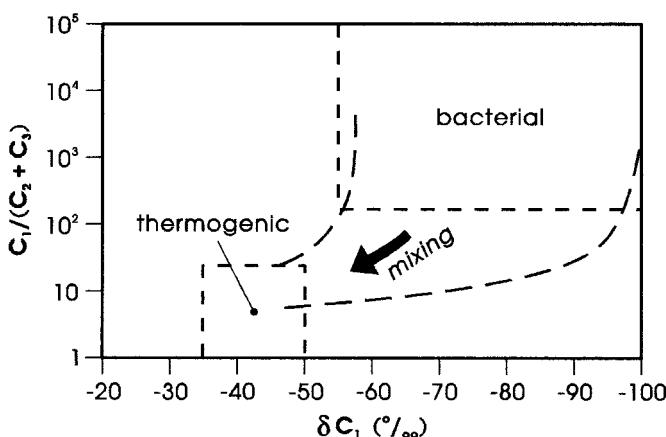


Figure 10-6. Modified Bernard diagram for naturally occurring methane. (From Wiese and Kvenvolden 1993.)

for petroleum gases at equal levels of thermal maturity. The difference is probably related to isotopic composition of source material (Fuex 1977).

Gas origin can be further defined by including hydrogen isotope composition of methane in isotopic analysis (Schoell 1980; Schoell 1983).

GAS INFLOWS AND GROUND CLASSIFICATION

An understanding of the nature of gas on a site, and potential mechanisms of gas inflow to the excavation, enables the estimation of inflow rates. Gas inflow mechanisms and rate calculations are described in Chapter 7 for natural gases and Chapter 9 for gasoline hydrocarbons. Estimating gas inflows is problematic, as it is analogous to estimating groundwater inflows to excavations below the water table. Of main interest are peak, short-term gas inflows from specific geologic features intercepted at the heading, as well as long-term gas inflows over the running length of the excavation. Since low-rate inflows can generate hazardous concentrations of gas in unventilated areas, they should also be identified.

Gas inflow estimates and other information on the nature of gas can then be used to classify the ground, to provide a general assessment of the potential severity of the gas hazard. A proposed scheme of ground classification is shown in Table 10-3. The classification is based mainly on information collected prior to excavation. Ground can be reclassified during excavation if new information justifies doing so, but reclassification to a higher level would generally necessitate redesign of the atmosphere control system, which would likely involve considerable delay and additional expense. Each classification is further defined as follows:

Class I—Most excavations will be made in this type of ground. Although gas is somewhat ubiquitous underground, in most cases it is present in low concentrations or is too widely distributed to produce significant inflows to excavations. However, to justify this classification, all the corresponding factors listed in Table 10-1 should be evident.

Class II—Most ground containing significant amounts of gas will fall under this class. It corresponds to conditions under which a fully operational ventilation system of low capacity could maintain safe atmospheric conditions in occupied areas of the excavation. In this classification, low capacity ventilation is arbitrarily assumed to equal one to two times the minimum required airflow velocity, or 30 to 60 ft min^{-1} in the United States and 9 to 18 m min^{-1} in the United Kingdom. Note that this type of ground could easily produce hazardous concentrations of gas in unventilated areas of the excavation, such as a TBM muck chamber. Evidence of one or more of the factors listed in Table 10-1 would justify this classification.

Table 10-3 Ground Classification for Gas

Class I: No evidence of gas on site
Absence of source strata in area
Absence of migration pathways from source strata in region
Site investigation shows no evidence of gas above potentially hazardous concentrations
No gas inflows to previous excavations or boreholes in comparable strata in area
No evidence of gas during advance of excavation
Class II: Low to occasional moderate inflows of gas
Source strata in area
Potential migration pathways from source strata in region
Site investigation shows natural gas above potentially hazardous concentrations
Gas in gaseous phase, in high-permeability ground above the water table
Gas in solution phase, in ground expected to produce low to occasional moderate inflows of groundwater
Gas in adsorbed or gaseous phase, in unconventional reservoirs characterized by tight and widely spaced fractures and low-permeability beds (excluding coal)
Reports of low to moderate gas inflows to previous excavations or boreholes in comparable strata in area
Low to moderate gas inflows detected during advance of excavation
Class III: Persistent moderate to occasional high inflows of gas
Site investigation shows natural gas above potentially hazardous concentrations
Gas in solution phase, in ground expected to produce persistent moderate to occasional high inflows of groundwater
Gas in adsorbed or gaseous phase, in unconventional reservoirs characterized by open or closely spaced fractures or high-permeability beds (including coal)
Gas in conventional reservoirs
Site investigation shows presence of gasoline

Class III—This class covers the widest range of potential gas inflow rates. It corresponds to conditions under which a high ventilation capacity would be necessary to maintain a safe atmosphere in occupied areas of the excavation, or under which a fully operational ventilation system is likely to be occasionally overwhelmed by gas, requiring shutdown of the excavation and evacuation of the crew to allow gas inflows to dissipate. Persistent moderate inflows of gas may originate from solution phase discharges from extensive aquifers or gaseous phase discharges from unconventional reservoirs. Occasional high inflows of gas are most likely to occur from accumulations intercepted at the heading. Class III includes all ground containing conventional reservoirs, even though they

may be few and of limited extent; the rate of gaseous phase discharges from conventional reservoirs is impossible to estimate, and a conservative approach is suggested. It also includes all ground containing gasoline contaminants, because very small amounts of gasoline can generate toxic or explosive atmospheres. Class III is more likely in ground well below the water table, where severe reduction in hydrostatic pressure during excavation may facilitate rapid inflows of natural gas. Evidence of the first and one or more of the factors listed in Table 10-1 would justify this classification.

Note that ground classification is not a direct measure of risk. Risk is a function of both gas inflows and atmosphere control measures; even low rates of gas inflow into a poorly ventilated excavation can pose an enormous risk. Also note that ignition of combustible gas in previous or ongoing excavations is not a primary factor in classification. Ignitions do not necessarily indicate a high rate of gas inflow, but more likely indicate a failure to control low to moderate inflows.

In some cases it may be advantageous to provide more than one ground classification to address different portions of an extensive excavation, such as long reaches of tunnel in dissimilar ground, and shafts. In any case, the ground classification should comprise the worst-case conditions anticipated along portions to be advanced using a single excavation system.

MEANS OF CONTROLLING THE EXCAVATION ATMOSPHERE

Excavations can be safely made in ground containing gas, by controlling the excavation atmosphere. Control measures include ventilation, gas monitoring, control of ignition hazards, and hazard awareness training for workers. Optimal efficiency and reliability can be achieved by designing control measures as a system of interacting components, using a system safety engineering approach. Design of atmosphere control systems is beyond the scope of this text; this section describes how a risk assessment for gas can be applied in a systems safety engineering approach to system design.

Ventilation Systems

Ventilation is the primary means of controlling the excavation atmosphere. In Class II and Class III ground it is advantageous to establish a ventilation capacity above the minimum required by government regulations, to control gas inflows from ground surrounding the excavation. In all excavations the ventilation system must control atmospheric contaminants generated from within, such as gases from diesel equipment and explosives, and dust. These contaminants are not addressed in this text, but because they often dictate the capacity of the ventilation system they must be considered.

The objective in sizing the ventilation system for hazardous gas inflows is to allow the work to proceed without serious interruption, while at the same time avoiding the unnecessary expense of excess capacity. The sizing concept is shown in Figure 10-7. The distribution curve for hazardous gas inflows from surrounding strata would be impossible to develop prior to construction, but the concept is nonetheless useful. The optimal size of the ventilation system would be sufficient for it to control all or nearly all of the highest inflows. An undersized system would result in frequent shutdowns and evacuations. An oversized system would produce little additional benefit with respect to controlling hazardous gas. In practice, the capacity of a fully operational ventilation system is not static, but decreases as the excavation is advanced, because of increasing friction losses and leakage. These losses are overcome by providing excess capacity, with design capacity being reached at maximum extension of the system. Although this excess capacity is lost as the excavation advances, it provides some factor of safety.

Design of ventilation systems for excavations has been addressed elsewhere (for example, Kissell 1989; Kissell 1996; McPherson 1993; National Coal Board 1979). If the amount of air supplied to the heading is insufficient to safely dilute and remove inflowing gas, excavation must cease for a period of time to allow the inflow to decrease to manageable levels. Other control measures are relied on to maintain control of the atmosphere in the event that the ventilation system

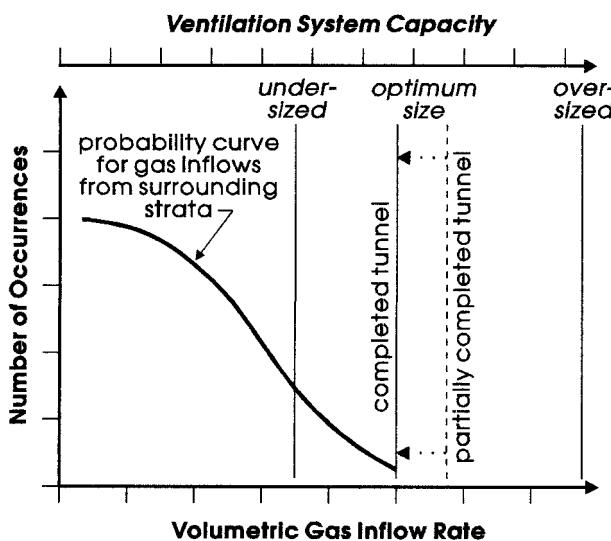


Figure 10-7. Sizing the ventilation system to suit hazardous gas inflow rate and frequency.

is overcome by gas. These are identified in the following section. The importance of mechanically ventilating shafts while they are being excavated should not be overlooked. Because shafts open directly to the surface, they are sometimes wrongly perceived as being sufficiently naturally ventilated.

Additional Control Measures

In the event that the ventilation system is overcome by gas inflows, additional control measures are employed. These include: gas monitors, to prompt personnel to respond to a developing hazardous condition; automatic power shutdown mechanisms, to eliminate electrical and frictional ignition hazards when combustible gas is detected at the face; explosion-proof and intrinsically safe electrical equipment (permissible equipment), to eliminate electrical ignition hazards from powered circuits; and hazard awareness training for workers, to ensure rapid and appropriate response to a hazardous condition.

These additional control measures are critical regardless of ground classification, because no ventilation system is invulnerable. A ventilation system functioning as designed may be overwhelmed by gas inflows in excess of those expected. The effect would be a rightward shift of the inflow distribution curve shown in Figure 10-7. The ventilation system might be rendered inoperative by power outage or fan failure, or it might be impaired by damage to fans or ducts, excessive leakage or friction losses, tardy advance of ducts toward the face, or other factors. The effect would be a leftward shift of the ventilation capacity line shown in Figure 10-7. Formal administrative procedures are important to ensure that all mechanical and procedural safeguards are in place and functioning at all times.

Other measures could also be used to reduce gas inflows to the excavation. These include grouting in advance of excavation, to reduce permeability; lining concurrent with excavation, to cut off inflows; dewatering, to reduce groundwater inflows; and drilling ahead of the excavation, to release large accumulations of gas from conventional reservoirs and coal beds.

System Safety Engineering and Fault Tree Analysis

Of construction projects seriously disrupted by gas, most exhibit deficiencies in atmosphere control measures. Few experience inflows sufficient to overcome a properly designed and fully operational ventilation system. Each atmosphere control measure, on close examination, performs a complex function. But to be completely effective, these measures must operate as integrated components of a system. Recognizing atmosphere control measures as a system is important to their reliable performance.

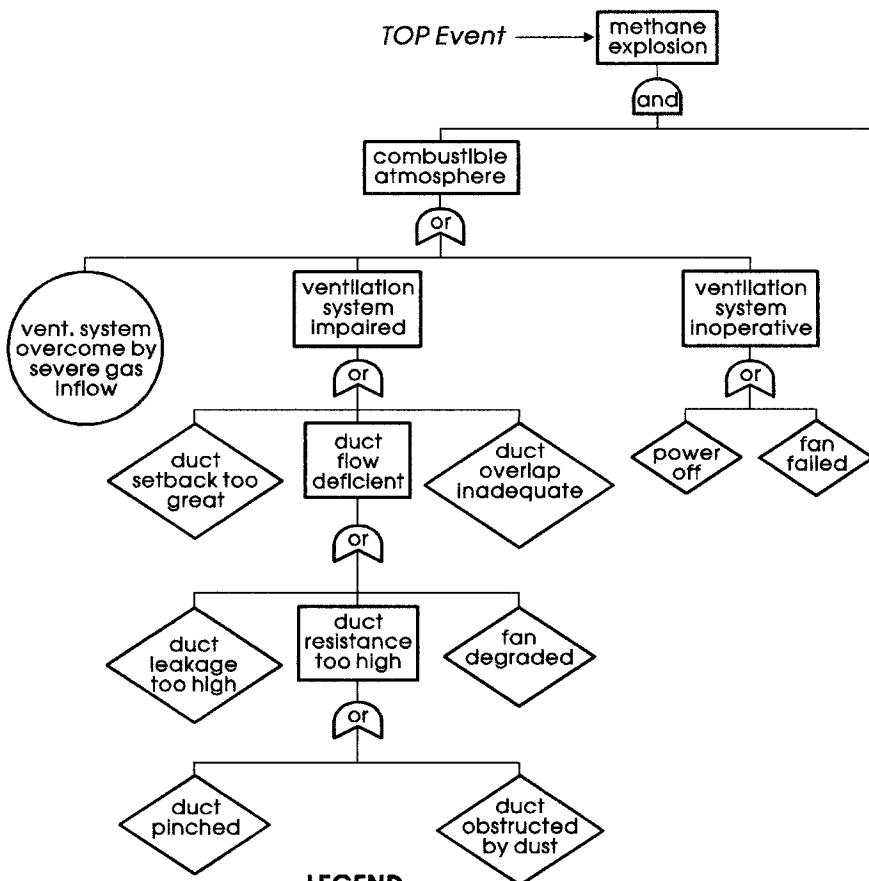
System safety engineering is an organized approach to imposing a state of safety on a complex system, by integrating system components to achieve maxi-

mum effectiveness (Roland and Moriarty 1983, pp. 3–11; MSHA 1985). It is a forward-looking approach to identifying and controlling hazards, as opposed to the traditional safety approach of responding to accidents that have already occurred (Brown 1993). This distinction is significant to underground construction, where the variety of geological conditions encountered and excavation methods employed make each project somewhat unique.

System safety engineering is based on the concept that 1) an accident is the result of a number of interacting causes within a system, 2) each cause and interaction can be logically identified and evaluated, and 3) solutions can be developed to control each cause (Brown 1993). An essential part of system safety engineering is *hazard analysis*, a formalized examination of a system to identify factors that contribute to hazards (Roland and Moriarty 1983, p. 187). A hazard is a potential condition that can be transferred from the potential state into a loss, by an initiating factor. For example, a combustible atmosphere constitutes a potential hazardous condition, and sources of ignition constitute initiating factors. Once identified, hazards can be controlled through system modification, by removing potential hazards or removing initiating factors. The approach can be applied to existing systems, but more control options are available if applied during system design.

Fault tree analysis (FTA) is a form of hazard analysis used to analyze a single catastrophic event (such as a gas explosion) that could occur within a defined system (Roland and Moriarty 1983, pp. 215–252). A fault tree is a logic diagram representing sequences of events that could lead to the catastrophic event. It is constructed by deductive reasoning from the principal undesired event, or TOP event, down through intermediate causation events, to basic events that cannot be subdivided further. At each step in the process the analyst asks “How can this occur?” In addition to exposing all credible sequences of events that lead to the TOP event, FTA clarifies the interaction of system components. A complete hazard analysis of a complex system may require that a number of potential catastrophic events be analyzed. FTA is a descriptive, qualitative form of analysis. A quantitative ranking of the importance of various control elements in a system can be derived, if probability data for basic events are available (Kissell and Goodman 1991; Roland and Moriarty 1983, pp. 252–271).

A general example of an FTA for a methane explosion in a tunnel heading is shown in Figure 10-8. The left half of the figure shows how a combustible atmosphere could develop, and the right half shows how a combustible atmosphere could be ignited. The following conditions are assumed: the ventilation system consists of a single main fan at the surface, a main duct extending to the back end of the trailing gear, and a forward fan and overlapping duct mounted on the trailing gear and extending to the face; the ventilation system is properly designed; the tunnel is excavated using a TBM; the TBM is equipped with an automatic power cutoff connected to a combustible gas monitor, with sensor head

**LEGEND**

- | | |
|--|---|
| | An output event. Should be developed further to see how they occur. |
| | A normal event. Should be expected to occur. |
| | An undeveloped event. Lack of information as to origin or significance. |
| | An independent event. Does not depend on other components to occur. |
| | And. All of the lower order events must occur for the higher event to occur. |
| | Or. Any or all of the lower order events may occur for the higher order event to occur. |
| | Transfer symbol. Eliminates repetition of sequence of events common to different areas of the tree. |

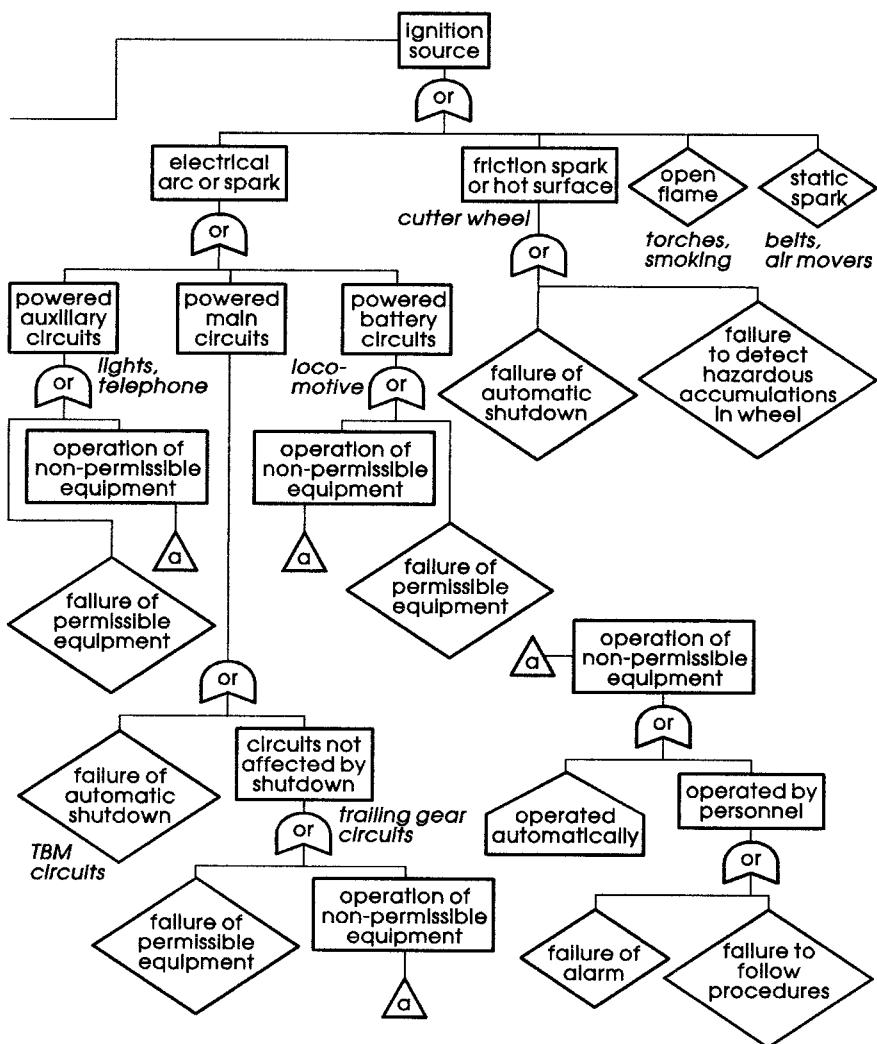


Figure 10-8. Fault tree analysis of methane explosion in tunnel heading. State of system described in text. (Developed in part from Doyle, Gronbeck, and Rose 1991; Kissel and Goodman 1991.)

positioned near the muck discharge point; a transformer mounted on the trailing gear distributes electrical power to the TBM and trailing gear equipment; and an electrical locomotive is used for muck haulage. This type of arrangement is common in underground construction, and would conform to U.S. OSHA Code requirements for construction in “unclassified” or “potentially gassy” ground (OSHA 1999, 29 CFR 1926.800).

Study of the fault tree reveals how this type of system could fail to control a gas inflow. The ventilation system could be overcome by a gas inflow far in excess of what was expected. Although uncommon, this is not an impossibility. The ventilation system could become impaired as a result of improper duct placement in the heading or lack of routine inspection. The ventilation system could be completely disabled by power failure or mechanical failure of either fan. Electrical ignition sources are numerous and the most difficult to control. In this example, only the electrical circuits on the TBM are affected by the automatic shutdown mechanism, leaving several others powered. Elimination of these circuits as initiating factors would require rapid response by the construction crew—at the heading, on the locomotive, and at the surface. Some pieces of electrical equipment may be essential to maintain the heading or facilitate safe and rapid evacuation of the crew (such as water pumps in a tunnel driven downgrade, lights, telephones, and the locomotive), a factor that could delay a decision to shut them down. Non-permissible electrical equipment that remains powered following TBM shutdown, and that operates automatically, could ignite a combustible atmosphere after the crew has evacuated the heading but before they have reached safety at the surface. Electrical equipment designed as permissible could fail in this function due to misuse, physical abuse, or lack of inspection and maintenance. Friction sparks and hot surfaces, and open flames (such as from smoking or use of cutting torches), are common sources of ignition. Static sparks are uncommon though not at all negligible sources of ignition (Vázquez, Ramón, and Remesal 1985). Many ignition sources are associated with the actions of workers in the heading, which attests to the importance of worker training.

The system described in the example may be vulnerable to other potential catastrophic events, which should be considered to complete the failure analysis. A frictional ignition of methane in the wheel chamber could result in a limited though not necessarily inconsequential explosion. An accumulation of methane could asphyxiate a worker entering the muck chamber. Significant gas inflows from behind the heading could generate hazardous concentrations elsewhere in the running length of the tunnel. The hazard assessment, by identifying manners of gas entry to the excavation, can be instrumental in identifying these potential catastrophic events.

There is no unique way to represent a fault tree (Caceres and Henley 1976). In structuring the tree through successive levels it is important to identify generic causes of upper-level events before identifying specific failures. This helps to

ensure that no system elements are bypassed (Roland and Moriarty 1983, pp. 229–230). Best results are obtained when personnel skilled in various aspects of the system are involved in constructing the tree, such as the ventilation specialist, the electrician, safety personnel, maintenance personnel, and management (Brown 1993; Main and McMurphy 1998).

A system safety engineering approach to design of atmosphere control measures has not yet become a standard of practice in underground construction. Current government safety regulations for underground construction reflect this lack of development, so they should not be perceived as reliable guides to safe practice with respect to gas inflows (Doyle, Hunt, and Kettler 1997). Where gas is expected, it may be appropriate to include in the construction contract additional performance or prescriptive specifications for atmosphere control, to lower the level of risk to an acceptable level. On contracts let to competitive bidding, this would help ensure that bidders are devoting similar and appropriate resources to this aspect of the project.

CONCLUDING REMARKS

A great deal of work has yet to be done to advance our standard of practice with respect to gas, to end the costly and sometimes tragic consequences of this geologic hazard that persist in the underground construction industry. This is not so much a matter of expending more resources, but of applying those resources in a more informed and focused manner. Characterizing gas on a site in advance of excavation, the subject of this text, is only part of this problem. Controlling gas inflows to the excavation is the other part, and comprehensive reliable guides to performing this work have yet to be developed. A broad body of detailed technical papers on the subject of gas underground is necessary to form a basis for a sound standard of practice. Underground construction literature at the present time is seriously lacking in this regard, despite the number of informative and useful papers that have been published. Readers are encouraged to contribute to the literature by sharing their experiences in dealing with gas, in a detailed, thorough, and objective manner. It is the author's hope that this text introduces some fresh solutions to this problem that can be applied within the time and financial constraints of every project.

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Appendix A: Units of Measure, Physical Quantities, and Miscellaneous Constants and Terms

Table A-1 Names and Symbols of Units of Measure

Physical quantity	Unit name	Unit symbol	Unit definition
Length	meter*	m	
	ångström	Å	10^{-10} m
Mass	kilogram*	kg	
	gram*	g	10^{-3} kg
Time	second*	s	
	minute	min	
Temperature	hour	h	
	degree Kelvin*	K	
	degree Celsius*	°C	
Amount of substance	mole*	mol	
Force	newton	N	$m \text{ kg s}^{-2}$
	dyne	dyn	10^{-5} N
Pressure	pascal*	Pa	$\text{kg m}^{-1} \text{ s}^{-2}$
	standard atmosphere	atm	101 325 Pa
Energy	bar	bar	10^5 Pa
	millibar	mb	10^2 Pa
Volume	joule*	J	$\text{kg m}^2 \text{ s}^{-1}$
	electronvolt	eV	
Volume	cubic meter*	m ³	
	liter	L	10^{-3} m ³
Absolute viscosity	milliliter	ml	10^{-3} L
	poise	P	$\text{g cm}^{-1} \text{ s}^{-1}$

* SI Unit.

Conversions:

1 atm = 10.33 m H ₂ O	1 m = 3.281 ft	K	= °C + 273.15
= 33.90 ft H ₂ O	1 km = 0.621 mile (stat.)	°C	= (5/9)(°F - 32)
= 760 mm Hg	1 mi = 5280 ft	1 P	= 100 cP
= 29.92 in Hg	1 m ³ = 1000 L		= 0.1 N s m ⁻²
= 14.70 psi	= 35.31 ft ³		= 0.0672 lbm ft ⁻¹ s ⁻¹
= 1013.25 mb	1 ft ³ = 7.481 gal(U.S.)	1 eV	= 1.60 × 10 ⁻¹⁹ J
1 bar = 100 kPa	1 L = 0.2642 gal(U.S.)	1 Btu lbm ⁻¹	= 0.002326 MJ kg ⁻¹
= 14.50 psi	1 kg = 2.205 lb		
= 2.79 in H ₂ O			
1 mb = 10 ⁵ g m ⁻¹ s ⁻²			
1 Pa = N m ⁻²			

Table A-2 Names and Symbols of Physical Quantities

Physical quantity	Quantity symbol	Definition	Units*
Amount of substance	n		mol
Amount concentration	c	n_i/V_t	mol L ⁻¹
Bunsen solubility coefficient	α		ml(g) ml(w) ⁻¹
Chlorinity	CL		g kg ⁻¹ (aq)
Compressibility factor	z	pV/nRT	—
Concentration	C, c		various
Diffusion coefficient	D		m ² s ⁻¹
Flux	J		mol m ⁻² s ⁻¹
Henry's constant	H		atm
Hydraulic conductivity	K		cm s ⁻¹
Mass	m		g
Mass density; mass concentration	ρ	m_i/V_t	g L ⁻¹
Mass flow rate	q_m		g min ⁻¹
Mass fraction	w	m_i/m_t	—
Molality	b	n_i/m_w	mol kg ⁻¹
Molarity	M	n_i/V_w	mol L ⁻¹
Molar mass	M	m/n	g mol ⁻¹
Molar volume	V_m	V/n	L mol ⁻¹
Mole fraction	x	n_i/n_t	—
Ostwald coefficient	L		ml(g) ml(aq) ⁻¹
Permeability	k		cm ² ; darcy
Porosity	ϕ		—
Pressure	p		atm
Salinity	S		g kg ⁻¹ (aq)
Saturation	S	V_i/V_{voids}	%
Solubility	S		various
Specific gravity	SG		—
Surface tension	γ		dyn cm ⁻¹
Temperature, absolute	T		K
Temperature, Celsius	θ		°C
Tortuosity	τ		—
Velocity	v		m s ⁻¹
Viscosity, absolute	μ		g cm ⁻¹ s ⁻¹
Viscosity, kinematic	ν	μ/ρ	cm ² s ⁻¹
Volume	V		L
Volume fraction	ϕ	V_i/V_t	—
Volume percent	P	$\phi' \times 100$	%
Volumetric flow rate	q		cm ³ s ⁻¹
Water content, volumetric	ω_v	V_w/V_t	—
Water content, gravimetric	ω	m_w/m_t	%
Wettability	θ		°

Source: Based in part on IUPAC 1993.

* Units shown for illustrative purposes. Other consistent units may be used.

Subscripts: i = constituent, g = gas, w = water, v = vapor, s = solution, t = total, gw = groundwater, ta = tunnel air, tw = tunnel water. Parenthetical terms: (g) = gas, (w) = water, (aq) = aqueous.

Table A-3 Miscellaneous Constants and Terms

Description	Symbol	Definition
<i>Constants</i>		
Gravitational acceleration	<i>G</i>	9.81 m s ⁻²
STP molar volume		22.414 L
SATP molar volume		24.789 L
Universal gas constant	<i>R</i>	8.206 × 10 ⁻² L atm mol ⁻¹ K ⁻¹
<i>SI prefixes</i>		
centi	c	10 ⁻²
milli	m	10 ⁻³
micro	μ	10 ⁻⁶
nano	n	10 ⁻⁹
kilo	k	10 ³
mega	M	10 ⁶
<i>Terms</i>		
Lower explosive limit	LEL	
Upper explosive limit	UEL	
Parts per million (vol.)	ppmv, ppm	
Parts per million (mass)	ppm	
Standard temperature and pressure	STP	0°C, 1 atm
Standard ambient temperature and pressure	SATP	25°C, 10 ⁵ Pa
Threshold limit value	TLV	
Time weighted average	TWA	
Short term exposure limit	STEL	
Fixed carbon content	FC	
Volatile matter content	VM	
Mineral matter content	MM	
Dissolved organic carbon	DOC	
Total organic carbon	TOC	
Total organic matter	TOM	
Tunnel boring machine	TBM	
<i>Units</i>		
age	ka B.P.	thousand years Before Present
time	Ma	million years

REFERENCE

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Appendix B: Data Tables

Table B-1 Weights and Densities of Gases

Gas	Density (g L ⁻¹)	Specific gravity	Molar mass (g mol ⁻¹)
Methane	0.7167	0.55	16.03
Hydrogen sulfide	1.5392	1.19	34.08
Carbon dioxide	1.9768	1.53	44.00
Nitrogen (N ₂)	1.2507	0.97	28.02
Oxygen (O ₂)	1.4289	1.11	32.00
Air (dry)	1.2928	1.00	28.94*

Density and specific gravity at 0°C and 1 atm.

* Apparent molar mass, calculated.

Source: From Liley et al. 1984.

Table B-2 Atmospheric Gases At Ground Level

Gas	Formula	Concentration	
		% by volume	Mole fraction
Nitrogen	N ₂	78.08	
Oxygen	O ₂	20.95	
Argon	Ar	0.93	9.3×10^{-3}
Neon	Ne		1.8×10^{-5}
Helium	He		5.2×10^{-6}
Krypton	Kr		1.1×10^{-6}
Xenon	Xe		8.6×10^{-8}
Water vapor	H ₂ O		$(0.4\text{--}400) \times 10^{-4}$
Ozone	O ₃		$(0\text{--}5) \times 10^{-8}$
Hydrogen	H ₂		$(0.4\text{--}1.0) \times 10^{-6}$
Carbon dioxide	CO ₂		$(2\text{--}4) \times 10^{-4}$
Carbon monoxide	CO		$(1\text{--}20) \times 10^{-8}$
Methane	CH ₄		$(1.2\text{--}1.5) \times 10^{-6}$
Formaldehyde	CH ₂ O		$(0\text{--}1) \times 10^{-8}$
Nitrous oxide	N ₂ O		$(2.5\text{--}6.0) \times 10^{-7}$
Nitrogen dioxide	NO ₂		$(0\text{--}3) \times 10^{-9}$
Ammonia	NH ₃		$(0\text{--}2) \times 10^{-8}$
Sulfur dioxide	SO ₂		$(0\text{--}20) \times 10^{-9}$
Hydrogen sulfide	H ₂ S		$(2\text{--}20) \times 10^{-9}$

To convert from mole fraction to ppm, multiply by 10⁶.

Source: Adapted from Junge 1963, Tbl. 1.

Table B-3 Solubility of Gases in Water

Temperature (°C)	Methane		Hydrogen sulfide		Carbon dioxide	
	Henry's constant (atm)	Bunsen coefficient* (ml(g)/ml(w))	Henry's constant (atm)	Bunsen coefficient* (ml(g)/ml(w))	Henry's constant (atm)	Bunsen coefficient* (ml(g)/ml(w))
0	21630	.05750	285.4	4.359	725.0	1.716
2	22970	.05416	302.5	4.113	782.8	1.589
4	24330	.05114	320.2	3.885	843.4	1.475
6	25710	.04838	338.5	3.675	906.7	1.372
8	27110	.04588	357.4	3.480	972.7	1.279
10	28530	.04360	376.9	3.300	1041	1.194
12	29950	.04152	397.0	3.132	1113	1.118
14	31390	.03961	417.7	2.976	1187	1.048
16	32820	.03786	438.9	2.832	1263	0.9841
18	34260	.03626	460.7	2.697	1342	0.9260
20	35690	.03479	483.0	2.571	1423	0.8729
22	37120	.03344	505.9	2.454	1506	0.8242
24	38540	.03220	529.3	2.344	1592	0.7795
26	39940	.03105	553.2	2.242	1679	0.7385
28	41330	.02999	577.6	2.146	1769	0.7008
30	42690	.02902	602.4	2.056	1860	0.6661
32	44030	.02811	627.7	1.972	1953	0.6340
34	45350	.02728	653.5	1.893	2047	0.6044
36	46640	.02651	679.6	1.819	2143	0.5770
38	47890	.02580	706.2	1.749	2240	0.5516
40	49110	.02514	733.1	1.684	2337	0.5281

* Gas volume at 0°C and 1 atm.

Source: Fog and Gerrard 1991.

(continued)

Table B-3 (Continued)

Temperature (°C)	Nitrogen		Oxygen	
	Henry's constant (atm)	Bunsen coefficient* (ml(g)/ml(w))	Henry's constant (atm)	Bunsen coefficient* (ml(g)/ml(w))
0	52420	.02373	25310	.04915
2	55040	.02260	26710	.04658
4	57670	.02157	28120	.04424
6	60320	.02062	29560	.04209
8	62970	.01976	31010	.04011
10	65610	.01896	32470	.03830
12	68240	.01822	33940	.03664
14	70840	.01755	35420	.03510
16	73430	.01693	36890	.03369
18	75980	.01635	38360	.03238
20	78490	.01582	39830	.03118
22	80950	.01533	41290	.03007
24	83370	.01488	42730	.02904
26	85720	.01447	44160	.02808
28	88020	.01408	45570	.02720
30	90240	.01373	46950	.02638
32	92390	.01340	48320	.02562
34	94470	.01310	49650	.02492
36	96460	.01282	50950	.02426
38	98360	.01256	52220	.02366
40	100180	.01232	53450	.02310

* Gas volume at 0°C and 1 atm.

Table B-4 Solubility of Gases in Seawater^a

Temperature (°C)	Bunsen Solubility Coefficient ^b (ml(g)/ml(w))				
	Methane ¹	Hydrogen sulfide ²	Carbon dioxide ³	Nitrogen ⁴	Oxygen ⁵
0	.04448	4.389	1.4490	.01826	.03866
2	.04205	4.121	1.3417	.01744	.03674
4	.03985	3.875	1.2454	.01669	.03498
6	.03784	3.650	1.1588	.01600	.03337
8	.03601	3.443	1.0807	.01536	.03190
10	.03433	3.252	1.0102	.01477	.03055
12	.03279	3.076	0.9464	.01422	.02930
14	.03139	2.914	0.8885	.01372	.02816
16	.03010	2.764	0.8359	.01326	.02711
18	.02891	2.626	0.7881	.01284	.02614
20	.02782	2.497	0.7445	.01245	.02524
22	.02682	2.377	0.7047	.01209	.02441
24	.02589	2.267	0.6683	.01176	.02365
26	.02504	2.163	0.6350	.01145	.02294
28	.02425	2.067	0.6045	.01118	.02229
30	.02352	1.977	0.5765	.01092	.02169
32	.02285	1.894	0.5508	.01069	.02113
34	.02223	1.815	0.5271	.01049	.02061
36	.02166	1.742	0.5053	.01030	.02014
38	.02113	1.673	0.4852	.01013	.01969
40	.02064	1.609	0.4667	.00998	.01929

^a Salinity = 35 gm kg⁻¹.^b Gas volume at 0°C and 1 atm.¹ Cleaver and Young 1987. ²Douabul and Riley 1979. ³Weiss 1974. ⁴Battino 1982. ⁵Weiss 1970.

Table B-5 Density of Water

Temperature (°C)	Density (g ml ⁻¹)
0	0.99984
3.98	1.00000
10	0.99970
20	0.99821
30	0.99565
40	0.99222

Source: Lide 1996.

Table B-6 Vapor Pressure of Water

Temperature (°C)	Vapor pressure (mb)
0	6.11
2	7.06
4	8.14
6	9.35
8	10.73
10	12.28
12	14.03
14	15.99
16	18.18
18	20.64
20	23.39
22	26.45
24	29.85
26	33.63
28	37.82
30	42.46
32	47.58
34	53.23
36	59.45
38	66.30
40	73.81

Source: Lide 1996.

Table B-7 Vapor Pressure of Gasoline

Temperature (°C)	Vapor pressure ^a (mb)	
	62 kPa gasoline ^b	90 kPa gasoline ^c
0	190	270
5	230	330
10	280	400
15	330	480
20	390	570
25	460	660
30	540	770
35	630	900
40	730	1050

^a Unweathered gasoline.^b Summer blend in United States.^c Winter blend in United States.

Source: Adapted from Gas Processors Suppliers Assoc. 1972.

Table B-8 The Error Function

ϕ	erf(ϕ)	ϕ	erf(ϕ)
0.00	0.0000	0.85	0.7707
0.025	0.0282	0.90	0.7970
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

Source: Thibodeaux 1979.

Table B-9 Properties of Selected Higher Hydrocarbons

Hydrocarbon	Chemical formula	Molar mass (g mol ⁻¹)	Specific gravity of gas or vapor	Net heat of combustion ΔH (kJ mol ⁻¹)	Flammability limits (% vol.)		Flashpoint (°C)	Auto-ignition temperature (°C)
					LEL	UEL		
<i>Straight-chain alkanes</i>								
methane	CH ₄	16.04	0.55	803	5.0	15.0	-188	630
ethane	C ₂ H ₆	30.07	1.04	1430	3.0	12.4	-135	515
propane	C ₃ H ₈	44.11	1.52	2050	2.1	9.5	-104	450
<i>n</i> -butane	C ₄ H ₁₀	58.12	2.01	2660	1.8	8.4	-74	370
<i>n</i> -pentane	C ₅ H ₁₂	72.15	2.49	3270	1.4	7.8	-49	260
<i>n</i> -hexane	C ₆ H ₁₄	86.18	2.98	3890	1.2	7.4	-23	225
<i>n</i> -heptane	C ₇ H ₁₆	100.21	3.46	4500	1.1	6.7	-3	225
<i>n</i> -octane	C ₈ H ₁₈	114.23	3.94	5120	0.95	6.5	14	220
<i>Cyclic alkanes</i>								
cyclopentane	C ₅ H ₁₀	70.14	2.42	3100	1.5	—	—	380
cyclohexane	C ₆ H ₁₂	84.16	2.91	3690	1.3	7.8	-20	245
<i>Alkenes</i>								
<i>cis</i> -2-butene	C ₄ H ₈	56.12	1.94	2540	1.7	9.7	—	325
3-methyl-1-butene	C ₅ H ₁₀	70.14	2.42	3150	1.5	9.1	—	365
<i>Aromatics</i>								
benzene	C ₆ H ₆	78.12	2.69	3170	1.3	7.9	-11	560
toluene	C ₇ H ₈	92.15	3.18	3770	1.2	7.1	4	480
ethylbenzene	C ₈ H ₁₀	106.17	3.67	4390	1.0	6.7	15	430
<i>o</i> -xylene	C ₈ H ₁₀	106.17	3.67	4380	1.1	6.4	32	530
<i>m</i> -xylene	C ₈ H ₁₀	106.17	3.67	4380	1.1	6.4	29	465
<i>p</i> -xylene	C ₈ H ₁₀	106.17	3.67	4380	1.1	6.6	27	530

Source: Kuchta 1985.

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Appendix C: Chemistry of Gases and Vapors

INTRODUCTION

Principles of physical chemistry of gases and vapors are fundamentally important to understanding gas and vapor behavior in the near-surface underground and in excavations. This appendix considers the hazardous gases methane, hydrogen sulfide, and carbon dioxide; and also nitrogen and oxygen, the major constituents of air. It introduces the concept of vapors, as are associated with gasoline. Chemistry principles are applied throughout the text, most frequently in Chapters 6 through 10.

Gas data are often reported under one of two sets of conditions of temperature and pressure. *Standard temperature and pressure* (STP) corresponds to 0°C and 1 atmosphere pressure. *Standard ambient temperature and pressure* (SATP) corresponds to 25°C and 1×10^5 Pa (0.987 atm). Unless otherwise noted, this text uses STP conditions.

GASES IN GASEOUS PHASE

A gas in gaseous phase is a physically very simple form of matter; it is a collection of small, largely independent molecules, in rapid, random, continuous motion. The molecules collide with each other, and they also batter constantly against contiguous solid and liquid surfaces, generating pressure proportional to their

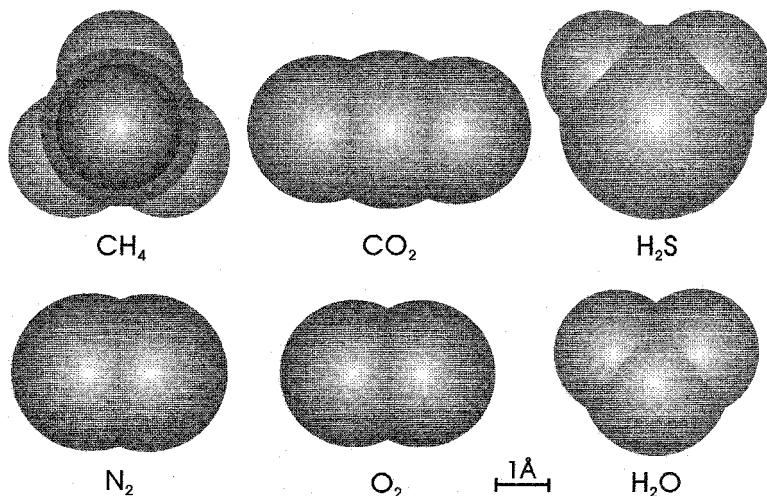


Figure C-1. Space-filling models of several gases. Water shown for size comparison.

average kinetic energy. Molecular structures of the subject gases are shown in Figure C-1.

Ideal Gas Behavior

The basic gas laws may be inferred from the hypothetical concept of an ideal gas. The molecules of an ideal gas are not acted upon by intermolecular forces of attraction or repulsion; they physically occupy zero space; and their average velocity is proportional to temperature. The appeal of the ideal gas concept is in the fundamental way that the physical behavior of gases can be modeled, with simple equations and a limited number of variables, largely independent of chemical properties of the gas.

The behavior of many real gases at normal temperatures and atmospheric pressure closely approximates the assumptions of an ideal gas. Distances between molecules are relatively large compared to molecular diameters, so intermolecular forces are almost nonexistent. That portion of the “container” volume physically occupied by gas molecules is minute—the container is largely empty space.

Boyle's Law

Boyle's law states that the volume of an ideal gas changes in inverse proportion to confining pressure, at constant temperature:

$$p_1V_1 = p_2V_2 \quad (\text{C-1})$$

where p is absolute pressure (as opposed to relative, or “gage” pressure), and V is volume. Doubling the container volume of a gas halves the number of molecules per unit volume, and so halves the average force exerted by molecules striking the walls of the container.

Charles' Law

Charles' law states that the volume of an ideal gas changes in direct proportion to absolute temperature, at constant pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{C-2})$$

where T is absolute temperature, measured on the Kelvin scale. Increasing the temperature of a gas increases the velocity and frequency at which molecules strike the walls of the container. Volume must increase proportionally to maintain a constant pressure.

Combined Gas Law

The combined gas law is derived by combining Equations C-1 and C-2 into:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad (\text{C-3})$$

For a given body of gas, pV/T is a constant.

Avogadro's Principle

The *amount* of a substance is defined as the number of atoms, molecules, or other entities present. A unit measure of amount is the *mole*:

$$n = \frac{m}{M} \quad (\text{C-4})$$

where n is moles, m is mass (g), and M is molar mass (g mol⁻¹; formerly, gram atomic weight, or gram molecular weight). A mole of any atomic or molecular substance contains 6.02×10^{23} atoms or molecules. Molar masses of the subject gases are shown in Table B-1.

Avogadro's principle states that equal volumes of gases, at the same temperature and pressure, contain equal numbers of molecules, or equal “amounts” of gas. A *molar volume* contains one mole of an ideal gas:

$$V_m = \frac{V}{n} \quad (\text{C-5})$$

where V_m is molar volume, and n is moles of gas. One mole of an ideal gas at STP occupies 22.414 L, defined as the *STP molar volume*. The *SATP molar volume* is 24.789 L.

Ideal Gas Law

The four properties that determine the state of an ideal gas are volume, temperature, pressure, and amount. The ideal gas law defines the relationship between these properties. It can be derived by combining Boyle's law, Charles' law, and Avagadro's principle to obtain:

$$pV = nRT \quad (\text{C-6})$$

where p is pressure, V is volume, n is amount of gas in moles, and T is absolute temperature. The term R is the universal gas constant, the value of pV/T for one mole of an ideal gas:

$$R = 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$$

Ideal Gas Mixtures

Dalton's Law

Dalton's law states that the total pressure generated by a gas mixture is equal to the sum of pressures that would be generated by each gas constituent occupying the volume alone:

$$p_t = p_1 + p_2 + p_3 + \dots \quad (\text{C-7})$$

where p_t is total pressure, and $p_1, p_2, \text{etc.}$ are partial pressures of the constituents. It follows that:

$$p_i = \frac{n_i R T}{V_t} \quad (\text{C-8})$$

where p_i is partial pressure of the constituent, n_i is amount of the constituent, and V_t is total volume of the mixture.

Mole Fraction

The total amount of gas in a gas mixture is equal to the sum of the constituents:

$$n_t = n_1 + n_2 + n_3 + \dots \quad (\text{C-9})$$

The mole fraction is:

$$x_i = \frac{n_i}{n_t} \quad (\text{C-10})$$

where x_i is mole fraction of constituent gas i .

Combining Equations C-8 and C-10 yields:

$$p_i = \frac{x_i n_t R T}{V_t} \quad (\text{C-11})$$

which can be simplified to:

$$p_i = x_i p_t \quad (\text{C-12})$$

Volume Fraction

Any gas will occupy the entire volume of its container. Each molecule of gas, in moving about the container, effectively occupies the same fraction of total volume. Volume fraction is defined as:

$$\phi_i = \frac{V_i}{V_t} \quad (\text{C-13})$$

where ϕ_i is volume fraction, V_i is volume effectively occupied by the constituent, and V_t is total volume of the mixture. Volume fraction is equivalent to mole fraction.

Apparent Molar Mass

Apparent molar mass is a concept that can be used to apply the ideal gas law to gas mixtures. Apparent molar mass is defined as:

$$M_g = x_1 M_1 + x_2 M_2 + x_3 M_3 \dots \quad (\text{C-14})$$

where M_g is apparent molar mass (g mol^{-1}), and x_i and M_i are mole fraction and molar mass, respectively, of the constituents.

Apparent molar mass can also be used to determine specific gravity, the ratio of the density of a gas mixture to the density of dry air:

$$SG_g = \frac{M_g}{M_{\text{air}}} \quad (\text{C-15})$$

where SG_g is specific gravity of the gas mixture. The apparent molar mass of dry air (M_{air}), calculated from the mole fraction and molar mass of N_2 , O_2 , and Ar , is 28.95 g mol^{-1} .

Real Gas Behavior

Compressibility

The behavior of real gases is not as simple as the ideal gas law describes. Gases deviate from ideal behavior as molecules are forced close together by high pressure, or their kinetic energy is reduced by low temperature. Pressure generated by a real gas is reduced by attractive forces between molecules, and increased

by the physical space occupied by molecules. The behavior of real gases is approximately described by Van der Waals' equation of state, a simple modification of the ideal gas law:

$$\left(p + \frac{n^2 a}{V^2} \right) (V - n b) = n R T \quad (\text{C-16})$$

where a is a constant representing attractive forces between molecules, and b is a constant representing space occupied by the molecules. Van der Waals' constants for several gases are shown in Table C-1.

A real gas deviates from ideal behavior according to:

$$z = \frac{p V}{n R T} \quad (\text{C-17})$$

where z is the compressibility factor. For one mole of an ideal gas, or a real gas at zero pressure and infinite volume, z is 1.0. Compressibility factors for the hazardous gases are plotted in Figure C-2.

For conditions commonly encountered in the near-surface underground, ideal gas behavior can be assumed with negligible error.

Chemical Reactions Between Gases

Ideal gases interact with each other only through momentary intermolecular collisions. In most cases such collisions merely redirect the trajectories of colliding molecules. If chemical reactions between gas molecules are possible, collisions may result in molecular rearrangements. Kinetic energy involved in the collision must be sufficient for these rearrangements to occur. Kinetic energy is a function of temperature. A heat source such as a spark or flame may raise molecular kinetic energy sufficiently to initiate the reaction. A local exothermic reaction may re-

Table C-1 Van Der Waals' Constants

Gas	a (L ² atm mol ⁻²)	b (L mol ⁻¹)
Methane	2.270	0.04301
Hydrogen sulfide	4.485	0.04339
Carbon dioxide	3.610	0.04286
Nitrogen	1.352	0.0387
Oxygen	1.364	0.03186

Source: Lide 1996.

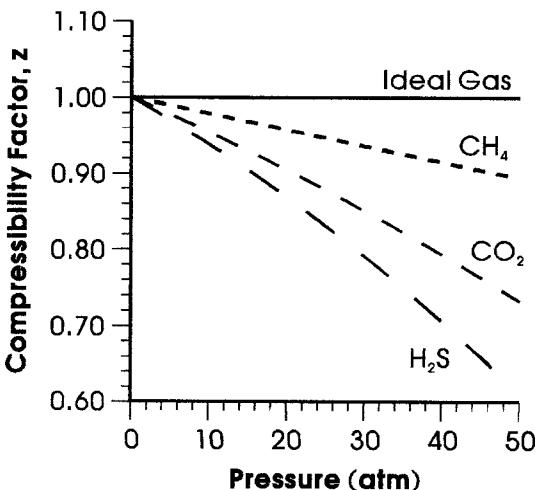


Figure C-2. Deviation of real gases from ideal behavior at 20°C. Calculated from virial form of van der Waals' equation. (Castellan 1971.)

lease enough energy to propagate the reaction completely through the gas mixture.

The behavior of methane in air provides an example. At normal temperatures, methane mixes passively with air. A scant heat source, such as a spark, flame, or hot surface, can initiate a highly exothermic chemical reaction between methane and oxygen. If these gases are present in appropriate concentrations, heat given off by the initial recombination drives the reaction rapidly forward to completion.

LeChatelier's Law

The bulk behavior of fuel gas mixtures is sometimes of more interest than the behavior of individual constituents. Combustibility limits of fuel gas mixtures in air can be calculated using LeChatelier's law:

$$L_m = \frac{100}{\frac{P_1}{L_1} + \frac{P_2}{L_2} + \frac{P_3}{L_3} \dots} \quad (\text{C-18})$$

where L_m is the explosive limit (LEL or UEL) of the fuel mixture (volume %), P_i is volume percent of fuel gas i , and L_i is flammable limit of fuel gas i (Kuchta 1985).

Petroleum gases typically consist predominantly of methane, with small proportions of higher hydrocarbon gases. The higher hydrocarbons alter the explosive limits from those for methane alone. For example, given a petroleum gas mixture of 95% methane, 4% ethane, and 1% propane:

$$LEL = \frac{100}{\frac{95}{5.0} + \frac{4}{3.0} + \frac{1}{2.1}} = 4.8\%$$

(Chemical properties of selected higher hydrocarbons are shown in Table B-9.)

Concentrations of Gases in Gaseous Mixtures

The concentration of a constituent gas in a gaseous mixture can be expressed on the basis of volume, pressure, or amount. In making unit conversions of gaseous concentrations, note that:

$$\frac{V_i}{V_t} = \frac{p_i}{p_t} = \frac{n_i}{n_t}$$

The following relationships assume ideal gas behavior.

Volume-Based Concentrations

Concentrations of combustible or asphyxiating gases, often CH₄ and CO₂, are commonly expressed as volume percent:

$$P_i = \phi_i \times 100 \quad (\text{C-19})$$

where ϕ_i is volume fraction, defined in Equation C-13. Volume fraction is independent of temperature and pressure.

Concentrations of toxic gases, which are commonly hazardous at much lower concentrations than combustible gases, are commonly expressed in terms of parts per million (ppm or ppmv), where:

$$C_i(\text{ppmv}) = \phi_i \times 10^6 \quad (\text{C-20})$$

Other volume-based units are amount concentration c (mol L⁻¹), and mass concentration ρ (g L⁻¹). Use of these terms requires that temperature and pressure conditions be specified. Amount concentration can be determined using the ideal gas law:

$$c_i = \frac{n_i}{V} = \frac{p_i}{R T} \quad (\text{C-21})$$

Amount concentration at STP conditions can be derived from volume fraction and STP molar volume:

$$c_i = \phi_i \left(\frac{1 \text{ mol}}{22.414 \text{ L}} \right) \quad (\text{C-22})$$

Mass concentration can be determined from the following equation, derived from Equations C-4 and C-6:

$$\rho_i = \frac{M_i p_i}{R T} \quad (\text{C-23})$$

where M_i is molar mass (g mol^{-1}). Mass concentration at STP conditions can be derived from volume fraction by:

$$\rho_i = \phi_i \left(\frac{1 \text{ mol}}{22.414 \text{ L}} \right) \left(M_i \frac{\text{g}}{\text{mol}} \right) \quad (\text{C-24})$$

Pressure-Based Concentrations

A pressure-based expression for concentration is partial pressure p_i , introduced in Equation C-7. Partial pressure is independent of temperature, but varies with total pressure p_t .

Amount-Based Concentrations

An amount-based expression for concentration is the mole fraction x_i , introduced in Equation C-10. Mole fraction is independent of temperature and pressure.

GASES IN SOLUTION IN WATER

The maximum amount of gas that can dissolve in water depends on three factors: 1) chemical properties of the gas, 2) temperature, and 3) pressure on the gaseous phase in contact with the water. *Solubility* is a measure of the maximum amount of a particular gas that can dissolve in a unit volume of water, under specific conditions of temperature and gas partial pressure. A *saturated* solution contains this solubility concentration of gas. Water saturated with gas is either in equilibrium with a contiguous gaseous phase or is on the verge of generating a gaseous phase in the form of bubbles. A solution in equilibrium with a gaseous phase exchanges gas molecules across the gas–water interface, though the net exchange is zero.

Solubility Expressions

Conventions used in this text to express solubility are Henry's constant, and the Bunsen solubility coefficient. Henry's constant is used with Henry's law, a fundamental expression of the solubility relationship. The Bunsen solubility coefficient is an equally correct but more explicit expression of solubility.

Henry's Constant

Henry's law states that the concentration of gas in solution, at equilibrium, is directly proportional to the concentration of the gaseous phase in contact with the solution:

$$x_i(\text{aq}) = \frac{p_i}{H_i} \quad (\text{C-25})$$

where $x_i(\text{aq})$ is concentration of gas i in solution, in terms of mole fraction; p_i is partial pressure of gas i in the gaseous phase (atm); and H_i is Henry's constant for constituent gas i at a specific temperature (atm). (Henry's constant may be expressed in units other than atm, consistent with its definition.) The mole fraction is:

$$x_i(\text{aq}) = \frac{n_i(\text{aq})}{n_w + n_i(\text{aq})} \quad (\text{C-26})$$

where $n_i(\text{aq})$ is moles of constituent gas i in solution, and n_w is moles of water. For dilute solutions Equation C-26 can be simplified to:

$$x_i(\text{aq}) = \frac{n_i(\text{aq})}{n_w} \quad (\text{C-27})$$

Henry's law is valid for dilute solutions at relatively low partial pressures. Gases that exhibit little chemical reaction with water generally satisfy the dilute solution condition. Henry's law applies to the subject gases of this text, when dissolved in water, at temperatures and pressures typical of the near-surface underground. Where several gases are dissolved simultaneously in water, Henry's law applies to each gas individually. Henry's law constants for several gases in water at 20°C are shown in Table C-2, and constants for a range of temperatures are shown in Table B-3.

Table C-2 Solubility of Gases in Water at 20°C

Gas	Henry's constant (atm)	Bunsen coefficient (ml(g)/ml(w))*	Mass concentration (ml(g)/L(w))
Methane	35690.	0.03479	24.93
Hydrogen sulfide	483.0	2.571	3957.
Carbon dioxide	1423.	0.8729	1726.
Nitrogen	78490.	0.01582	19.79
Oxygen	39830.	0.03118	44.55

* Gas volume at 0°C and 1 atm.

Source: Fogg and Gerrard 1991.

As an example of the application of Henry's law, consider a column of water in a thermally stratified lake. Surface waters contain little methane, due to the low partial pressure of methane in the atmosphere. Sediments and bottom waters are anoxic, as the result of limited water circulation. Anaerobic bacteria decomposing organic matter in sediments continuously generate methane. Methane molecules diffuse upward from the sediments into bottom waters. But molecular diffusion is a very slow process. If methane is generated faster than it can be dispersed by diffusion, the concentration of methane in bottom waters rises to a limiting value, at which time bubbles form. This excess methane will be removed by ebullition (boiling up). Bubbles form when the concentration of methane in bottom waters reaches that prescribed by Henry's law, for a partial pressure of methane equal to the sum of barometric pressure at the water surface and hydrostatic pressure at the bottom. For a lake 90 m deep and bottom waters at 20°C, the maximum concentration of methane that could exist, at the onset of bubble formation, is 0.25 g methane per L water, corresponding to a methane partial pressure of about 10 atm (1 atm barometric pressure + 9 atm hydrostatic pressure). Gaseous methane rising through the water column tends to go into solution in upper waters unsaturated with methane, but as a practical matter the bubbles rise too rapidly to be absorbed completely, and they escape to the atmosphere.

Consider another example: a column of water equal in depth to that described above, uniform in temperature, in which no gas is being generated or consumed. Gases in the atmosphere and in solution in water are in equilibrium. The concentration of nitrogen in bottom waters is the same as in surface waters, a function only of temperature and the partial pressure of nitrogen in the atmosphere. Note that under equilibrium conditions solubility is not a function of hydrostatic pressure.

Bunsen Solubility Coefficient

The Bunsen solubility coefficient is defined as the volume of gas held in a unit volume of solution, where the solution is in contact with a gaseous phase at a partial pressure of 1 standard atmosphere. The volume of gas in solution is expressed as a gaseous volume at 0°C and 1 standard atmosphere.

The Bunsen solubility coefficient can be derived from Henry's law. Assuming a dilute solution, the amount of water in moles is:

$$n_w = \frac{V_w \rho_w}{M_w} \quad (C-28)$$

where V_w is the volume of water, ρ_w is the mass density of water, and M_w is the molar mass of water. Substituting Equations C-27 and C-28 into Equation C-25 yields:

$$\frac{n_i(\text{aq}) M_w}{V_w \rho_w} = \frac{p_i}{H_i} \quad (\text{C-29})$$

According to the ideal gas law, n_i moles of gas would occupy a gaseous volume of:

$$V_i = \frac{n_i R T'}{H'} \quad (\text{C-30})$$

Solving Equation C-30 for n_i , substituting for $n_i(\text{aq})$ in Equation C-29, and rearranging terms:

$$\alpha = \frac{V_i}{V_w} = \frac{1}{H_i} \frac{p_i \rho_w}{p' M_w} R T' \quad (\text{C-31})$$

where α is the Bunsen solubility coefficient. By definition, the partial pressure p_i of the gaseous phase in contact with the solution is 1 atm, and the amount of gas in solution is expressed as a gaseous volume at $T' = 0^\circ\text{C}$ and $p' = 1 \text{ atm}$. Solving Equation C-31 for a solution of gas in water at 20°C :

$$\begin{aligned} \alpha &= \left(\frac{1}{H_i} \right) \left(\frac{1 \text{ atm}}{1 \text{ atm}} \right) \left(\frac{1.0 \text{ g}}{\text{ml}} \right) \left(\frac{\text{mol}}{18.015 \text{ g}} \right) \left(\frac{0.08206 \text{ L atm}}{\text{mol K}} \right) \\ &\times \left(\frac{1000 \text{ ml}}{\text{L}} \right) (273.15 \text{ K}) \\ &= \left(\frac{1}{H_i} \right) 1240 \text{ atm (at } 20^\circ\text{C)} \end{aligned}$$

where H_i is in atmospheres. Henry's constant for methane in water at 20°C is 35690 atm, so $\alpha = 0.0348 \text{ ml methane / ml water}$. Bunsen coefficients for several gases in water at 20°C are shown in Table C-2, and coefficients for a range of temperatures are shown in Table B-3.

If the gaseous phase in contact with water is at a partial pressure other than 1 atm, solubility can be calculated by multiplying the Bunsen coefficient by the partial pressure in atmospheres:

$$\frac{V'_i}{V_w} = p_i \alpha \quad (\text{C-32})$$

Solubility in Seawater

The solubility of gas in water declines with increasing dissolved minerals concentration. The average dissolved minerals concentration, or salinity, of seawater is

35 grams of minerals per kilogram of seawater. Bunsen solubility coefficients for gases in seawater are shown in Table B-4. Solubility of gases in saline waters other than average seawater can be calculated from the data of Tables B-3 and B-4 using the Setchénov equation:

$$\ln \alpha = b_1 + b_2 S \quad (\text{C-33})$$

where b_1 and b_2 are constants, and S is salinity. Given the solubilities for fresh water ($S = 0 \text{ g kg}^{-1}(\text{aq})$) and seawater ($S = 35 \text{ g kg}^{-1}(\text{aq})$), the constants b_1 and b_2 can be derived for a particular temperature, and solubility at other salinities obtained. Salinity is related to chlorinity (dissolved chloride concentration) by $S = 1.80655 Cl$, using consistent units among variables (Wooster, Lee, and Dietrich 1969).

Concentrations of Gases in Solution

The concentration of a gas in solution in water can be expressed on the basis of volume, amount, or mass. In each case the temperature and pressure should be specified. Natural solution concentrations of gas in groundwaters may be at, as well as below, saturation concentrations.

Volume-Based Concentrations

A common expression for solution concentrations in water is mass concentration, defined as:

$$\rho_i(\text{aq}) = \frac{m_i(\text{aq})}{V_s} \quad (\text{C-34})$$

where $\rho_i(\text{aq})$ is mass concentration, $m_i(\text{aq})$ is mass of gas (mg) in solution, and V_s is total volume of the solution.

Another volume-based unit is amount concentration:

$$c_i(\text{aq}) = \frac{n_i(\text{aq})}{V_s} \quad (\text{C-35})$$

where $c_i(\text{aq})$ is amount concentration, and $n_i(\text{aq})$ is amount of gas (mol) in solution. Amount concentration in mol L⁻¹ is termed *molarity*.

The Ostwald coefficient expresses the solution concentration as a gaseous phase volume at solution temperature and stated pressure:

$$L = \frac{V_i(\text{g})}{V_s} \quad (\text{C-36})$$

where L is Ostwald coefficient (ml L⁻¹). This is a convenient expression for use in calculating the volume of gas that may be released from groundwater inflowing

to an excavation, where water and air temperatures are similar. In this application, gaseous phase volume would be expressed at atmospheric pressure.

Volume-based concentrations of gases in water can generally be converted to mass-based units by assuming an aqueous solution density of 1 g ml⁻¹. The error introduced is negligible for solutions containing a dissolved solids concentration less than 7000 mg L⁻¹ (Hem 1985, p. 55). The actual density of water for a range of temperatures is shown in Table B-5.

The degree of saturation is

$$S_q = \frac{V_i}{V_{sat}} \times 100 \quad (\text{C-37})$$

where V_i is the volume of gas in solution, and V_{sat} is the solubility of the gas.

Amount-Based Concentrations

An amount-based concentration expression is the mole fraction $x_i(\text{aq})$, defined in Equations C-26 and C-27.

Mole fraction of a gas in solution in water is related to amount concentration (a volume-based expression) by:

$$x_i(\text{aq}) = \frac{c_i V_m(\text{w})}{1 + c_i V_m(\text{w})} \quad (\text{C-38})$$

where $V_m(\text{w})$ is the molar volume of water (18 ml mol⁻¹). This is an approximation based on the assumption that gas makes negligible contribution to solution volume. For normal gas solutions the error involved is minimal.

Mass-Based Concentrations

A mass-based concentration expression includes *molality*:

$$b_i = \frac{n_i}{m_w} \quad (\text{C-39})$$

where b_i is molality, and m_w is mass of water in kg.

Another mass-based expression is mass fraction:

$$w_i = \frac{m_i}{m_s} \quad (\text{C-40})$$

where w_i is mass fraction, m_i is mass of the constituent gas, and m_s is total mass of the solution.

Other mass-based fractional terms are “parts per thousand” (ppt) and “parts per million” (ppm or ppml), the number of grams of solvent per thousand or million grams of solution. For gases in fresh water, the ppm unit can be interchanged with mass concentration in mg L⁻¹ with minimal error. The ppt and ppm

terms for solutions will not be used in this text, to avoid confusion with the volume-based ppm term for gaseous mixtures.

VAPORS

A vapor is the gaseous form of a substance that commonly exists as a liquid (or solid) under normal conditions of temperature and pressure. On a molecular level, a vapor is identical to a gas. Vapor is formed from molecules that manage to escape the retentive intermolecular interactions of the liquid, through their higher-than-average kinetic energy and proximity to the surface. Evaporation rate is controlled by temperature and volatility of the liquid. Liquids held together by weak intermolecular forces of attraction, such as the light hydrocarbons of gasoline, vaporize readily.

Vapor is continually released from the surface of a liquid. If the liquid is in a tightly closed container, gas pressure over the liquid will gradually increase by contribution of the partial pressure of the vapor. Eventually an equilibrium will be reached where vaporized molecules are recaptured by the liquid at a rate equal to evaporation. Vapor pressure is defined as the partial pressure of the vapor over the liquid at equilibrium, at the existing temperature. If this equilibrium is upset by enlarging the volume available to the vapor, the partial pressure of the vapor will drop, the rate of condensation will decrease temporarily, and the partial pressure of the vapor will gradually increase to the vapor pressure of the liquid. The release of pressure observed upon opening a tightly closed container of gasoline is evidence of a buildup of vapor pressure. The vapor pressure of water is often accounted for in calculating partial pressures of gases over water. Vapor pressures for water and gasoline are shown in Tables B-6 and B-7.

A vapor behaves the same as a gas, provided that the vapor is separated from its source and the partial pressure of the vapor is below vapor pressure. If the partial pressure is brought to vapor pressure, by increasing total pressure or decreasing temperature, part of the vapor will condense into liquid and will be removed from the gaseous phase.

Volatile multi-constituent liquids such as gasoline generate multi-constituent vapors. The partial pressure of each constituent over liquid gasoline, at equilibrium and at moderate pressures, can be determined using *Raoult's law*:

$$p_i = x_i \times p_{vi} \quad (\text{C-41})$$

where x_i is mole fraction of the constituent in the liquid phase, and p_{vi} is vapor pressure of the pure constituent. The vapor phase over a multi-constituent liquid will be enriched in the most volatile constituents, compared to constituent concentrations in the liquid.

COMPOSITION OF NORMAL AIR

Normal air is that mixture of gases that surrounds the earth and constitutes an uncontaminated atmosphere. Dry air consists of about 78% nitrogen, 21% oxygen, and 0.9% argon (by volume). Other gases compose the remaining 0.1%. The composition of atmospheric air near the ground surface is shown in Table B-2. Concentrations of carbon dioxide and methane in the atmosphere have been increasing due to man's influences. The carbon dioxide concentration in 1996 was about 360 ppmv and is increasing at the rate of 1.8 ppm per year; the methane concentration was about 1.6 ppmv and is increasing at the rate of 0.015 ppmv per year (Meszaros 1993, Table 2.1; Brimblecombe 1996, Table 1.1).

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