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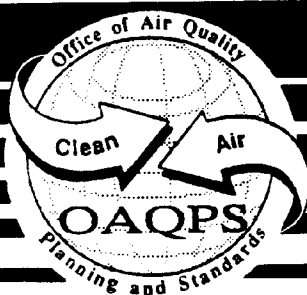
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Report to Congress on Hydrogen Sulfide Air Emissions Associated with the Extraction of Oil and Natural Gas



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HYDROGEN SULFIDE REPORT TO CONGRESS -- EXECUTIVE SUMMARY

Under section 112(n)(5) of the Clean Air Act (CAA), as amended, Congress required the Administrator of the United States Environmental Protection Agency (EPA) to carry out a study to assess the hazards to public health and the environment resulting from the emission of hydrogen sulfide (H_2S) associated with the extraction of oil and natural gas. The assessment must include a review of existing State and industry control standards, techniques, and enforcement. This report, developed in fulfillment of section 112 (n)(5), evaluates the hazards to the public and the environment posed by these emissions.

This study was added to the CAA by the Committee on Environment and Public Works, chaired by the late Senator Quentin N. Burdick of North Dakota, because of concern about the health and environmental hazards associated with H_2S emissions from oil and gas wells. Witnesses testified before Congress that these emissions resulted in deterioration of air quality, death and injury to livestock, and evacuation and hospitalization of residents located near the release point of such emissions.

Congress considered listing H_2S as a hazardous air pollutant (HAP) under section 112(b) of the CAA, which regulates industrial sources of routine emissions of HAPs. On the basis of information contained in accident records, it was determined that H_2S is a concern from an accidental release standpoint and it would be listed under the accidental release provisions in section 112(r) of the Act, and not under section 112(b). Substances regulated under 112(r) are known or may be anticipated to cause death, injury, or serious adverse effects to human health or the environment upon accidental release.

Hydrogen sulfide is produced in nature primarily through the decomposition of organic material by bacteria. It develops in stagnant water that is low in oxygen content, such as bogs, swamps, and polluted water. The gas also occurs as a natural constituent of natural gas, petroleum, sulfur deposits, volcanic gases, and sulfur springs. Natural sources constitute approximately 90 percent of the atmospheric burden of H_2S . Ambient air concentrations of H_2S due to natural sources are estimated to be between 0.11 and 0.33 ppb (0.15 and 0.46 $\mu g/m^3$).

H_2S is a colorless gas with an offensive odor characteristic of rotten eggs. H_2S is flammable and highly corrosive to metals. It is toxic and care should be exercised in its presence. There have been several incidences in the United States of deaths of workers exposed to H_2S gases. Other symptoms of exposure include irritation, breathing disorders, nausea, vomiting, diarrhea, giddiness, headaches, dizziness, confusion, rapid heart rate, sweating, weakness, and profuse salivation. Levels above 1.5×10^5 ppb are considered life threatening. Few studies exist measuring effects of natural or accidental exposure of wildlife to H_2S ; however, wildlife deaths have been reported in connection with blowouts (a sudden expulsion of gas or oil well fluids with great velocity).

Natural gas and oil formations may be composed of many gases. The largest volume and most beneficial gases in this composition are generally the light hydrocarbons (methane, ethane, propane, and butane). H_2S is the most common impurity in hydrocarbon gases. If an oil and gas formation contains H_2S , it is said to be "sour." Although a sour well's oil and gas can be sweetened by removing the H_2S after extraction, the well is always considered sour once H_2S is present.

Certain areas of the United States are especially prone to contain H_2S in oil and gas reservoirs at varying depths underground. Vulnerability zones have been characterized as 14 major H_2S prone areas found in 20 States. Texas has four discrete H_2S prone areas. Concentrations as high as 42 percent H_2S (by volume) have been found in gas from central Wyoming.

In the oil and gas industry, H_2S may be emitted or released during exploration, development, extraction, crude treatment and storage, transportation (e.g., pipeline), and refining. This report focuses on potential hazards of routine emissions and accidental releases of H_2S from the extraction and storage of crude oil and natural gas at well sites. Potential sources of emissions include flares/vapor incinerators, heater-treaters (an oil/water/gas separation device), storage tanks, equipment (valves, flanges, etc.), and both active and abandoned wells.

When H_2S is released to the air from an oil or gas well, several factors determine its possible effects on surrounding residents and the environment. Accidental releases of sour gas, such as from a well blowout or pipe rupture, are usually at high pressure and will entrain surrounding air. This causes significant, immediate dilution of the H_2S and other components of the gas, thereby reducing the potential magnitude of the consequences of the release. Factors such as chemical composition of the expelled gas, release rate, release orientation, topography and meteorological conditions also determine the effects of such a release.

Human fatalities from H_2S exposure from oil wells in the United States have virtually all been work-related. Significant public impacts are rare although evacuations have been initiated in response to accidental releases and at least one case of loss of consciousness has been reported as a result of exposure.

Eighteen states have developed ambient air quality guidelines for H_2S . Most, however, do not collect continuous data but rather only monitor for H_2S when a complaint is made. These guidelines range from 160 ppb per 24-hr averaging time to 14 ppb per 24-hr averaging time. Little data exist to determine actual levels of H_2S near oil and gas extraction sites. North Dakota was the only State found to have a continuous record of H_2S atmospheric levels at several sites. Exceedences of the North Dakota air quality standard have been minimal in recent years at these monitoring locations. No specific H_2S environmental (i.e., ecological) protection standards were found to exist. Some States require notification of the regulatory authority upon accidental release of H_2S from oil and

gas wells but few maintain an inventory of such incidences. Reporting of routine emissions (emissions of small quantities from equipment, pipelines, flares, and storage tanks) was not required by the States reviewed in this report.

H₂S is regulated under a number of United States statutes. It is listed as a hazardous substance under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). It is listed under the Emergency Planning and Community Right-to-Know Act (EPCRA) for emergency planning and preparedness, community right-to-know reporting, and toxic chemical release reporting. The Occupational Safety and Health Administration (OSHA) has established General Industry Standards that list worker exposure concentration limits, and Respirator Standards. The National Institute for Occupational Safety and Health (NIOSH) has produced a criteria document containing recommendations for safe worker exposure levels and work practices. The United States EPA has the potential for regulation of new oil and gas well sources through the Prevention of Significant Deterioration (PSD) program and, as mentioned previously, H₂S is listed under the CAA section 112(r) accidental release provisions.

Other standards for worker and public protection from H₂S emissions come from the Bureau of Land Management, Minerals Management Service, and the American Conference of Governmental Industrial Hygienists.

The oil and gas production industry has guidelines for safe practices regarding H₂S. The American Petroleum Institute, an industry-wide technical organization, has published six documents regarding H₂S in the industry. They pertain to safety practices for drilling, operation, and equipment.

Findings and Recommendations

As a result of this study, EPA finds that the potential for human and environmental exposures from routine emissions of H₂S from oil and gas wells exists, but insufficient evidence exists to suggest that these exposures present any significant threat. On the other hand, an accidental release of H₂S from an oil or gas well could have severe consequences because of its toxicity and its potential to travel significant distances downwind under certain circumstances. The likelihood (and thus the risk) of an accidental release of H₂S or any other hazardous substance, can be greatly reduced if facility owners/operators exercise the general duty and responsibility to design and operate safe facilities and if they comply with existing industry standards and practices, existing regulations, and future guidance and regulations. Such actions should result in: (1) the safe management of H₂S and other hazardous substances with an emphasis on accident prevention; (2) the preparedness to properly and quickly respond to chemical emergencies and to provide specialized medical treatment if necessary; and (3) community understanding of the risks involved. Industry should ensure that H₂S is safely handled and that accidental releases are prevented; that any releases that do occur are quickly discovered, controlled, and mitigated; and that workers and the community are informed and prepared to properly respond to a H₂S emergency.

From the limited data available, there appears to be no evidence that a significant threat to public health or the environment exists from routine emissions from sour oil and gas wells. States and industry are encouraged to evaluate existing design, construction, and operation principles within the framework of process safety management. EPA recommends no further legislation pertaining to routine H₂S emissions or accidental releases from oil and gas wells at this time. However, the Agency does recommend that the owner/operators of oil and gas extraction conduct drills and exercises with workers, the community, first responders, and others to test mitigation, response, and medical treatment for a simulated H₂S accident. Sour oil and gas extraction facilities should be able to rapidly detect, mitigate, and respond to accidental releases in order to minimize the consequences. The Agency will continue to investigate the need for additional rulemaking under the accidental release prevention provisions of the Clean Air Act.

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CHAPTER I INTRODUCTION

STATUTORY REQUIREMENTS

Section 112(n)(5) of the Clean Air Act (CAA or Act), as amended in 1990, requires the Environmental Protection Agency (EPA) "to assess the hazards to the public and the environment resulting from the emissions of hydrogen sulfide (H_2S) associated with the extraction of oil and natural gas resources." This assessment must reflect consultation with the States and shall include a review of State and industry control standards, techniques, and enforcement. To avoid duplication of work by other EPA offices, the assessment must build upon a report from the Office of Solid Waste conducted under Section 8002(m) of the Solid Waste Disposal Act. The Section 8002(m) study is a three-volume report to Congress entitled *Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* (1987).

The EPA Administrator is required by the Act to report to Congress with the findings of the assessment along with any recommendations. Moreover, under Section 112(n)(5) (or 42 U.S.C. 7412(n)(5)), the Administrator "shall, as appropriate, develop and implement a control strategy for emissions of hydrogen sulfide to protect human health and the environment."

This study was added to the Act by the Committee on Environment and Public Works chaired by the late Senator Quentin N. Burdick of North Dakota. The study was included in the Act because of concern about the health and environmental hazards associated with H_2S emissions from oil and gas wells. In 1987, Congress received testimony in which witnesses urged that H_2S should be listed as a hazardous air pollutant under the provisions of Section 112 of the Clean Air Act. The witnesses testified that lack of emission controls resulted in significant deterioration of air quality. There was also testimony that H_2S releases from oil and gas facilities caused death and injury to livestock and required the evacuation and hospitalization of residents from affected areas.

Congress considered listing H_2S as a hazardous air pollutant (HAP) under Section 112(b), which regulates industrial sources for routine emissions of HAPs. On the basis of information contained in accident records, it was determined that H_2S is a concern from an accidental release standpoint and should be listed under the accidental release provisions in Section 112(r) of the Act. The substances regulated under Section 112(r) are known or may be anticipated to cause death, injury, or serious adverse effects to human health or the environment from accidental releases. Under the provisions of Section 112(r) of the Act, the EPA must develop a list of at least 100 substances that pose the greatest risk from accidental releases. The Act listed 16 chemicals, including H_2S , which must be included in the Section 112(r) list.

A clerical error led to the inadvertent addition of H₂S to the Section 112(b) list of HAPs. However, a Joint Resolution to remove H₂S from the Section 112(b) list was passed by the Senate on August 1, 1991, and the House of Representatives on November 25, 1991. The Joint Resolution was approved by the President on December 4, 1991. It should be emphasized that the purpose of this report is not to examine whether or not H₂S should be included in the Section 112(b) list.

SCOPE OF REPORT

The scope of this report is determined by the Congressional directive found in Section 112(n)(5), which is quoted in its entirety in Exhibit 1. For clarity, the Agency has designed the report to respond to specific items in the directive within separate chapters or sections of chapters. It is important to note that although all issues relevant to this study have been weighed in arriving at the conclusions and recommendations of this report, no single issue has a determining influence on the conclusions and recommendations.

The directive in Section 112(n)(5) is expanded upon in the paragraphs below. Detailed methodologies used to analyze and respond to the directive can be found later in this report and in the supporting documentation and appendices. The principal components of the Congressional mandate are:

- 1. Review existing State and industry control standards, techniques, and enforcement programs.**

Currently, there are no Federal ambient air quality standards for H₂S. Most oil- and gas-producing States have their own regulations and enforcement programs. Some States, such as some hosting major producers, have large H₂S programs in place. However, the risk may exist in States that do not have large programs simply because of the lack of State regulatory overview. Although Occupational Safety and Health Administration (OSHA) standards exist that are applicable to oil and gas production, there are no industry-specific standards. However, the industry has developed recommended practices and technologies to reduce the potential for H₂S emissions.

Current State regulations regarding H₂S emissions from the extraction of oil and gas are summarized in this report, with emphasis on four oil-producing States—California, Michigan, Oklahoma, and Texas. Industry safety procedures as well as regulations promulgated and proposed by OSHA and other Federal regulatory programs are reviewed.

- 2. Assess the hazards to public health and the environment resulting from the emission of H₂S associated with extraction of oil and natural gas resources.**

Hydrogen sulfide is a colorless gas almost as toxic as hydrogen cyanide and 5 to 6 times more toxic than carbon monoxide. The principal threat of H₂S gas to human life is poisoning by inhalation (Dosch and Hodgson, 1986). Over the years, there have been

112(n)(5) Hydrogen Sulfide.— The Administrator is directed to assess the hazards to public health and the environment resulting from the emission of hydrogen sulfide associated with the extraction of oil and natural gas resources. To the extent practicable, the assessment shall build upon and not duplicate work conducted for an assessment pursuant to section 8002(m) of the Solid Waste Disposal Act and shall reflect consultation with the States. The assessment shall include a review of existing State and industry control standards, techniques, and enforcement. The Administrator shall report to the Congress within 24 months after the date of enactment of the Clean Air Act Amendments of 1990 with the findings of such assessment, together with any recommendations, and shall, as appropriate, develop and implement a control strategy for emissions of hydrogen sulfide to protect human health and the environment, based on the findings of such assessment, using authorities under this Act including sections 111 and this section.

Exhibit 1. 1990 Clean Air Act Amendments: Mandate for a Report to Congress on H₂S Emissions Associated with Oil and Gas Extraction.

incidents involving exposure to H₂S resulting from accidental releases from oil and gas extraction facilities that have caused death or injury to humans or animals (Layton, D.W., et al; Texas Oil and Gas Pipeline Corporation).

Oil and gas extraction, as defined in this study (see Appendix A), includes only the activities involved in removing oil and/or gas from an established (developed) well. This report includes not only a review of oil and gas extraction, but also other associated components of oil and gas extraction such as piping to a separator, separation, and storage. However, in following the Congressional mandate to address extraction, this report does not cover activities primarily associated with exploration or well development, nor does it cover sources such as gas processing plants. It is noteworthy that these plants are potential sources of H₂S releases since one of their functions is to remove impurities such as produced water, H₂S and/or carbon dioxide. Personnel at these plants are trained in H₂S safety. However, this operation falls outside the definition of extraction.

In addition to assessing the sources of H₂S emissions in the extraction industry, this report discusses related control technologies as well as the health and environmental effects associated with exposure to accidental H₂S releases and routine H₂S emissions during extraction and closely associated production activities. When possible, monitored ambient air concentrations of H₂S and cases of death or injury to humans, wildlife, and/or livestock from exposure to H₂S releases and emissions are documented.

The report culminates with a hazard assessment of H₂S routine emissions and accidental releases from oil and gas extraction activities based on information obtained in the efforts described in the previous paragraphs. Past and potential hazards from both routine emissions and accidental releases are identified, the degree of hazard is assessed, and potentially exposed human and ecological populations are identified.

3. **Recommend and, as appropriate, develop and implement a control strategy for H₂S emissions to protect human health and the environment, based on the findings of such assessment, using authorities under this act including sections 111 and 112.**

As stated in a 1987 Senate report on the Clean Air Act Amendments, "Although many State [H₂S regulatory] programs are implemented conscientiously, in some instances concerns have been raised that some oil- and gas-producing States may not be enforcing their regulatory programs sufficiently or may have deficient regulatory programs. The purpose of this subsection is to assess the effectiveness and the level of enforcement of various hydrogen sulfide control programs. The assessment should assure more uniform application of control technology, standards and enforcement. The Administrator should examine in particular means of preventing accidental releases of hydrogen sulfide at remote facilities" (U.S. Senate, 1987). [EPA identifies and reviews current State and Federal regulatory programs and industry-recommended procedures to reduce routine emissions and accidental releases. However, the ability to assess the effectiveness of these programs is limited by the lack of

available emissions-monitoring data and the limited information available on accidental release incidents.]

In this report, EPA makes recommendations regarding the release of H₂S from oil and gas extraction activities. The recommendations presented in this report do not constitute a regulatory determination. The Agency is, in several important areas, presenting optional approaches involving further research and consultation with the States and other affected parties.

ORGANIZATION OF REPORT

This report addresses two forms of H₂S losses to the atmosphere: routine emissions and accidental releases. (These terms are defined in the Glossary and examples are provided in Chapter II.)

Chapter II provides an overview of H₂S formation in oil and natural gas deposits and its presence in numerous industries. Potential sources of routine emissions and accidental releases from the oil and natural gas extraction industry are identified along with their causes. Chapter III is a hazard assessment of H₂S losses from oil and gas wells. It contains information on the nature of hydrogen sulfide's hazardous properties; exposure and consequence analyses for routine emissions and accidental releases; protective guidelines, prevention, mitigation, and emergency response procedures; and a characterization of land use around wells and of affected human populations and environmental settings. Chapter IV reviews and evaluates current State, Federal, and industry-recommended procedures related to H₂S in the oil and natural gas extraction industry. At the end of both Chapters III and IV are lists of findings to provide the reader with a condensed summary of key information identified during the development of this report. Chapter V completes the report with EPA recommendations regarding routine emissions and accidental releases of H₂S from oil and gas extraction operations.

This report contains a glossary of terms commonly used, and three appendices providing:

- background information on oil and gas production;
- subjects of State H₂S regulations and guidelines; and
- atmospheric dispersion calculations for accidental H₂S releases.

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CHAPTER II

HYDROGEN SULFIDE FORMATION AND ITS ROLE IN OIL AND GAS PRODUCTION

OVERVIEW

Petroleum oil and natural gas originate in organic-rich sedimentary source rocks composed of decayed marine algae and bacteria and terrestrial plants. In rock formations, temperature increases with depth. The organic matter (kerogen) in sedimentary rock is thermally converted to oil and gas at a specific temperature and migrates from the source rock formation into a reservoir, or trap, formed by less porous cap rock, usually shale. Once the well has been drilled into the reservoir, the oil and gas flow through the interconnected pore spaces to the well.

Natural gas may be composed of many gases. Only a few of these gases are typically found in large concentrations. The largest volume and most beneficial gases in natural gas are the light hydrocarbons (methane, ethane, propane and butane). Other gases that may occur in large concentrations are carbon dioxide, nitrogen, and hydrogen sulfide. H_2S is the most common impurity in hydrocarbon gases.


H_2S is generated under reducing conditions from high-sulfur kerogens or oils and is most commonly formed in sedimentary rock formations such as limestone (calcite or calcium carbonate). H_2S can also be generated from hydrocarbon reactions with sulfates in carbonate rock formations containing anhydrites. Oil and gas formations that do not contain H_2S are called "sweet." Oil and gas formations that contain H_2S are described as "sour." Sour gas is defined by the U.S. EPA as natural gas with an H_2S concentration greater than 0.25 grains per 100 cubic feet (GRI, 1990). Others have defined sour gas as having H_2S concentrations greater than 1.0 grain per 100 cubic feet (Amyx, Bass, and Whiting, 1960) or greater than 2 percent (Curtis and Showalter, 1989). The American Petroleum Institute recommends special practices (described in Chapter IV) for sour gas when the natural gas's total pressure is greater than or equal to 65 psia (448 kPa) and the partial pressure of H_2S in the gas is greater than 0.05 psia (0.34 kPa) (API, 1987). It is not known how many sour wells exist in the United States. Sweet oil wells can become sour due to the introduction of sulfur-reducing bacteria during enhanced oil recovery injection. Once an oil or gas field becomes sour, it cannot be made sweet again. However, after extraction from the well, the oil and gas can be sweetened by processing to remove H_2S , and this is a common procedure.

In relatively low concentrations, H_2S has a strong rotten-egg odor (Landes, 1953). However, the sense of smell rapidly becomes fatigued and cannot be relied on to warn of the continuous presence of H_2S . In fact, high concentrations of H_2S may cause a loss of smell. Concentrations of H_2S in crude oil vary greatly. In California alone, the Shiells Canyon oil field measures only 6×10^4 ppb of H_2S , while the Santa Maria Valley oil field has reported H_2S concentrations of 2.7×10^7 ppb (27 percent by weight) (Dosch and Hodgson, 1986).

Table II-1. Physical/Chemical Properties of H₂S

Chemical Formula: H₂S

Molecular Structure:



Molecular Weight: 34.08

Boiling Point: -60.33 °C (-76.59 °F)

Specific Gravity (H₂O=1): 0.916 at -60 °C (-76 °F) (Liquid) 1.54 g/L vapor at 0 °C (32 °F)

Vapor Pressure: 20 atmospheres at 25.5 °C (77.9 °F)

Melting Point: -85.49 °C (-121.9 °F)

Vapor Density (AIR=1): 1.19

Solubility in Water: 1 gram dissolves in 242 mL at 20 °C (68 °F)

Flammable Limits: Lower Explosive Limit - (4.3 x 10⁷ ppb)
Upper Explosive Limit - (45.5 x 10⁸ ppb)

Odor Threshold: 20 ppb^a

Olfactory Fatigue Level: 1 x 10⁵ ppb^a

Conditions or Materials to Avoid: Avoid physical damage to containers; sources of ignition; and storage near nitric acid, strong oxidizing materials, and corrosive liquids or gases (NFPA, 1978). Hydrogen sulfide is incompatible with many materials, including strong oxidizers, metals (NIOSH/OSHA, 1978, p. 112), strong nitric acid, bromine pentafluoride, chlorine trifluoride, nitrogen triiodide, nitrogen trichloride, oxygen difluoride, and phenyl diazonium chloride (NFPA, 1978).

Hazardous Decomposition or Byproducts: When heated, it emits highly toxic fumes of oxides of sulfur (Sax, 1984, p. 1552)

Source: U.S. EPA, 1993.

^aNIOSH, 1977.

Hydrogen sulfide is also called hydrosulfuric acid, sulfurated hydrogen, sulfur hydride, rotten-egg gas, swamp gas, and stink damp. Table II-1 lists some of the chemical and physical properties of H_2S . It is colorless, has a very low odor threshold, and being more dense than air, it tends to settle to the ground when released to the atmosphere as a pure gas (NIOSH, 1977). H_2S oxidizes to form sulfur dioxide (SO_2).

Exposure to H_2S is one potential health and environmental concern associated with extraction and related operations. H_2S is found in Paleozoic carbonates in the Rockies, Mid-Continent, Permian Basin, and Michigan and Illinois Basins (GRI, 1990). Figure II-1 shows the areas of naturally occurring H_2S . The Gas Research Institute reported in 1990 that H_2S can often occur in association with carbon dioxide (CO_2) within the deep portions of a basin and can comprise more than 30 percent of the composition.

Among the natural gas deposits in the United States, large deposits in central and north-central Wyoming, in western Texas, in southeastern New Mexico, and in Arkansas were singled out as rich in H_2S . The Health Effects Research Laboratory (HERL) also reported that H_2S concentrations as high as 42 percent may be present in gas from central Wyoming. According to the *Wyoming State Review* (1991), released by the Interstate Oil and Gas Compact Commission (IOGCC), gas reserves in Wyoming were estimated to be approximately 11 trillion cubic feet. The IOGCC also reported that the reserves of liquid hydrocarbons found in western Wyoming are approximately 5 percent H_2S . Fifty percent of the oil produced in Wyoming in 1989 was reported to be sour.

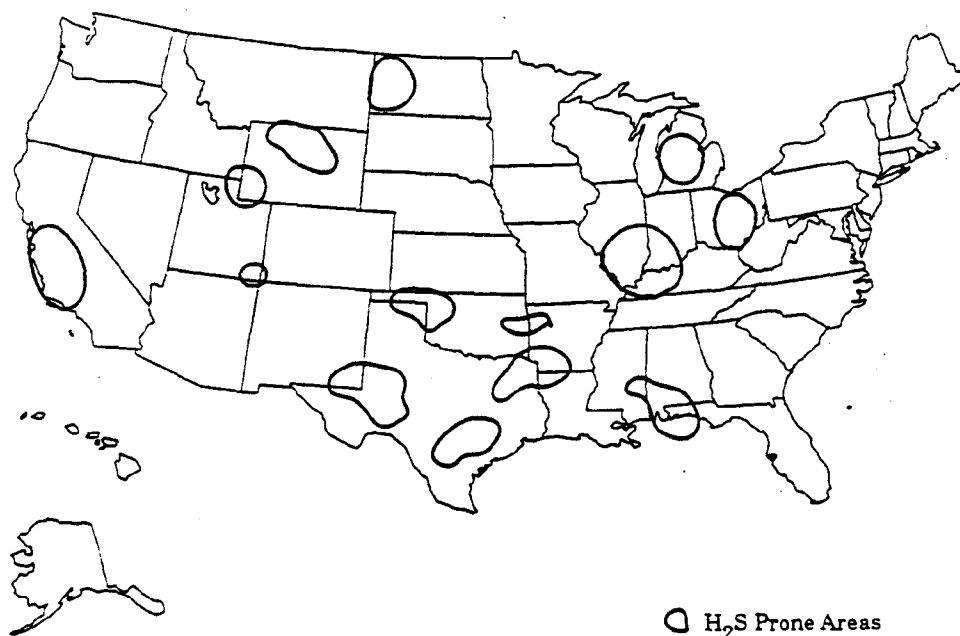
HYDROGEN SULFIDE IN INDUSTRY

Hydrogen sulfide has been cited as a potential hazard for approximately 125,000 employees in 73 industries (U.S. EPA, 1993). Industries with a potential exposure are listed in Table II-2. The health effects of H_2S were recognized in the petroleum industry more than 50 years ago with the discovery of large deposits of high-sulfur oil in the United States (Davenport, 1945). In the oil and gas industry, H_2S may be emitted or released during exploration, development, extraction, crude treatment and storage, transportation (e.g., pipeline transmission), and refining. This report focuses on potential hazards of H_2S routine emissions and accidental releases from the extraction and storage of crude oil and natural gas.

POTENTIAL H_2S EMISSION SOURCES IN THE OIL AND NATURAL GAS EXTRACTION INDUSTRY

Appendix A provides a general overview of the oil and gas extraction industry. Both the exploration/development and extraction sectors of the industry are described along with production data for recent years.

Hydrogen sulfide (H_2S) complicates oil and gas extraction operations because of its toxic effects and its corrosive properties. H_2S exists as a gas at atmospheric pressure, but it



Source: Gas Research Institute. 1990.

Figure II-1. Major H₂S prone areas.

Table II-2. Occupations with Potential H₂S Exposure

| | |
|--------------------------------------------------|-----------------------------------------------|
| Animal fat and oil processors | Lithopone makers |
| Animal manure removers | Livestock farmers |
| Artificial-flavor makers | Manhole and trench workers |
| Asphalt storage workers | Metallurgists |
| Barium carbonate makers | Miners |
| Barium salt makers | Natural gas production and processing workers |
| Blast furnace workers | Painters using polysulfide caulking compounds |
| Brewery workers | Papermakers |
| Bromide-brine workers | Petroleum production and refinery workers |
| Cable splicers | Phosphate purifiers |
| Caisson workers | Photoengravers |
| Carbon disulfide makers | Pipeline maintenance workers |
| Cellophane makers | Pyrite burners |
| Chemical laboratory workers, teachers, students | Rayon makers |
| Cistern cleaners | Refrigerant makers |
| Citrus root fumigators | Rubber and plastics processors |
| Coal gasification workers | Septic tank cleaners |
| Coke oven workers | Sewage treatment plant workers |
| Copper-ore sulfidizers | Sewer workers |
| Depilatory makers | Sheepdippers |
| Dyemakers | Silk makers |
| Excavators | Slaughterhouse workers |
| Felt makers | Smelting workers |
| Fermentation process workers | Soapmakers |
| Fertilizer makers | Sugar beet and cane processors |
| Fishing and fish-processing workers | Sulfur spa workers |
| Fur dressers | Sulfur products processors |
| Geothermal-power drilling and production workers | Synthetic-fiber makers |
| Glue makers | Tank gagers |
| Gold-ore workers | Tannery workers |
| Heavy-metal precipitators | Textiles printers |
| Heavy-water manufacturers | Thiophene makers |
| Hydrochloric acid purifiers | Tunnel workers |
| Hydrogen sulfide production and sales workers | Well diggers and cleaners |
| Landfill workers | Wool pullers |
| Lead ore sulfidizers | |
| Lead removers | |
| Lithographers | |

Source: NIOSH, 1977.

is soluble in oil and water. As a result of this solubility, H_2S can enter the environment by a variety of pathways. It can enter the atmosphere as a result of releases of gas containing H_2S or as a result of venting tanks or vessels which contain or have contained oil or water with significant concentrations of H_2S . Waters in the general environment can become contaminated with H_2S by contact with either gaseous plumes or waters that contain H_2S .

The potential sources of H_2S emissions associated with oil and gas extraction are summarized in Table II-3.

Routine emission sources may include—

- inefficient air emission control devices
- tank venting due to diurnal temperature changes;
- volatilization;
- generation by sulfur-reducing bacteria in oil deposits; and
- migration through poorly plugged wells.

Potential accidental release sources include —

- equipment failures, e.g., valves, flanges;
- piping ruptures due to corrosion, embrittlement, or stress; and
- venting due to unanticipated pressure changes.

Background information on these potential sources is provided in Appendix A.

The crude oil and natural gas industries use a large number of similar yet distinct industrial processes that together serve a common purpose: to remove hydrocarbons from subterranean deposits of oil and gas and to produce marketable products for industrial, commercial, and residential use. Figure II-2 shows the basic components of a typical oil and gas production operation. From the wellhead, the oil/gas mixture is piped to an oil/gas separator. Oil/water emulsions and mixtures are then transferred to a heater-treater, which separates the oil from the water. The treated crude oil is next piped to storage tanks, and the produced water is piped to a holding tank prior to further treatment and/or disposal. An emergency pit (a wastewater basin) is also provided. Each of these operations, as well as other equipment found at a well site, may be a source of H_2S in sour oil and gas operations.

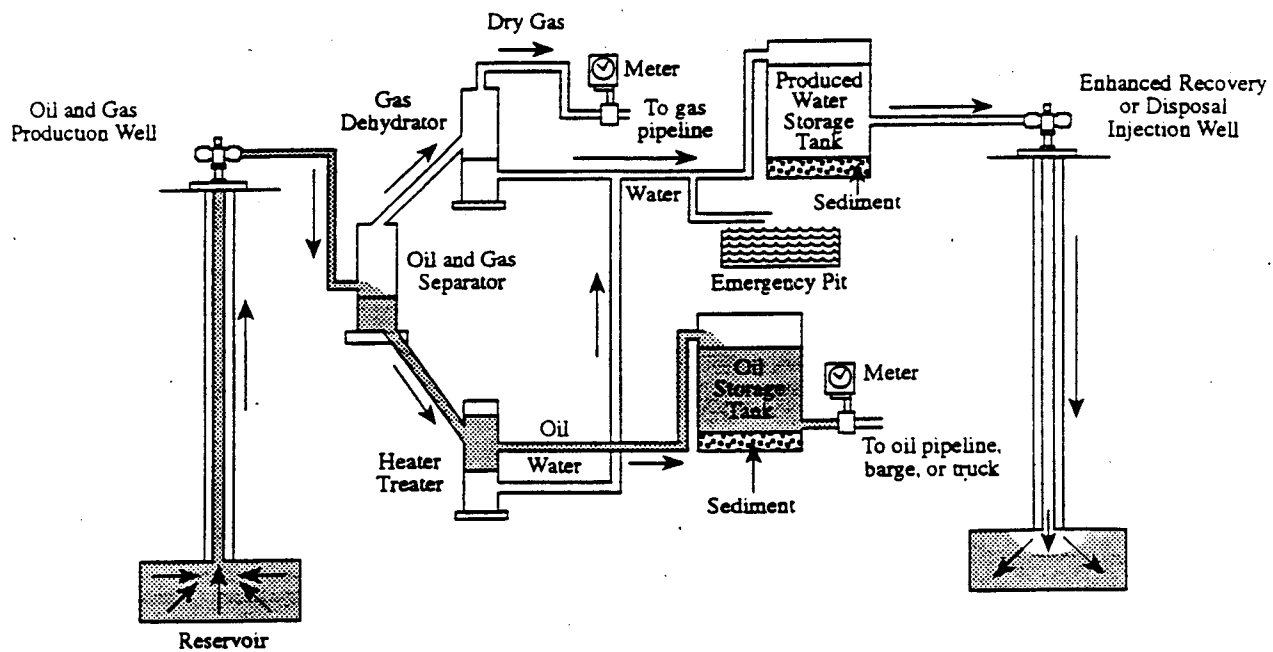
Oil and Gas Production Operations

Crude Oil

In the crude oil production process, releases or emissions of H_2S to the environment may occur from a variety of sources, including wellheads, piping, flares, separation devices, storage vessels, and pumps.

**Table II-3. Examples of Potential Routine H₂S Emission Sources and
Accidental H₂S Release Sources from Sour Oil and Gas Extraction**

| Source | Mechanism | Cause |
|-----------------------------------------------------------|----------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Flares/vapor incinerators | Incomplete combustion | Design; lack of maintenance |
| Heater-treaters | Pressure change, high pressure | Pressure above design specifications |
| Crude oil storage tanks | Diurnal temperature change; filling operations; volatilization | Lack of controls; design |
| Water storage vessels | Volatilization; sulfur-reducing bacteria | Lack of controls; design |
| Equipment (valves, flanges, etc.) Oil/gas separator | Corrosion and embrittlement | Reaction of water with metal and H ₂ S; lack of maintenance; poor materials |
| Well plugging | Migration from well bore to atmosphere | Improper plugging |



Source: U.S. EPA, 1987.

Figure II-2. Typical extraction operation showing separation of oil, gas, and water.

Flares are connected to points in the system where gas might be directed in case of an operating problem. Subject to regulatory approval, flares may also burn gases that cannot be sold. The gases are vented up a tall vertical pipe and then ignited at the top of the pipe, releasing heat and combustion products. Flares are connected to production vessel pressure-relief valves, rupture disks, and tank vents, among other places. Few data are available on the efficiency of flares used in a crude oil production setting; however, the operating efficiency of a common flare, regardless of industry application, is about 95 to 99 percent (personal communication, Donelson, Texaco, 12/9/92). The combustion product of H_2S is sulfur dioxide (SO_2). Incomplete combustion from flares is one possible source of H_2S emissions, and actual pollutant emissions vary depending on the combustion efficiency of the flare.

Devices, such as heater-treaters, break down water/oil emulsions or mixtures. These devices operate under pressure and do not normally emit H_2S . However, H_2S may be released in accidental situations when the vessel becomes subjected to pressures above design specifications. The pressure relief valve or a rupture disk will open in a high-pressure situation, and the gas will be sent through these openings via pipeline to a flare (personal communication, Donelson, Texaco, 12/9/92).

H_2S can potentially be emitted by two processes from vessels used to store water produced during extraction:

- Dissolved H_2S may be contained in the produced water and brought up from the reservoir. Pressure reductions from subsurface to surface change the solubility of H_2S in water and can release some H_2S from solution.
- H_2S may be produced by the action of sulfate-reducing bacteria in some aqueous and oil media. Biocides are used to kill these bacteria and eliminate H_2S formation.

Tanks storing crude oil are another potential source of H_2S emissions. H_2S can be discharged to the atmosphere from a storage tank as a result of diurnal temperature change, filling operations, and volatilization. The process of filling oil-transport vessels is another potential source of H_2S emissions. As the crude oil is loaded, gases containing the pollutant are displaced to the atmosphere. If the gas amounts do not warrant repressuring into the gas sales line, a flare may operate to burn the gas given off (personal communication, Donelson, Texaco, 12/9/92). There have been several accidents involving tanks that have H_2S in them. This is typically a worker safety issue.

Pumps that move the oil during the extraction process can leak oil at the seals between the moving shaft and the stationary casing, causing a possible release of H_2S .

Natural Gas

Two additional items in natural gas extraction can contribute emissions and releases of sulfur compounds into the atmosphere: (1) equipment failure (e.g., leaks and ruptured pipes) due to corrosion or embrittlement, and (2) improperly plugged wells.

Equipment Failure. H_2S can attack the crystalline matrix of the steel, leading to embrittlement and cracking of the steel, which could, in turn, lead to possible leakage of H_2S . This embrittlement is invisible and can occur in a short period of time. Corrosion, which is caused by chemical reactions of metal with water and H_2S , can also cause H_2S leakage. Because of the corrosive nature of H_2S in the presence of water, oil and gas operations take precautions to remove water from gas streams containing H_2S . The National Association of Corrosion Engineers has a "Standard Material Requirement" entitled "MR-0175-92, Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment" which describes corrosion prevention measures. Corrosion resistant materials, coatings, and chemical corrosion inhibitors may be used to prevent equipment failure and gas releases where H_2S and other corrosives are known to be present (personal communication, Donelson, Texaco, 12/9/92). This type of accidental release is discussed in greater detail in Chapter III.

Well Plugging. Improper well plugging may also be a potential source of H_2S emissions. After all of the recoverable natural resources have been removed from a well, it must be properly plugged to avoid degradation of groundwater and surface water. Plugging involves placing cement within a wellbore at specific intervals to permanently block the possible migration of formation fluids containing H_2S . Improper plugging may allow H_2S (if present) to migrate out of the wellbore and into the atmosphere. Well plugging is regulated by the individual states. Plugging bonds are posted and procedures are subject to the regulatory agency's approval and on-site witness (personal communication, Donelson, Texaco, 12/9/92). This type of accidental release is also discussed in Chapter III.

Stripper Wells

Stripper wells are defined in Appendix A as producing at most 10 barrels of oil per day or 100 thousand cubic feet of gas per day. The owners or operators of these wells are typically smaller producing companies. Although stripper wells are often in remote areas, many are not completely isolated from the public. The potential exists for livestock, wildlife, or humans to come into contact with high levels of H_2S from stripper wells due to routine emissions and accidental releases. Although these wells are a potential hazard, no data were available on the number of sour stripper wells in the United States.

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CHAPTER III

HAZARD ASSESSMENT OF OIL AND GAS WELLS

INTRODUCTION

Objective

The objective of this chapter is to evaluate the potential hazards to public health and the environment resulting from routine emissions and accidental releases of hydrogen sulfide (H_2S) from oil and gas production, i.e., extraction; piping to a separator; oil, gas, and water separation; and associated storage.

Focus of Assessment

This hazard assessment was performed in two parts. First, existing H_2S ambient air monitoring data were compared to studies of human health and environmental effects to determine whether the H_2S concentrations measured from routine emissions have potentially harmful effects. Second, the threat of accidental releases was assessed by identifying past accidents and their impacts, reviewing atmospheric dispersion analyses (i.e., modeling) of accidental release scenarios in the literature, and conducting additional analyses. The result is an assessment of whether routine emissions and accidental releases are at levels that would require a national control strategy. In addition, this assessment identifies the hazards of H_2S , recommended protective levels, and the areas of the United States potentially vulnerable to routine emissions and accidental releases of H_2S .

Scope and Limitations

This hazard assessment addresses hydrogen sulfide emissions and releases that may potentially originate from a range of sources beginning with oil and gas wells (after well development) up through their associated treatment processes, storage units, and piping. However, it does not include gas processing or oil refining plants. For the potential H_2S emission sources described in Chapter II, non-occupational health impacts are considered along with environmental impacts (i.e., wildlife, livestock, and vegetation). For wildlife and livestock, the assessment includes animals that may be exposed to H_2S when they wander onto the well site.

For routine H_2S emissions, this hazard assessment is limited by the lack of data available on ambient air quality around well sites. Only a small amount of ambient monitoring data collected by States was identified. In addition, no national statistics on the health and environmental effects of chronic H_2S exposure exist. Nor are national statistics on the frequency and severity of accidental H_2S emissions or releases available. Only case records were located for the assessment of accidental releases. Therefore, the conclusions drawn from this assessment are based primarily on predictive modeling of accidental releases

and on a semi-quantitative comparison of ambient monitoring data and non-specific health effects data.

Hazard Assessment Steps

This hazard assessment was divided into three major parts:

- **Hazard Identification**
- **Exposure Analysis**
- **Consequence Analysis**

Figure III-1 displays the various components of this assessment.

The first step in this assessment was hazard identification. It entailed collecting information on the physical and chemical properties of H_2S and its location in the United States as it occurs (1) naturally in petroleum deposits, and (2) where it has been generated by sulfur-reducing bacteria that are introduced by enhanced oil recovery processes. The primary component of hazard identification is determining hydrogen sulfide's hazardous properties: ignitability, corrosivity, explosivity, and toxicity to human health and the environment.

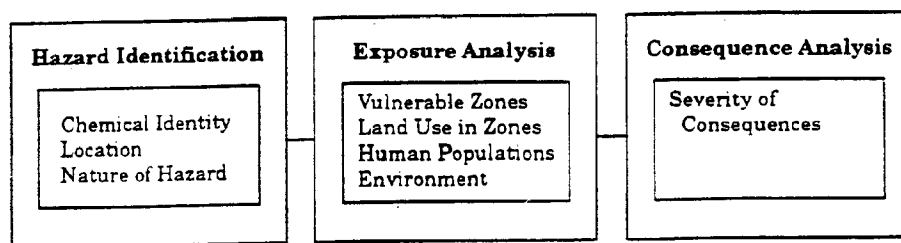
The second step, exposure analysis, included identification of the H_2S prone areas for H_2S exposure in the United States and the human and ecological populations expected to be in these zones. The final part of the assessment, consequence analysis, was an examination of H_2S routine emissions and accidental releases occurring at oil and gas wells and the severity of the consequences.

Since this report examines routine emissions and accidental releases separately, this chapter first presents hazard identification, which is the same for both routine and accidental releases. Next, routine exposure and its consequences are discussed. Finally, exposure to accidental releases and its consequences are presented.

HAZARD IDENTIFICATION

Chemical Identity

Hydrogen sulfide is a colorless, flammable gas which, in low concentrations, has a characteristic odor of rotten eggs. It is a frequent component of crude oil and natural gas. Hydrogen sulfide gas has the Chemical Abstracts Services (CAS) registry number 7783-06-4; its physical and chemical properties are summarized in Table II-1.



Adapted from: U.S. EPA, 1987.

Figure III-1. Components of the hazard assessment exercise.

Location

H₂S is found at varying depths in the earth's geological formations. Underground sources of the gas are often referred to as pockets of H₂S. Other natural sources of H₂S include volcanic gases, sulfur deposits, sulfur springs, and swamp gas from anaerobic decay. Approximately 90 percent of the air emissions of H₂S are produced by natural sources (U.S. EPA, 1993). A portion of this 90 percent results from the routine emissions and accidental releases resulting from the extraction of oil and gas containing H₂S. Figure II-1 shows major H₂S-prone areas of the United States.

Nature of Hazard

Exposure Routes, Absorption, Metabolism, and Elimination

As described in previous chapters, the most rapid route of exposure to H₂S is through the air. Although eye irritation is the basis for the OSHA Permissible Exposure Limit (PEL), inhalation is the quickest lethal exposure to humans and wildlife. The solubility of H₂S in water decreases as temperature increases; however, drinking groundwater has been found with noticeable H₂S concentrations.

Sullivan and Krieger's *Hazardous Materials Toxicology* (1992) summarizes the effects of H₂S exposure as follows:

In environmental and occupational exposures, the lung rather than the skin is the primary route of absorption (Burgess, 1979; Yant, 1930). The dermal absorption of H₂S is minimal (Laug and Draize, 1942). Results from animal inhalation studies indicate that H₂S is distributed in the body to the brain, liver, kidneys, pancreas, and small intestine (Voigt and Muller, 1955). Within the body, H₂S is metabolized by oxidation, methylation, and reaction with metallo- or disulfide-containing proteins. Orally, intraperitoneally, and intravenously administered H₂S is primarily oxidized and directly excreted as either free sulfate or conjugated sulfate in the urine (Curtis et al., 1972). The importance of methylation in the detoxification processes of H₂S, however, is unknown (Weisiger and Jakoby, 1980). The reaction of H₂S with vital metalloenzymes such as cytochrome oxidase is the likely toxic mechanism of H₂S (NRC, 1979; Smith and Gosselin, 1979). Reaction with nonessential proteins may also serve as a detoxification pathway (Smith, Kroszyna, and Kruszyna, 1976; Smith and Gosselin, 1964). Systemic poisoning occurs when the amount of H₂S absorbed exceeds that which can be detoxified and eliminated (Yant, 1930; Milby, 1962). Because of its rapid oxidation in the blood, H₂S is not considered a cumulative poison (Yant, 1930; Ahlborg, 1951; Haggard, 1925)....

There are no animal data available regarding the exhalation of H_2S after inhalation exposure. In animals, the excretion of H_2S by the lungs is minimal after peritoneal administration of H_2S (Evans, 1967; Gunina, 1957; Susman et al., 1978). However, because rescue personnel have developed H_2S poisoning shortly after starting mouth-to-mouth resuscitation on victims who had been poisoned, it is likely that significant H_2S is excreted from the lungs (Kleinfeld, Giel, and Rosso, 1964).

Acute Human Toxicity

The odor perception threshold for H_2S is very low. At concentrations between 3 and 20 ppb, the characteristic rotten egg odor is detectable. However, higher concentrations of H_2S in the 1.5×10^5 to 2.5×10^5 ppb range can cause olfactory paralysis. At these concentrations, the olfactory sense may be lost and exposed persons may be unaware of the presence of the toxic gas. Thus, odor cannot be relied upon as a warning sign of possible exposure to H_2S . Pulmonary edema, resulting from inhalation of levels between 3×10^5 and 5×10^5 ppb, can be fatal. (See Table III-1.) Inhaling levels between 5×10^5 and 1×10^6 ppb can cause a stimulation of the respiratory system, and rapid breathing (hyperpnea) will occur followed by cessation of breathing (apnea). The effect of inhaling levels above 1×10^6 ppb is immediate respiratory paralysis followed by death.

Inhalation of levels above 2.5×10^5 ppb can damage organs and the nervous system. Much of this damage is a result of a lack of oxygen (anoxia) caused by the depression of cellular metabolism which can occur at 2.5×10^5 ppb. Instances of permanent neurological damage in humans resulting from acute exposure have been described. Furthermore, animal data have revealed that changes in the tissues of the brain, lungs and heart can occur from exposure to the gas.

Irritation of the respiratory tract and eyes is another major effect of H_2S exposure. The gas is readily absorbed through the nasal and lung mucosa. It is very irritating to the respiratory tract and eyes and can cause serious eye injury above 5×10^4 ppb. The gas can affect the epithelium of the eye causing inflammation and lacrimation. The Integrated Risk Information System (IRIS) (U.S. EPA, 1992) lists several signs and symptoms of H_2S exposure including painful conjunctivitis, sensitivity to light, tearing, and clouding of vision. In addition, permanent scarring of the cornea can occur. At high, and potentially lethal concentrations, the mucous membranes can be anesthetized so that irritation effects cannot be relied upon to warn individuals of H_2S exposure.

In addition to irritation, IRIS lists other signs and symptoms of H_2S exposure including labored breathing and shortness of breath, profuse salivation, nausea, vomiting, diarrhea, giddiness, headache, dizziness, confusion, rapid breathing, rapid heart rate, sweating, and weakness.

Table III-1. Effects of Exposure in Humans at Various Concentrations in Air

| Clinical Effect | Level of Hydrogen Sulfide | | Reference |
|-------------------------------------------|-----------------------------------------|-------------------|---------------------------------------------|
| | ppb | mg/m ³ | |
| Odor perception threshold | 3-20 | 0.004 - 0.028 | Indiana Air Pollution Control Board (1964) |
| Offensive odor (rotten eggs) | <3x10 ⁴ | <42 | Ahlborg (1951) |
| Offensive odor (sickening sweet) | >3x10 ⁴ | >42 | National Research Council (1977) |
| Occupational Exposure Limit (OEL) | 1x10 ⁴ | 14 | National Research Council (1977) |
| Serious eye injury | 5x10 ⁴ - 1x10 ⁵ | 70 - 140 | National Research Council (1977) |
| Olfactory paralysis | 1.5x10 ⁵ - 2x10 ⁵ | 210 - 350 | National Research Council (1977) |
| Pulmonary edema, threat to life | 3x10 ⁵ - 5x10 ⁵ | 420 - 700 | National Research Council (1977) |
| Strong stimulation of respiration | 5x10 ⁵ - 1x10 ⁶ | 700 - 1400 | National Research Council (1977) |
| Respiratory paralysis, collapse and death | 1x10 ⁶ - 2x10 ⁶ | 1400 - 2800 | National Research Council (1977) |

Source: U.S. EPA, 1993.

Hydrogen sulfide may also decrease the body's ability to withstand infection. A toxicological study exposed rats to 4.5×10^4 ppb of hydrogen sulfide for 2, 4, or 6 hours, followed by a challenge with an aerosol of *staphylococcus epidermis* (Rogers and Ferin, 1981). A significant dose-response effect was seen in the number of colonies formed, when the exsanguinated lungs were harvested from the rats at 30 minutes, 3 hours and 6 hours post-challenge, and homogenized and grown in a selective growth medium for staphylococci. Rats exposed to hydrogen sulfide for 4 hours had a 6.5-fold greater percent of colony-forming units than controls, while those exposed to hydrogen sulfide for 6 hours had a 52-fold greater percent of colony-forming units. The conclusion reached was that hydrogen sulfide significantly affected the antibacterial system of the rats by impairing alveolar macrophages.

However, Higashi et al. (1983), in a cross-sectional study of viscose rayon textile workers exposed to hydrogen sulfide (average concentration, 3×10^3 ppb) and carbon disulfide, found no difference between exposed employees and controls in respiratory and spirometric variables. Similarly, Kangas et al. (1984) found no increased prevalence of subjective symptoms among cellulose mill workers exposed to hydrogen sulfide concentrations of up to 2×10^4 ppb and methyl mercaptan levels as high as 1.5×10^4 ppb, and much smaller amounts of dimethyl disulfide.

Chronic Human Toxicity

The toxicological data based was reviewed and an inhalation reference concentration (RfC) was verified by the U.S. EPA Reference Dose (RfD)/RfC Work Group on June 21, 1990. The documentation is available via the Integrated Risk Information System (IRIS) (U.S. EPA, 1991). The Integrated Risk Information System is an on-line data base containing EPA risk assessment results and regulatory information. An RfC is defined as an estimate, with uncertainty spanning perhaps an order of magnitude, of a daily exposure to the human population (including sensitive subgroups) which is likely to be without adverse effects during a lifetime (U.S. EPA, 1990). The derivation of the RfC is based on a complete review of the toxicological literature and encompasses adjustments for exposure duration and dosimetry. It utilizes uncertainty factors to account for specific extrapolations between the population in which the effect was observed and the human population. The critical, usually the most sensitive, effect is the focus of the RfC derivation; for this effect the no-observed-adverse-effect level (NOAEL), or lowest-observed-adverse-effect level (LOAEL) if a NOAEL is not available, is identified. Detailed discussion concerning these issues can be found in U.S. Environmental Protection Agency, 1990.

The RfC for H_2S is 9×10^{-4} mg/m³ (6.7×10^{-1} ppb) and was derived from the NOAEL for inflammation of the nasal mucosa in mice (Toxigenics, 1983). The subchronic study revealed a lowest-observed-adverse-effect level (LOAEL) of 110 mg/m³ (8×10^4 ppb) and a no-observed-adverse-effect level (NOAEL) of 42.5 mg/m³ (3.05×10^4 ppb). Since the RfC may change due to evaluation of additional data, the reader is referred to IRIS for the most current information regarding the RfC for H_2S .

The extrapolation of the NOAEL to the RfC follows several steps. First, the NOAEL is adjusted to account for the daily length of exposure in the study; and second, it is extrapolated to humans, and a human equivalent concentration (HEC) is calculated. Finally an uncertainty factor is applied. The RfC for hydrogen sulfide is derived using an uncertainty factor of 1000. The 1000 reflects a factor of 10 to protect sensitive individuals, 10 to adjust from subchronic studies to a chronic study (a subchronic study is carried out over a shorter period of time and may not accurately reflect cumulative effects), and 10 to adjust for interspecies conversions and database deficiencies.

Very little data exist on whether H₂S can cause carcinogenic, mutagenic, reproductive or developmental effects in humans or animals. Because of a lack of adequate test data, H₂S is currently placed in Group D, based on the weight-of-evidence criteria in the EPA's Carcinogen Risk Assessment Guidelines issued in August 1986. A Group D ranking means that the available data are inadequate to assess a chemical's human carcinogenic potential. Furthermore, data are inadequate to state that H₂S is mutagenic or that it causes reproductive effects. Limited animal data do suggest that H₂S appears to have potential to alter normal developmental processes. No data on human developmental effects of inhaled H₂S have been located (U.S. EPA, 1993).

Ecological Effects

Data on the ecological effects of H₂S are limited (Table III-2). McCallan, Hartzell, and Wilcoxon (1936) and Benedict and Breem (1955) conducted high-exposure fumigation studies, which noted that young, growing plants were the most susceptible to injury from exposure to H₂S. However, they noted that temperature, soil moisture, and species differences were important factors affecting the results. Heck, Daines, and Hindawi (1970) noted that mature leaves were unaffected while damage to the young shoots and leaves consisted of scorching. Among the plants determined to be sensitive to H₂S are clover, soybean, tomatoes, tobacco, and buckwheat.

According to the EPA *Health Assessment Document for H₂S* (U.S. EPA, 1993), few studies exist that evaluate natural or accidental exposure of wildlife and/or domestic animals to H₂S. However, H₂S has been determined to be highly toxic to some fish species. Animal surveys conducted after a gas well blowout in Lodgepole, Alberta, Canada (Lodgepole Blowout Inquiry Panel, 1984; Harris, 1986) revealed that large animals were exhibiting signs of mucous membrane irritation and were avoiding the geographic area. Most cattle in the exposed area were unaffected. Concentrations of H₂S as high as 1.5×10^4 ppb (sampling time unknown) were measured in the blowout area.

Flammability, Explosivity, and Corrosivity

"Hydrogen sulfide is generally stable when properly stored in cylinders at room temperature. However, in the air, it is flammable and explosive and may be ignited by static discharge. It may react with metals, oxidizing agents, and acids such as nitric acid, bromine

Table III-2. Effects of Ecological Exposure to H₂S

| Studies | Species | Level | Source |
|------------------|----------------------------------------|---------------------------------------------------------|--------|
| Aquatic | Bluegill | LC ₅₀ 0.009 - 0.0478 mg/L | AQUIRE |
| | Rainbow Trout | LC ₅₀ 0.013 - 0.047 mg/L | AQUIRE |
| | Fathead Minnow | LC ₅₀ 0.007 - 0.776 mg/L | AQUIRE |
| Mammalian | Mouse | NOAEL 42.5 mg/m ³ (3.05x10 ⁴ ppb) | IRIS |
| | | LOAEL 100 mg/m ³ (8x10 ⁴ ppb) | IRIS |
| | Rat | NOAEL 42.5 mg/m ³ (3.05x10 ⁴ ppb) | IRIS |
| | | LOAEL 100 mg/m ³ (8x10 ⁴ ppb) | IRIS |
| AQUIRE | Aquatic Toxicity Information Retrieval | | |
| IRIS | Integrated Risk Information Service | | |
| LC ₅₀ | Lethal Concentration 50 | | |
| NOAEL | No-observed-adverse-effect-level | | |
| LOAEL | Lowest-observed-adverse-effect-level | | |

pentafluoride, chlorine trifluoride, nitrogen triiodide, nitrogen trichloride, oxygen difluoride, and phenyldiazonium chloride. When heated to decomposition, it emits highly toxic sulfur oxide fumes" (Sullivan and Krieger, 1992). In pure form, its lower and upper explosive limits are 4.3 percent (4.3×10^7 ppb) and 45.5 percent (45.5×10^7 ppb), and its auto-ignition temperature is 260 °C (500 °F) (NIOSH, 1977). The National Fire Protection Association (NFPA) has classified hydrogen sulfide in the highest flammability class (NFPA, 1974).

In the presence of water, hydrogen sulfide gas is highly corrosive to metals, including high-tensile steel, which hydrogen sulfide can embrittle. These properties can lead to loss of containment and accidental releases from ruptures if not controlled. Special precautions must be taken to prevent spontaneous ignition fires when vessels that previously contained concentrated hydrogen sulfide are opened. Ignition is caused by reaction of iron sulfide with air to form iron oxide. The conversion of sulfide to oxide produces enough heat to ignite flammable vapors (Dosch and Hodgson, 1986).

ACGIH Threshold Limits

The American Conference of Governmental Industrial Hygienists (ACGIH) publishes a book of threshold limit values for chemical substances in the work environment (ACGIH, 1992). The limits are intended for use in the practice of industrial hygiene as guidelines or recommendations in the control of potential health hazards. When OSHA began setting standards for employee exposure in the 1970s, they adopted the ACGIH threshold limit values (TLV's) as their permissible exposure limits. The ACGIH standards are recommendations rather than regulations; they are updated annually and respond to current research more quickly than OSHA's regulations.

The current limits for H₂S were adopted by ACGIH in 1976. The Threshold Limit Value-Time Weighted Average (TLV-TWA) is 1×10^4 ppb or 14 mg/m³, and the TLV short-term exposure limit (TLV-STEL) is 1.5×10^4 ppb or 21 mg/m³. The TLV-TWA is defined as the time-weighted average concentration for a normal 8-hour workday and 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. The TLV-STEL is defined as the concentration to which workers can be exposed continuously for a short period of time without suffering from 1) irritation, 2) chronic or irreversible tissue damage, or 3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or reduce work efficiency, also provided that the daily TLV-TWA is not exceeded. A STEL is further defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the TLV-STEL should not be longer than 15-minutes and should not occur more than 4 times a day, and should be separated by 60 minutes each.

LC₀₁

One measure of the airborne concentrations of toxic materials that might cause fatality is the LC₀₁, which is the concentration that could prove fatal to one percent of those exposed to it. The LC₀₁ is related to the exposure time, t, by a relationship of the form $LC_{01} = (k/t)^{1/n}$, where k and n are constants that depend on the material in question. This relationship is a manifestation of the probit equation, which is a well-established way of presenting the relationship between concentration, exposure time, and probability of fatality.

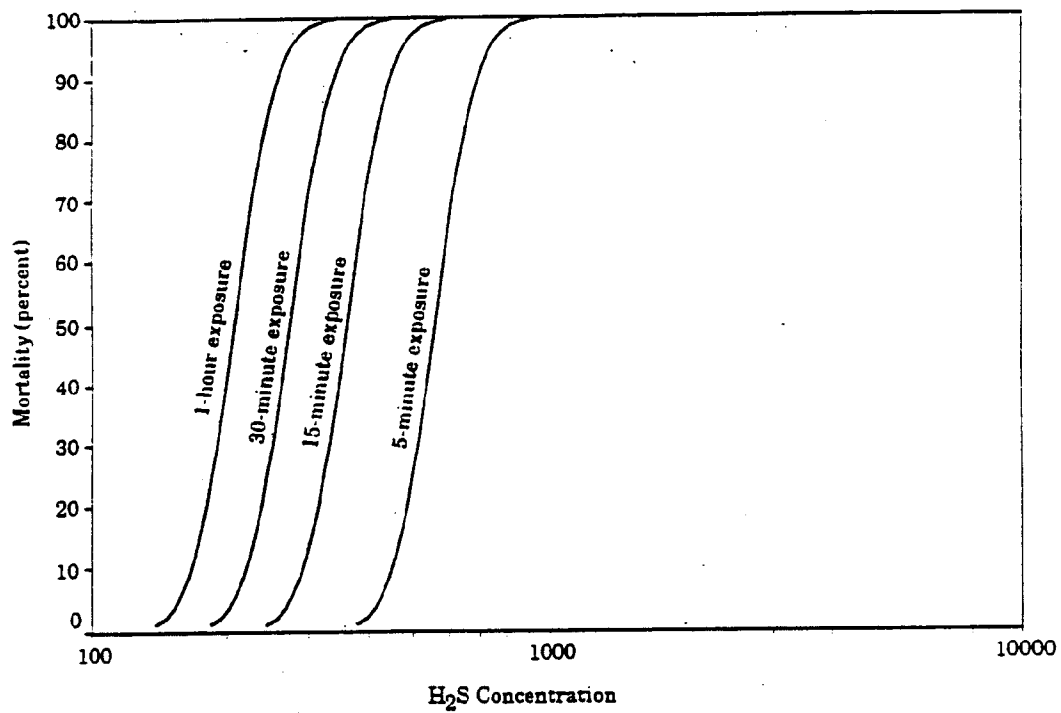
For H₂S, the Center for Chemical Process Safety of the American Institute of Chemical Engineers (AIChE) has a probit equation which gives k = 83,500 and n = 1.43, with C in ppb and t in minutes (AIChE, 1989). Thus, for a five minute exposure, LC₀₁ = 8.95 x 10⁵ ppb and, for a one hour exposure, LC₀₁ = 1.6 x 10⁵ ppb.

The Energy Resources Conservation Board (ERCB) of Alberta, Canada (Alp et al., 1990) has developed an alternative probit equation (shown in Figure III-2) which, for the LC₀₁, gives k = 1.364x10⁸ and n = 2.5. For a five minute exposure, this gives LC₀₁ = 3.75 x 10⁵ ppb and for a one hour exposure gives LC₀₁ = 1.4 x 10⁵ ppb. The ERCB values are thus more conservative.

AIHA Guidelines

The American Industrial Hygiene Association (AIHA) sets Emergency Response Planning Guidelines (ERPGs) to protect the general public in the event of an emergency release. The three ERPGs for H₂S, which are time-dependent levels for varying degrees of potential harm, are defined as follows:

- | | |
|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ERPG-3 | <u>1 x 10⁵ ppb</u> , the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects; |
| ERPG-2 | <u>3 x 10⁴ ppb</u> , the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. |
| ERPG-1 | <u>100 ppb</u> , the maximum airborne concentrations below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor. |



Note: Concentrations intentionally left in ppm.
Source: Alp et al., 1990.

Figure III-2. ERCB H₂S probit relations.

For hydrogen sulfide, the ERPG-3 is based on human experience, while the ERPG-2 is based on animal studies and the ERPG-1 is based on the fact that the objectionable odor of hydrogen sulfide is distinct at 300 ppb (AIHA, 1991). For the purposes of accidental release dispersion analysis, the ERPG-2 was considered conservative and used as a threshold for emergency countermeasures.

As stated above, these ERPG values are for an exposure time of one hour. At the time of writing, there is no definitive guidance on how to extrapolate to shorter durations of exposure. However, Gephart and Moses (1989) suggest that a constant dosage extrapolation might be reasonable; that is, (ERPG in ppb) × (exposure time, t, in minutes) = constant, k. Discussions with one of the AIHA authors have suggested that, for $t < 15$ min, k should be divided by two. Thus, for H_2S , the ERPG-2 is as follows:

- 3×10^4 ppb for an exposure time of one hour
- 1.8×10^5 ppb for an exposure time of five minutes.

The reader should recognize that these extrapolations are tentative and included for purposes of illustration. They represent one of the greater sources of uncertainty in the calculations.

NAS/NRC Guidelines

For the last forty years, the NRC's Committee on Toxicology has submitted emergency exposure guidelines for chemicals of concern to the Department of Defense (DOD) (NRC, 1986). These guidelines are used in planning for sudden contamination of air during military and space operations; specifically, they are used to choose protective equipment and response plans after non-routine but predictable occurrences such as line breaks, spills, and fires. These guidelines are for peak levels of exposure considered acceptable for rare situations, but are not to be applied in instances of repeated exposure.

An Emergency Exposure Guidance Level (EEGL) is defined as a concentration of a substance in air (gas, vapor, or aerosol) judged by DOD to be acceptable for the performance of specific tasks by military personnel during emergency conditions lasting 1 to 24 hours. Exposure to an EEGL is not considered safe, but acceptable during tasks which are necessary to prevent greater risks, such as fire or explosion. Exposures at the EEGLs may produce transient central nervous system effects and eye or respiratory irritation, but nothing serious enough to prevent proper responses to emergency conditions.

Since the 1940's, the NRC has developed EEGLs for 41 chemicals, 15 of which are listed in Section 302 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) as extremely hazardous substances (EHSs). Although acute toxicity is the primary basis for selecting EEGLs, long-term effects from a single acute exposure are also evaluated for developmental, reproductive (in both sexes), carcinogenic, neurotoxic, respiratory and other organ-related effects. The effect determined to be the most seriously debilitating,

work-limiting, or sensitive is selected as the basis for deriving the EEGL. This concentration is intended to be sufficiently low to protect against other toxic effects that may occur at higher concentrations. Factors such as age of the exposed population, length of exposure, and susceptibility or sensitivity of the exposed population are also considered in determining EEGLs.

Safety factors are used in developing EEGLs to reflect the nature and quality of the data. Safety factors for single exposures may differ from those used in chronic studies. In the absence of better information, a safety factor of 10 is suggested for EEGLs (i.e., the reported toxicity value should be divided by 10) if only animal data are available and extrapolation from animals to humans is necessary for acute, short-term effects (NRC, 1986). The safety factor of 10 takes into account the possibility that some individuals might be more sensitive than the animal species tested. A factor of 10 is also suggested if the likely route of human exposure differs from the route reported experimentally (NRC, 1986), for example, if oral data are reported and inhalation is the most likely exposure route for humans.

As noted by NRC (1986, p. 7), development of an EEGL for different durations of exposure usually begins with the shortest exposure anticipated (i.e., 10-15 minutes) and works up to the longest, such as 24 hours. For H_2S , 10-minute emergency exposure guideline level (EEGL) is 5×10^4 ppb; 1×10^4 ppb is the 24-hour EEGL. The 24-hour/day, 90-day continuous exposure guide level (CEGL) for H_2S has been recommended at 1×10^3 ppb (NCCT, 1985). Under the simplest framework, Haber's law is assumed to operate, with the product of concentration (C) and time (t) as a constant (k) for all the short periods used ($Ct=k$) (Casarett and Doull, 1986). If Ct is 30 and t is 10, then C is 3; if Ct is 30 and t is 30, then C is 1. If detoxification or recovery occurs and data are available on 24-hour exposures, this is taken into account in modifying Ct. In some instances, the Ct concept will be inappropriate, as for materials such as ammonia that can be more toxic with high concentrations over short periods. Each material is considered in relation to the applicability of Haber's law.

Generally, EEGLs have been developed for exposure to single substances, although emergency exposures often involve complex mixtures of substances and, thus, present the possibility of toxic effects resulting from several substances. In the absence of other information, guidance levels for complex mixtures can be developed from EEGLs by assuming as a first approximation that the toxic effects are additive. When the chemical under evaluation for development of an EEGL is an animal or human carcinogen, a separate qualitative risk assessment is undertaken in recognition of the fact that even limited exposure to such an agent can theoretically increase the risk of cancer. The risk assessment is performed with the aim of providing an estimate of the acute exposure that would not lead to an excess risk of cancer greater than 1 in 10,000 exposed persons. The following mathematical approach, taken directly from NRC (1986, pp. 26-27), is applicable for EEGL computations for carcinogens:

1. If there has been computed an exposure level d (usually in ppm in air), which after a lifetime of exposure is estimated to produce some "acceptable" level of excess risk of cancer — say, 1×10^{-6} — this has been called a "virtually safe dose" (VSD). Computation of the dose d , if not already done by a regulatory agency, will be computed by the Committee on Toxicology in accordance with generally accepted procedures used by the major regulatory agencies, i.e., using the multistage no-threshold model for carcinogenesis and the appropriate body weight/surface area adjustments when extrapolating from an animal species to humans.
2. If carcinogenic effect is assumed to be a linear function of the total (cumulative) dose, then for a single 1-day human exposure an acceptable dose (to yield the same total lifetime exposure) would be d times 25,600 (there being approximately 25,600 days in an average lifetime); the allowable 1-day (24-h) dose rate would be

$$d \times 25,600$$

3. Because of uncertainties about which of several stages in the carcinogenic process a material may operate in, and because of the likely low age of military persons, it can be shown from data of Crump and Howe (1984) that the maximal additional risk that these considerations contribute is a factor of 2.8. As a conservative approach, the acceptable dose is divided by 2.8, i.e.,

$$\frac{d \times 25,600}{2.8}$$

If a lifetime excess risk, R , is established by DOD (for example, at 1×10^{-4} , as has been suggested by the International Council on Radiation Protection for nuclear power plant workers), then the appropriate extent of risk at the EEGL would be

$$\frac{d \times 25,600}{2.8} \times \frac{R}{\text{level of risk at } d}$$

(In the example given here, the level of risk at d was no more than 1×10^{-6} .) If R is 1×10^{-4} , then $R/\text{risk at } d = 10^{-4}/10^{-6} = 100$ (NRC, 1986).

4. If a further element of conservatism is required (for example, where animal data need to be extrapolated to estimate human risk), an additional safety factor can be used as divisor.

The NRC's Committee on Toxicology has also developed special public exposure guidelines upon request from Department of Defense. The Short-term Public Exposure Guidance Level (SPEGL) is defined as an acceptable ceiling concentration for a single,

unpredicted short-term exposure to the public. The exposure period is usually calculated to be one hour or less and never more than 24 hours. SPEGLs are generally set at 0.1 to 0.5 times the EEGL. A safety factor of 2 is often used to take into account effects on sensitive subpopulations, such as children, the aged, and people with debilitating diseases. A safety factor of 10 may be used to take into account the effects of an exposure on fetuses and newborns. Effects on the reproductive capacity of both men and women are also considered. Five SPEGLs (for hydrazine, dimethylhydrazine, monomethyl hydrazine, nitrogen dioxide, and hydrogen chloride) have been developed by the NRC; all five chemicals are on the list of EHSs. (U.S. EPA, 1987).

EXPOSURE AND CONSEQUENCE ANALYSES

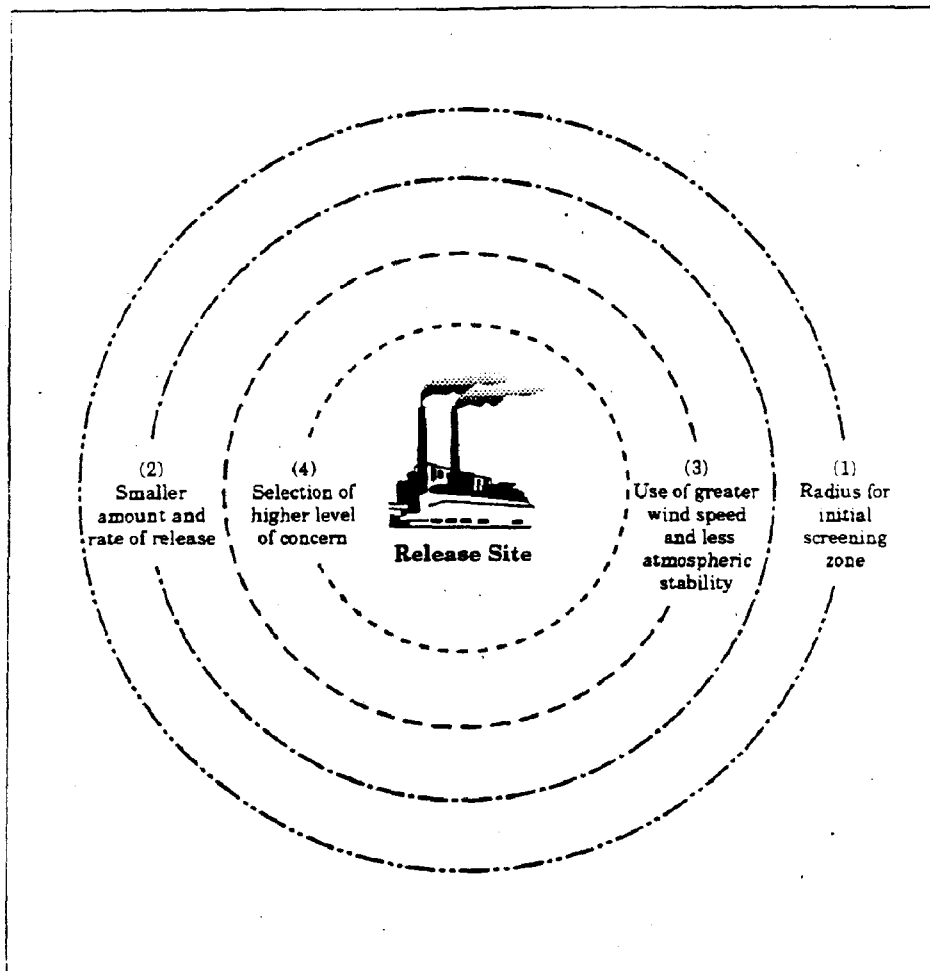
In this section, potential exposures to and consequences of exposure to H_2S from oil and gas wells are analyzed. The zones of the United States most likely to contain H_2S are identified and the potentially exposed human and ecological populations are discussed. Routine emissions and accidental releases of H_2S are characterized using monitoring records and dispersion modeling and the consequences are discussed. For accidental releases, prevention, mitigation and emergency response policies and procedures are also identified.

Vulnerability Zones

Vulnerability zones are estimated geographical areas that may be subject to concentrations of H_2S at levels that could cause irreversible acute health effects or death to human populations within the area following an accidental release. For detailed hazard analyses recommended under the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), see Chapter IV; vulnerability zones are based on estimates of the quantity of hazardous substances released to air, the rate of release to air, airborne dispersion, and the airborne concentration that could cause irreversible health effects or death. This concept of vulnerability is used to assess regions most likely to encounter routine emissions or accidental H_2S releases from oil and gas production. This report does not use the EPCRA methodology. Rather, the basic tools of a hazard analysis are used to alert the reader to areas with potential H_2S hazards.

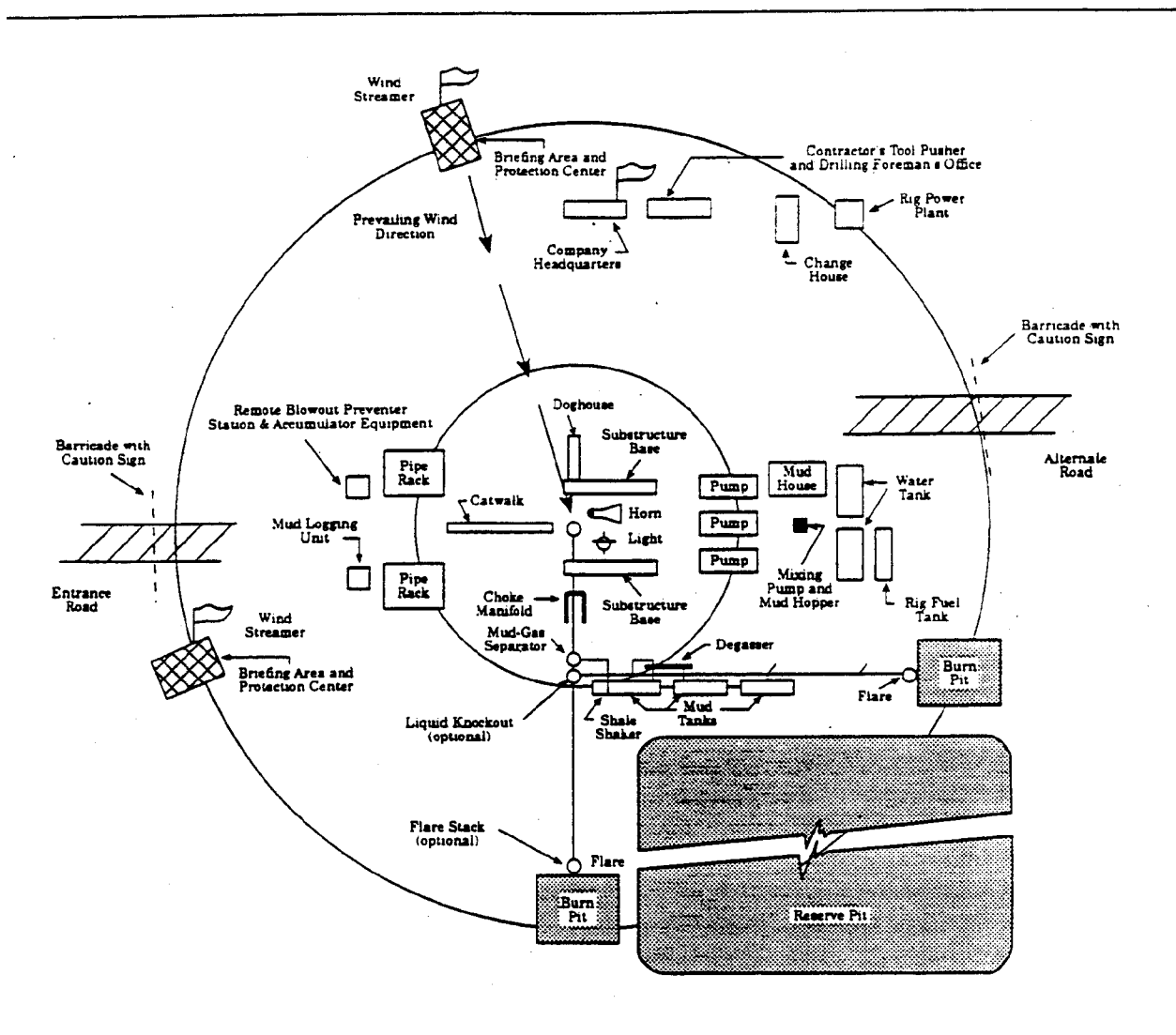
Estimated vulnerability zones are shown in Figure III-3 as circles with different radii to illustrate how changing conditions or assumptions can influence the vulnerability zone estimate. With most atmospheric releases, the actual concentration of the airborne chemical tends to decrease as it moves further downwind from the release site because of continual mixing and dilution (i.e., dispersion).

The American Petroleum Institute (API), an industry-wide technical organization, has published several recommended practices (RP) pertaining to hydrogen sulfide in the oil and gas production industry. Figure III-4 shows API's RP 49 recommended equipment layout to minimize vulnerability zones for an unconfined area, taking the potential for H_2S releases into consideration. Confinement refers to offshore sites and some land locations confined by



Source: U.S. EPA, 1987.

Figure III-3. The effect of different assumptions on the calculation of the radius of estimated vulnerable zones.



Source: API, 1987.

Figure III-4. Example of drilling equipment layout - unconfined location.

the restriction of area, method of access, terrain, surrounding population distribution, etc. In an H_2S environment, well plot areas should be larger than usual, (i.e., larger reserve pits, turnaround room, etc.). The extra space allows for a greater margin of safety in well site activities and, in turn, a smaller vulnerability zone.

The California Division of Oil and Gas provides guidance on H_2S exposure prevention. In their report, *Drilling and Operating Oil, Gas, and Geothermal Wells in an H_2S Environment*, the State recommends calculating the well area's potential toxicity from H_2S emissions, if the volume of oil or gas produced and the concentration of the H_2S in the oil or gas are known (Dosch and Hodgson, 1986). From these data, the radius from the source to the 3×10^5 ppb and 1×10^5 ppb H_2S concentration area can be determined on dispersion-based scales. Potential sources of toxic gas emissions considered in calculating the toxicity of the well area include wells and associated production, treatment, processing, and storage facilities.

Calculating vulnerability zones for H_2S on a nationwide basis, as in EPCRA hazard analyses, is difficult because vulnerability zones are designed for site-specific studies. Therefore, this assessment will take a broader approach to identifying vulnerability zones, which will be referred to as H_2S prone areas. These areas are considered the major areas of the United States prone to natural occurrences of hydrogen sulfide. Figure II-1 identified 14 major H_2S prone areas in the United States. The 20 states having H_2S prone areas are Alabama, Arizona, Arkansas, California, Colorado, Florida, Idaho, Indiana, Illinois, Kentucky, Louisiana, Michigan, Mississippi, Missouri, Nebraska, North Dakota, Oklahoma, Texas, Utah, and Wyoming. Texas has four discrete areas prone to H_2S . However, some States, such as Louisiana, do not drill to depths of known H_2S deposits; in Louisiana, oil and gas wells appear to be located in more shallow depths.

Exposure Analysis — Routine Emissions

Monitoring Records

Ambient air monitoring programs measure the concentration of pollutants after they have dispersed from one or more sources. These levels are recorded and tracked continuously so that the level of exposure and air quality can be assessed over the long term and under varying meteorological and emission scenarios. Ambient air monitoring is also used to determine compliance with air quality standards by measuring pollutant concentrations. With a dispersed, relatively unreactive primary pollutant such as hydrogen sulfide, often the emissions can be traced back to the specific source.

Many States require ambient air monitoring for hydrogen sulfide at gas plants and refineries; however, monitoring is not frequently required at oil and gas extraction facilities. In the preparation of this report, six States (California, Michigan, North Dakota, Oklahoma, Texas, and Wyoming) were contacted and questioned about the availability of monitoring

data. California, Michigan, Oklahoma, Texas and Wyoming had not conducted pertinent ambient air monitoring.

The North Dakota State Department of Health and Consolidated Laboratories (NDSDH&CL) performs ambient monitoring for routine emissions of H_2S and has collected the data since 1980. The following discussion summarizes North Dakota's program to provide an indication of historical, routine emissions of H_2S from wells. Since no other States have such monitoring data available, this report relies on North Dakota's data to assess hazards and draw conclusions.

The North Dakota database contains site name, year/month/day monitored, and H_2S value measured. The database reflects three background and six special purpose monitors (i.e., monitors set up as a result of a complaint). Monitoring periods vary in length from months to over a decade for a total of 393 months (32.75 years) of data (personal communication, D. Harman, NDSDH&CL, 8/11/92). Table III-3 shows the North Dakota data. The data were in half-hour average concentrations up to January 1, 1988, when the averages recorded were changed to hourly, to correspond with the change in the North Dakota Ambient Air Quality Standards (NDAAQS). Some monitoring lasted less than a year; however, monitoring in the Theodore Roosevelt National Park-north unit was begun in 1980 and continues today.

North Dakota's Hydrogen Sulfide Standards - An Historical Review. At the time of the early monitoring activities, there were two NDAAQS for hydrogen sulfide, both based on half-hour averages and on odor thresholds but over different time spans. Adopted in 1970, they were based upon guidelines established in the Interstate Air Pollution Study conducted in St. Louis in the late 1960s. Those standards were 54 ppb ($75 \mu g/m^3$), 1/2-hour maximum concentration not to be exceeded more than twice per year; and 32 ppb ($45 \mu g/m^3$), 1/2-hour maximum concentration not to be exceeded more than twice in any five consecutive days. The 1/2-hour hydrogen sulfide standards were inconvenient because all of the other pollutants were being tracked on an hourly basis. To correct the situation, North Dakota developed a 1-hour standard that would afford the same degree of protection as the old 1/2-hour standards did, while still based on an odor threshold value. Statistically, they narrowed the proposed standard down to a range of concentrations between 48 ppb and 52 ppb. Montana had an existing hydrogen sulfide standard of 50 ppb for a 1-hour period, not to be exceeded more than once per year, and North Dakota decided to adopt the same standard to provide consistency on both sides of the North Dakota-Montana State border. The 50 ppb ($70 \mu g/m^3$) 1-hour hydrogen sulfide standard became effective October 1, 1987.

At the same time that the new standard became effective, a new chapter (Chapter 20) was added to North Dakota's Air Pollution Control Rules entitled "Control of Emissions from Oil and Gas Well Production Facilities." The oil companies expressed concern that the hydrogen sulfide standard was included in North Dakota's table of ambient air quality standards (NDAAQS) and, by law, exceptions could not be granted. Their position was that they could not guarantee compliance with the standard at all times, and that the standard was

Table III-3. North Dakota H₂S Monitoring Studies

| Study | Location | Dates | Year | Ambient Std. (ppb) | Violation* (hours) | Maximum (ppb) |
|--------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------|------|--------------------|--------------------|---------------|
| Roffler | Farmyard within 1/2 mile of well and tank battery | 5/11/80 - 9/29/80 | 1980 | 32 | 0 | 13 |
| Theodore Roosevelt National Memorial Park - North Unit | Little Missouri River Valley, near the north unit park headquarters | 4/24/80 - 8/2/92 (1990 missing) | 1980 | 32 | 0 | 4 |
| | | | 1981 | 32 | 1 | 220 |
| | | | 1982 | 32 | 34 | 500 |
| | | | 1983 | 32 | 31 | 158 |
| | | | 1984 | 32 | 27 | 415 |
| | | | 1985 | 32 | 35 | 137 |
| | | | 1986 | 32 | 12 | 87 |
| | | | 1987 | 32/50 | 0 | 73** |
| | | | 1988 | 50 | 0 | 39 |
| | | | 1989 | 50 | 0 | 10 |
| | | | 1990 | 50/200 | 0 | 10 |
| | | | 1991 | 200 | 0 | 32 |
| | | | 1992 | 200 | 0 | 6 |
| Jorgenson | Valley with several oil wells within 1 mile | 10/2/80 - 5/13/82 | 1980 | 32 | 8 | 160 |
| | | | 1981 | 32 | 19 | 230 |
| | | | 1982 | 32 | 13 | 250 |
| Kadrmaz | Farmyard within 1 mile of several wells | 6/30/82 - 10/31/83 | 1982 | 32 | 9 | 541 |
| | | | 1983 | 32 | 7 | 353 |
| Theodore Roosevelt National Memorial Park - South Unit | Painted Canyon Rest Area | 10/17/85 - 6/30/90 | 1985 | 32 | 0 | 12 |
| | | | 1986 | 32 | 0 | 16 |
| | | | 1987 | 32/50 | 0 | 18 |
| | | | 1988 | 50 | 0 | 9 |
| | | | 1989 | 50 | 0 | 10 |
| | | | 1990 | 50/200 | 0 | 0* |
| Lone Butte | Little Missouri River Valley near an oil tank battery in Little Knife Oil Field | 1/17/84 - 7/11/89 | 1984 | 32 | 1808 | 1630 |
| | | | 1985 | 32 | 1859 | 2734 |
| | | | 1986 | 32 | 1653 | 2182 |
| | | | 1987 | 32/50 | 1130 | 2420 |
| | | | 1988 | 50 | 320 | 1515 |
| | | | 1989 | 50 | 25 | 122 |
| Lostwood | Lostwood National Wildlife Refuge Headquarters | 12/26/85 - 1/14/91 | 1985 | 32 | 0 | 0 |
| | | | 1986 | 32 | 0 | 18 |
| | | | 1987 | 32/50 | 0 | 45 |
| | | | 1988 | 50 | 0 | 46 |
| | | | 1989 | 50 | 0 | 47 |
| | | | 1990 | 50/200 | 0 | 88 |
| | | | 1991 | 200 | 0 | 0 |
| Olson | Farmyard within 1.5 miles of several wells | 7/20/89 - 9/18/90 | 1989 | 50 | 2 | 88 |
| | | | 1990 | 50/200 | 0 | 73 |
| Plaza | Town of Plaza, within 2 miles of several wells and tank batteries | 9/4/90 - 8/3/92 | 1990 | 50/200 | 0 | 152 |
| | | | 1991 | 200 | 0 | 358 |
| | | | 1992 | 200 | 1 | 269 |

Source: Personal correspondence, D. Harman, NDSOH & CL, 8/11/92.

Analysis of data prior to 10/1/87 based upon 32 ppb, 1/2-hour average standard, not to be exceeded more than twice in any 5 consecutive days.

Analysis of data between 10/1/87 and 6/1/90 based upon 50 ppb 1-hour average standard, not to be exceeded more than once per year.

Analysis of data after 6/1/90 based upon 200 ppb 1-hour average standard, not to be exceeded more than 1 time per month.

* A violation occurs the second time the standard is exceeded.

* Monitor out of service much of the time period.

** Exceedance defined as 2 times the standard.

not based on health-related concerns but on odor recognition levels. As a result, a joint Health Department/Industry task force was established and four new health-based standards were developed (effective June 1, 1990). These included raising the 50 ppb, 1-hr standard to a 200 ppb, 1-hr standard - a decrease in H_2S protection by a factor of four. These standards, which remain in effect today, are as follows:

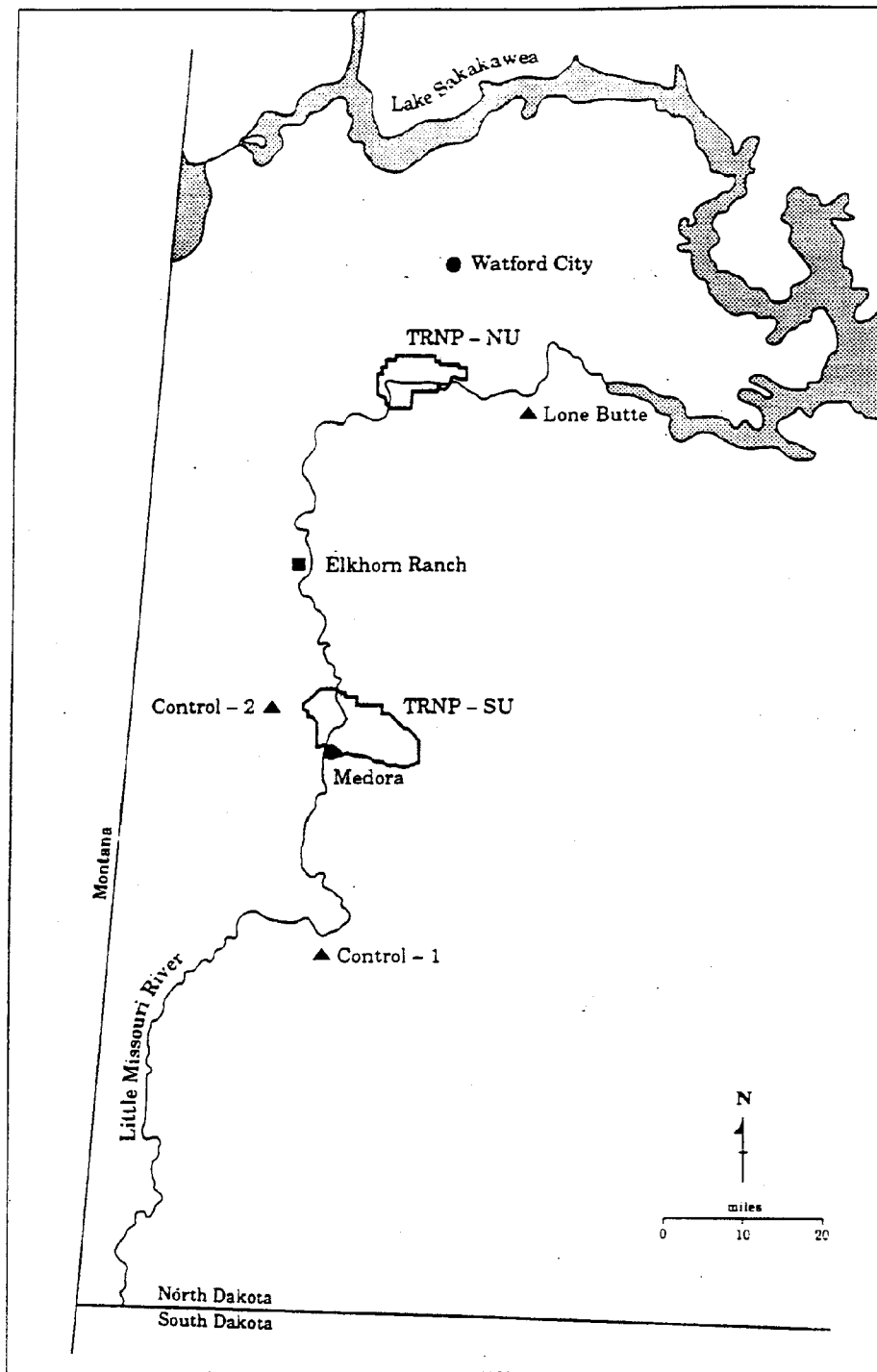
- 1 x 10⁴ ppb or 14 mg/m³) maximum instantaneous concentration not to be exceeded;
- 200 ppb or 280 µg/m³) maximum 1-hour average concentration not to be exceeded more than once per month;
- 100 ppb or 140 µg/m³) maximum 24-hour average concentration not to be exceeded more than once per year;
- 20 ppb or 28 µg/m³) maximum arithmetic mean concentration averaged over three consecutive months (personal communication, D. Harman, NDSDH&CL, 8/11/92).

Methodology for Analysis of Monitoring Data. For the analysis of the monitoring data, only one of the standards was evaluated for each time period. Prior to October 1, 1987, the data were compared to the 32 ppb 1/2-hour average standard, not to be exceeded more than twice in any five consecutive days. After October 1, 1987, and prior to June 1, 1990, 50 ppb was the only standard in effect, not to be exceeded more than once per year. The data collected after June 1, 1990, were compared to the 200 ppb standard which was not to be exceeded more than once per month. The results of the analysis are tabulated in Table III-3.

PSD Class I Areas. Several of the North Dakota monitoring programs were conducted to monitor air quality changes resulting from the oil and gas production industry at national parks and wildlife refuges. The Federal government established the Prevention of Significant Deterioration permit program (PSD) to protect areas with good air quality. In North Dakota, the most important, or Class I, areas include the Lostwood National Wildlife Refuge and the northern, southern and Elkhorn Ranch portions of the Theodore Roosevelt National Park (see Figure III-5). Monitoring sites for hydrogen sulfide were set up at all of these locations except the Elkhorn Ranch locations.

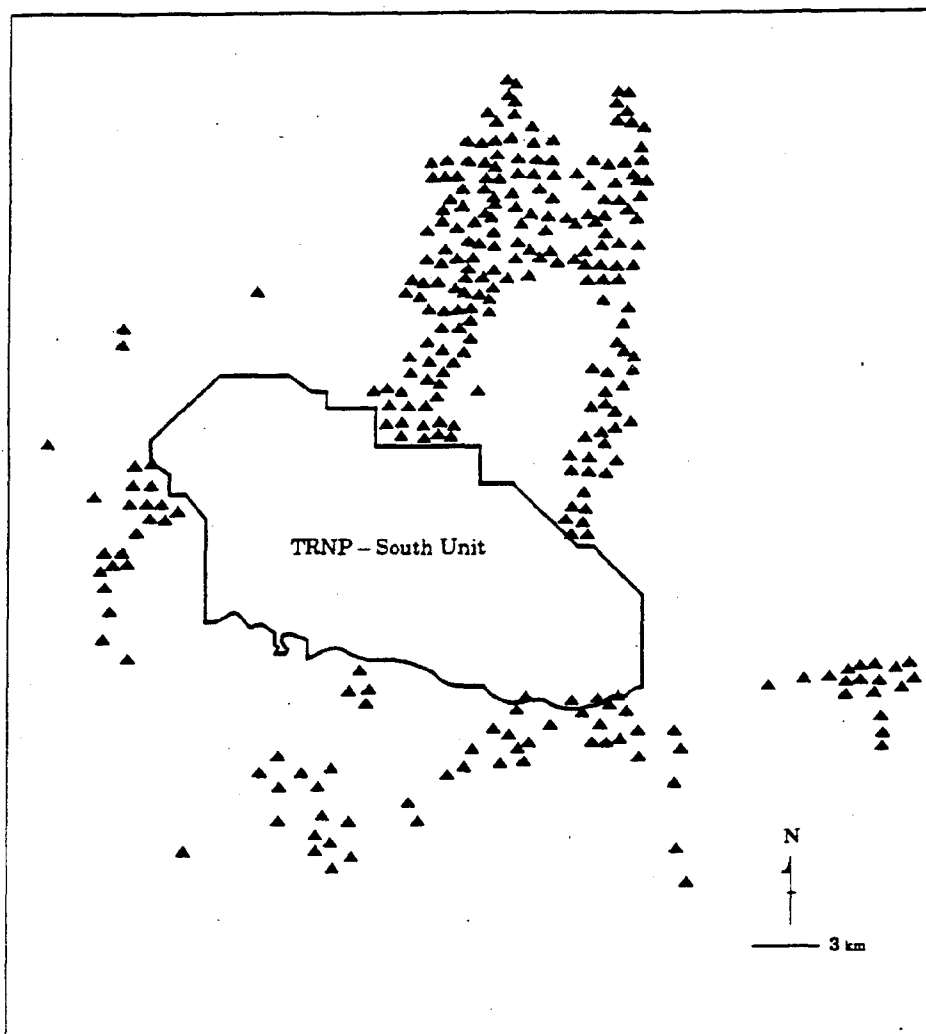
At the Lostwood Wildlife Refuge, data were obtained for the period from December 26, 1985, until January 14, 1991. Throughout the time period the maximum average concentration was 88 ppb, recorded as a 1-hour average in 1990. Overall, this was a site with acceptable air quality with respect to hydrogen sulfide because there were no NDAAQS violations.

In the Theodore Roosevelt National Park system (see Figures III-6 and III-7 for well distribution around the park), data were received by NDSDH&CL for the south unit (obtained at the Painted Canyon Rest Area) from October 17, 1985, to June 30, 1990. The air quality was very good, with no NDAAQS violations, and a maximum half-hour average



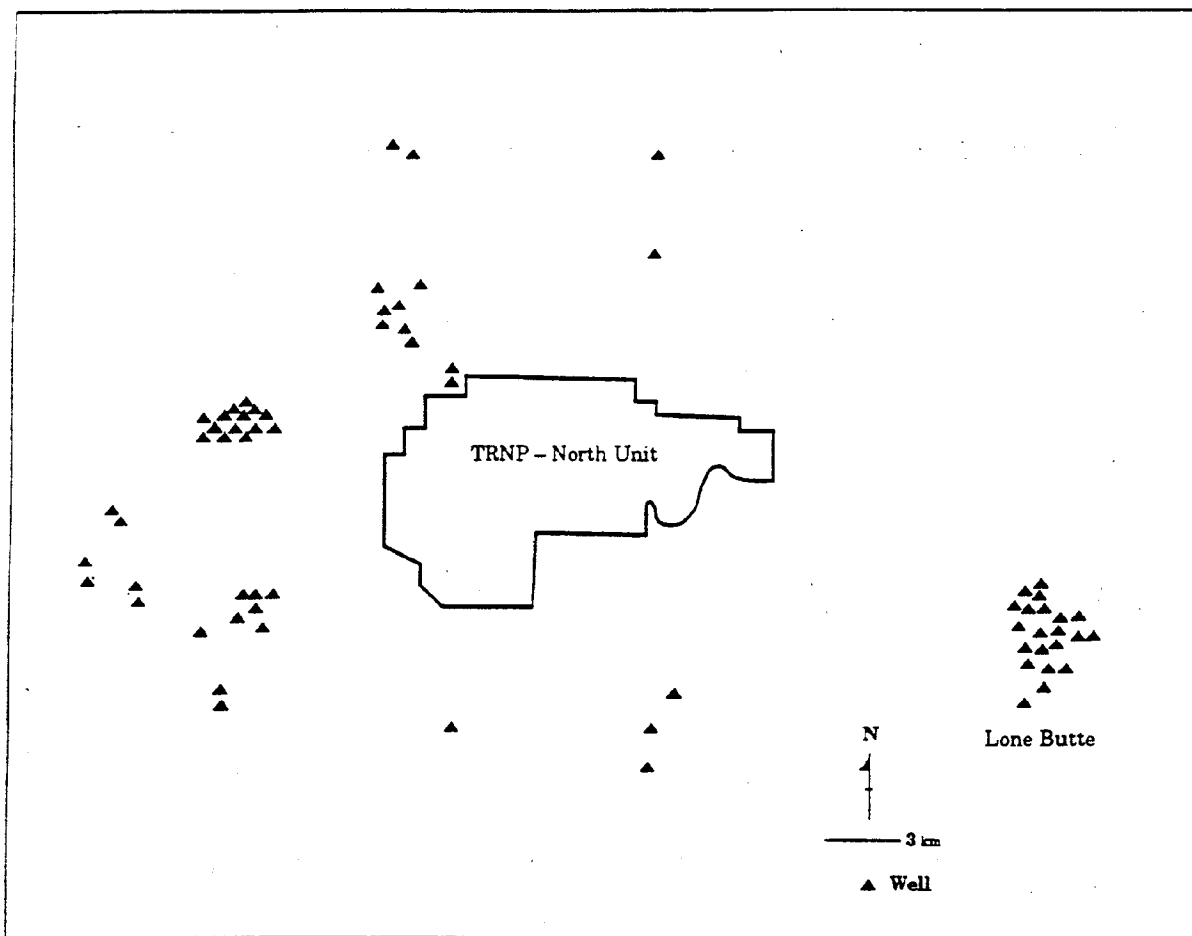
Source: Bilderbeck, 1988.

Figure III-5. Class I and II areas of North Dakota including Lone Butte and Theodore Roosevelt National Park (TRNP). Bold outlined areas are Class I; remaining area is Class II.



Source: Bilderbeck, 1988.

Figure III-6. Well distribution around Theodore Roosevelt National Park, South Unit.



Source: Bilderbeck, 1988.

Figure III-7. Well distribution around Theodore Roosevelt National Park, North Unit.

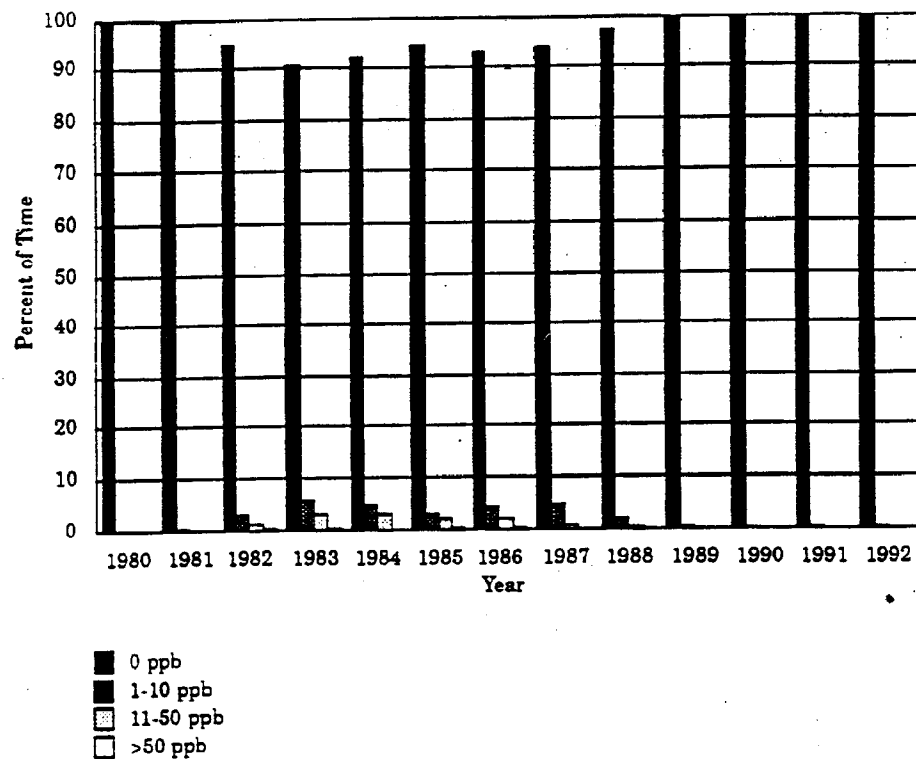
concentration of 18 ppb. The longest period of monitoring data received was from the north unit (recorded in the Little Missouri River Valley), covering the period from April 24, 1980, to August 2, 1992 (1990 data were not received by NDSDH&CL). In the early years, numerous violations of the 1/2-hour, 32 ppb NDAAQS occurred (e.g., 68 in 1982, 62 in 1983, and 70 in 1985). The maximum 1/2 hr time-weighted average concentration recorded during this period was 500 ppb in 1982. Air quality did improve during the second half of the study period, with several years of no NDAAQS violations. This was a result of NDSDH&CL mandated implementation of rigorous operations and maintenance programs by well operators involved in the field and tank vapor collection. Also, expansion of a gas-gathering pipeline network contributed to the decrease in H₂S concentrations because gases were previously released to the atmosphere.

From 1988 to 1990, the Williston Basin Regional Air Quality Study (BLM, 1990) was undertaken as a joint project between North Dakota and the Bureau of Land Management (BLM) to forecast compliance with Federal standards for sulfur dioxide, the resulting product of hydrogen sulfide combustion. Figure III-8 shows the range of concentrations measured at the site. Although over the entire period, 0 ppb was the concentration most frequently recorded, a decrease in air quality is charted, from 1982 through 1987.

Lone Butte. Lone Butte, is located approximately 11 km from the north unit of Theodore Roosevelt National Memorial Park (see Figure III-5). Lone Butte had concentrations of hydrogen sulfide an order of magnitude higher than the other sites. The monitor at Lone Butte (see Figure III-9), in the Little Missouri River Valley near an oil tank battery in the Lone Butte Oil Field, recorded more than 3000 violations of the 1/2-hour average 32 ppb NDAAQS per year from 1984 to 1986. Air quality did improve at the end of the monitoring period, although not to levels continuously below the NDAAQS of 50 ppb which was the standard at that time.

Figures III-10 depicts the range of concentrations measured at the Lone Butte site. Zero ppb is recorded more than 50 percent of the time through the early years, with an improvement towards 80 percent of the time by 1989. (The detection limit of the monitoring equipment was 1 ppb.) The improving trend toward the hydrogen sulfide standard occurred when the NDSDH&CL correlated the sources of the hydrogen sulfide with the ambient monitor levels through the use of the prevailing wind direction. The possibility of NDSDH&CL requiring individual monitoring at each well site convinced the producers to reduce their emissions (personal communication, D. Harman, NDSDH&CL, 8/11/92).

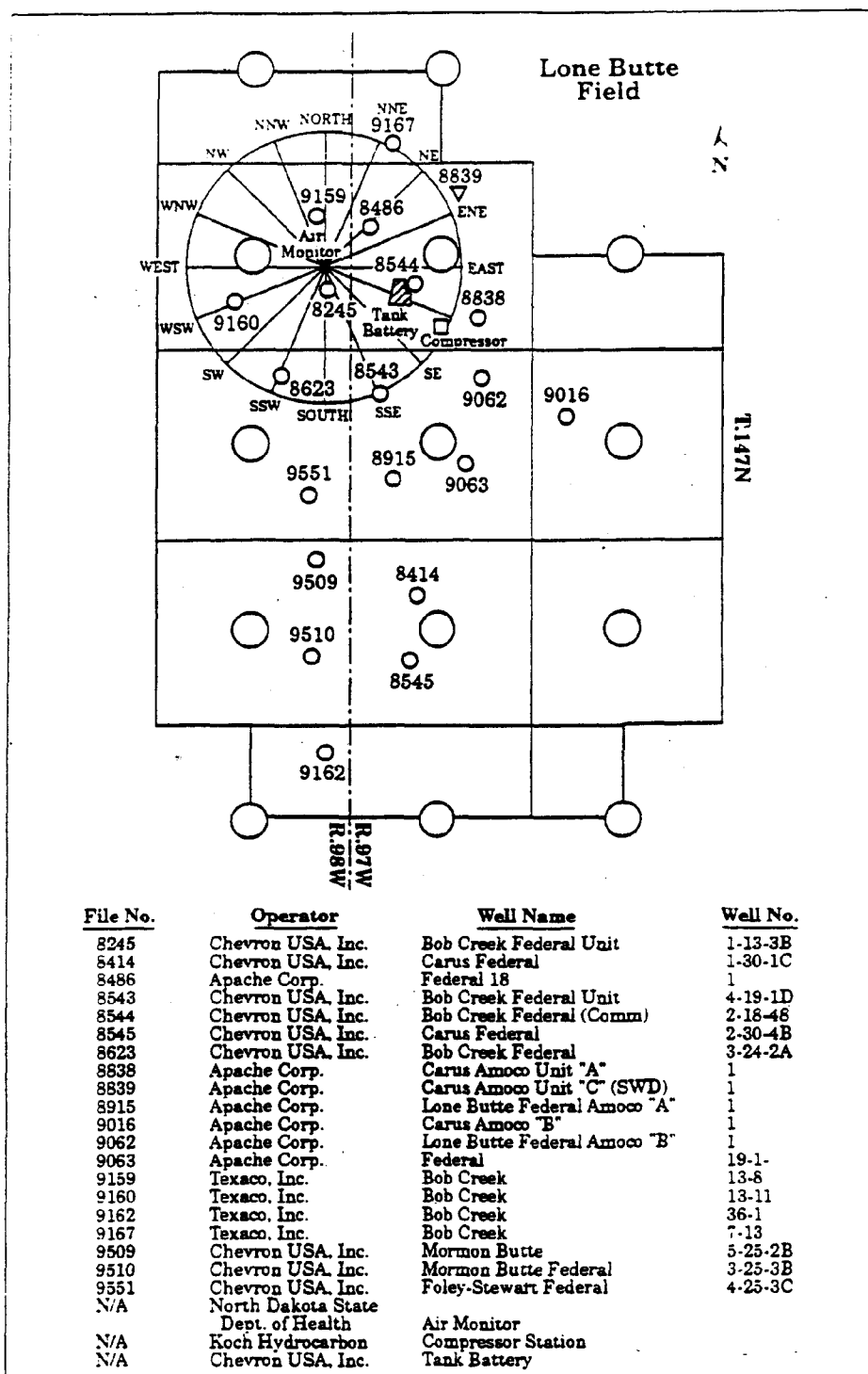
Other Monitoring Sites. Data from thirteen months of monitoring during 1989-1990 were recorded at the Olson farmyard, 1.5 miles from several wells in North Dakota. A maximum 1-hour average concentration of 88 ppb was recorded. Data were also obtained from September 4, 1990, to August 3, 1992, from a monitor in the town of Plaza, North Dakota, within 2 miles of several wells and tank batteries. The maximum concentration recorded on this monitor was 358 ppb, in 1991, with one violation of the NDAAQS recorded.



H₂S monitor detection limit = 1ppb

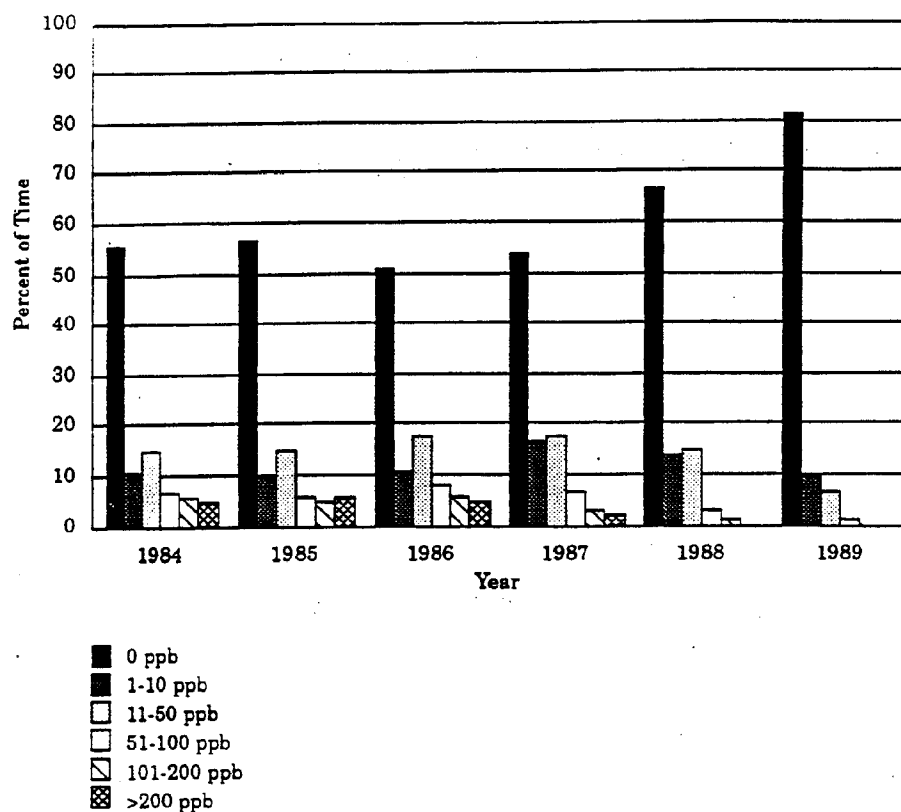
Source: Personal correspondence, D. Harman, NDSDH & CL, 8/11/92.

Figure III-8. Percentage of times designated H₂S concentrations were measured at the Theodore Roosevelt National Park - North Unit monitoring site.



Source: Personal correspondence, D. Harman. NDS DH & CL. 8/11/92.

Figure III-9. Wells producing between July 1986 and December 1987 surrounding Lone Butte H₂S ambient air monitoring site.



H₂S monitor detection limit = 1ppb

Source: Personal correspondence, D. Harman, NDS DH & CL, 8/11/92.

Figure III-10. Percentage of times designated H₂S concentrations were measured at the Lone Butte monitoring site.

Only four months of monitoring data from the Roffler site were received by NDSDH&CL, dating from April 11, 1980, to September 29, 1980. Located in a farmyard within 1/2 mile of a well and tank battery, the monitor measured very low concentrations (usually 0 ppb) with a maximum, time-weighted average of 13 ppb recorded. In contrast, at the Jorgenson monitor, the recorded concentration was as high as 250 ppb. The Jorgenson monitor was located in a valley within one mile of several wells, and the data received dated from October 2, 1980, to May 13, 1982. Data from sixteen months of monitoring, from June 30, 1982, to October 31, 1983, were received for the Kadrmas site. Located in a farmyard within a mile of several wells, the maximum half-hour averages recorded were 541 ppb, in 1982, and 353 ppb, in 1983. From these three studies, an analysis was performed on the monitoring data in comparison to the 32 ppb half-hour standard. The results showed that the concentration of hydrogen sulfide never exceeded the NDAAQS during the four months of the Roffler study. Conversely, at the Jorgenson site, the 32 ppb standard was violated 16 times in 1980, 38 times in 1981, and 26 times in 1982. At the Kadrmas site, the violation count was 18 times in 1982 and 14 times in 1983.

Williston Basin Study. The Williston Basin Regional Air Quality Study was undertaken in the late 1980s to assess the air quality impact of oil and gas production in western North Dakota (BLM, 1990). Emissions inventories were prepared and air quality models were applied to project the impact of sulfur dioxide and hydrogen sulfide emissions in these 12 selected oil fields with respect to applicable ambient air quality standards and PSD increments. Study results suggested that exceedances of both sulfur dioxide and hydrogen sulfide ambient air quality standards could be expected for some fields. Exceedances of Class I PSD increments for sulfur dioxide were expected for three of the four Class I areas studied. Further development of the oil and gas fields, where the emissions of sulfur dioxide and hydrogen sulfide would be possible, would not be permitted unless these exceedances were addressed.

To arrive at estimated hydrogen sulfide concentrations for the study, two types of hydrogen sulfide emissions were considered. First a hydrogen sulfide concentration was obtained through back calculation of the output sulfur dioxide concentrations from the Industrial Source Complex Model. The predicted sulfur dioxide concentrations were the result of modeled dispersion of the point source emissions from heater-treaters firing on H₂S contaminated wellhead gas and from flares which burn H₂S contaminated wellhead gas when a gas gathering pipeline is not available. To provide conservative results, combustion efficiency of 75 percent was used in these calculations, meaning that 25 percent of the hydrogen sulfide remained unchanged. [Note: As stated in Chapter II, flares, in most applications, operate at 95 to 99 percent efficiency.] The second emission source used represented fugitive emissions from leaky valves, tank hatches or pipe connections. These fugitive sources were estimated as contributing a background concentration of 7 µg/m³ (50 ppb), derived from the 99th percentile of the 1-hr average monitored ambient air concentrations at three remote monitor locations (the Theodore Roosevelt National Park's two sites and the Lostwood site) during portions of 1987 and 1988.

At the time of the study, the NDAAQS for H_2S was 50 ppb 1-hour average concentration not to be exceeded more than once a year. NDAAQS exceedances were predicted for 6 of the 12 fields studied using current emissions estimates, with exceedances predicted for 7 of the 12 fields using future emissions estimates. Of the sites where modeling suggested NDAAQS exceedances, the yearly second highest (the first occurrence of ambient hydrogen sulfide concentrations above 50 ppb would be allowed by the law) expected concentrations exceeded 700 ppb for the Lost Bridge Field and 900 ppb for the Rough Rider Field.

Modeling results are only an estimate and are often considered accurate when they are within a factor of two of the actual ambient concentrations. Except for the Lone Butte Field, ambient monitoring data were not available for the other fields to verify or contradict the modeled estimates.

Conclusions. At several locations, for example, Lostwood and the Theodore Roosevelt-south unit, the monitoring program served as a verification that the air quality was within the levels allowed by the law. In two cases, the monitoring programs were of too short of a duration to support any conclusions. When an area is monitored for a short period of time, as at the Roffler and Olson sites, the full range of meteorological conditions and emissions scenarios are not represented in the ambient air measurements. Monitoring was discontinued at Jorgenson and Kadmas (both monitored in the early 1980s) and at Lone Butte (the site with the worst air quality) even though numerous NDAAQS violations were experienced during their last monitored year. This occurred because rigorous inspection and maintenance scheduling was established and/or the data indicated no air quality problems existed (personal communication, D. Harman, NDSDH&CL, 11/9/92).

Ambient concentrations of hydrogen sulfide varied for the sites, with maximum yearly concentrations ranging from half-hour averages, below the 1 ppb detection limit, to 2734 ppb (2.734×10^3 ppb). Two common factors were the median and mode values. For all of the monitoring data received from North Dakota, the median and mode values were 0 ppb. In other words, for each site more than half of all observations recorded below the 1 ppb monitor detection limit.

Severity of Consequences. No epidemiological studies have been carried out to assess the effects of hydrogen sulfide exposure resulting from the production of oil and gas. Many States have enacted ambient air quality standards based upon odor for hydrogen sulfide, since its odor recognition threshold is so low (i.e., 3 to 20 ppb).

Annual average H_2S concentrations, which can more appropriately be compared to a long-term concentration benchmark such as the RfC, were also calculated from the Lone Butte site. These values exceeded the RfC by about an order of magnitude from 1984-1987, dropping to about the RfC level in 1988 and 1989. Since these values indicate the combined impacts of 9 separate wells, it is reasonable to conclude that: 1) the long-term impact of routine releases from any individual well is probably not significantly greater than the RfC;

and 2) the use of a gas-collection system with manifolded flares and rigorous operation and maintenance programs can significantly reduce long-term H₂S impacts.

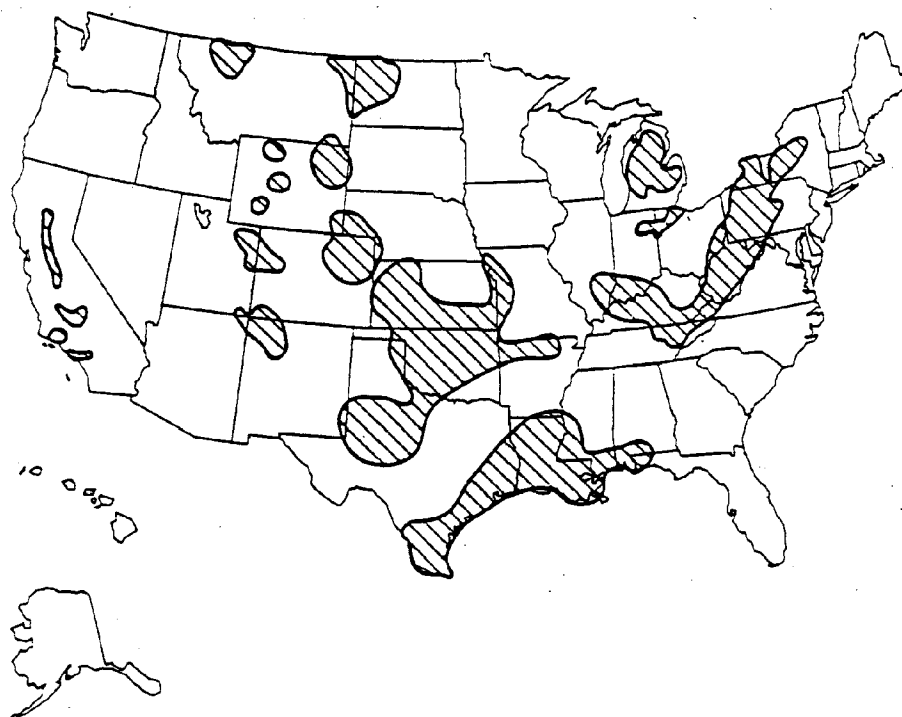
At low concentrations, odor nuisance and eye and respiratory tract irritation are the consequences of exposure rather than the toxic properties of the gas. An explanation for an increased perception of ill health could be related to low level exposure to hydrogen sulfide and pulmonary infections. A study by Rogers and Ferin (1981) concluded that hydrogen sulfide significantly affected the antibacterial system of rats by impairing pulmonary macrophage. However, additional research would be required before any definitive judgements could be made in human exposure scenarios.

Elevated ambient concentrations in two episodes (one in the Great Kanawha River Valley, WV, in 1950, and one in Terre Haute, IN, in 1964) were reported as 0.41 mg/m³ (293 ppb) and 0.46 mg/m³ (329 ppb), respectively (West Virginia Department of Health, 1952; U.S. Public Health Service, 1964). These incidents did not result from oil and gas production; however, the ambient concentrations recorded were comparable to some measurements in North Dakota. General symptoms of malaise, irritability, headache, insomnia, and nausea were reported by exposed populations. In the Terre Haute incident, levels measured at a nearby lagoon ranged from 2×10^3 to 8×10^3 ppb). The most common symptoms reported were offensive odor, foul-tasting water, nausea, vomiting, diarrhea, throat irritation, shortness of breath, burning eyes and asthma. Milder symptoms included cough, headache, anorexia, acute asthma attacks, nervousness, weight loss, fever, gagging and heaviness of chest. The symptoms ceased when the odor disappeared. In an episode in Alton, IL in 1973 similar symptoms were reported (Illinois Institute for Environmental Quality, 1974; NRC, 1979). Ambient hydrogen sulfide levels ranged from 25 ppb to higher than 1×10^3 ppb. Other contaminants, such as ozone and nitrogen oxides were also detected during this episode (Hoyle, 1973).

A study of the levels of sulfur compounds in vegetation near the Lone Butte oilfield and Theodore Roosevelt National Park, was conducted during the summer of 1987 (Bilderback, 1988). The study's conclusions confirmed what ambient monitoring had suggested: the South Unit of the national park may have been impacted by moderately high levels of atmospheric sulfur pollution, and the Lone Butte oil field was impacted by high levels of reactive atmospheric sulfur. Visible signs of vegetation damage were also detected at the Lone Butte oilfield. Furthermore, Bilderback attributes the elevated levels of hydrogen sulfide at the North Unit of the Park to the Lone Butte oilfield.

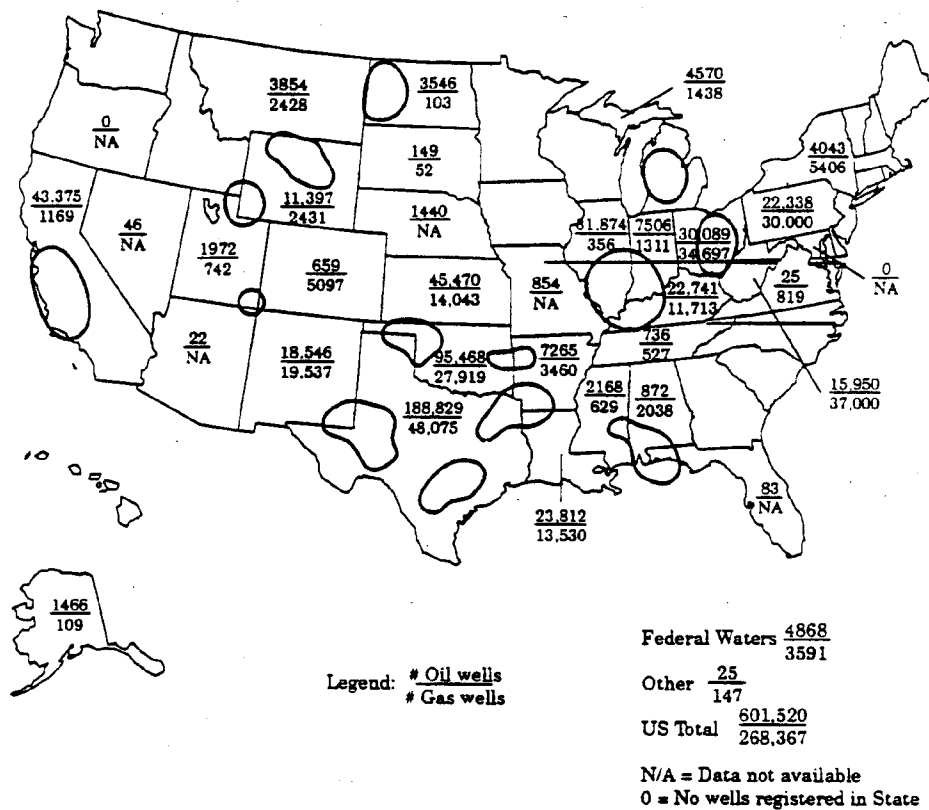
Consequence Analysis — Routine Emissions

As described in Chapter II, several potential sources of routine H₂S emissions can be found at oil and gas production facilities. Figures III-11 and III-12 indicate that 8 States have a significant overlaps of well fields and H₂S prone areas. Using the estimated number of producing wells in these States (Figure III-12) as a conservative measure, it appears that as many as 280,000 oil wells and 54,000 gas wells have the potential for location in an H₂S



Source: IOGCC, 1990.

Figure III-11. Oil and gas fields.



Source: Gas Research Institute, 1990.

Figure III-12. Major H₂S prone areas shown in relation to number of producing oil and gas wells in 1990.

prone area. Although only a fraction of these wells would actually be sour, these figures imply that the potential for routine H_2S emissions is significant. However, no national statistics are available to predict the probability of such emissions. The only record of routine emissions identified is ambient air quality monitoring data from the State of North Dakota. Nine monitoring studies in 12 years resulted in more than 3,300 violations of the NDAAQS. The majority of these violations occurred when the standard was developed based on the more conservative odor threshold rather than on health considerations. Only one violation was recorded after the health-based (higher concentration limits) standards were implemented.

A routine emission scenario would be the incomplete combustion of the wellhead gases, allowing some percentage of the hydrogen sulfide to be emitted. In the oilfields of North Dakota, the concentration of hydrogen sulfide in waste gas stream to flares can reach 30 percent, with the conversion efficiencies of the flaring operations varying from 30 to 100 percent (NDS DH&CL, 1983). (Note, however, that in Chapter II, the common efficiency of a flare, regardless of industrial application is 95-99 percent.) This scenario would result in releases of 0 to 70 percent of the hydrogen sulfide contained in the wellhead gas. In western North Dakota, the amount of natural gas flared exceeded 1 million cubic feet per month in mid-1982, dropping to less than half of that amount by mid-1985, as more wells were tied into a central gas collection system (Liebsch, 1985). As a worst case scenario, if the gas content were 30 percent hydrogen sulfide, and the combustion efficiency were 30 percent (70 percent of the hydrogen sulfide was emitted unconverted), 210,000 cubic feet of hydrogen sulfide per month could have been routinely emitted in the mid-1982 time period.

No H_2S health or ecological effects studies have been conducted which specifically target oil and gas production. The most common consequences of exposure to routine emissions of H_2S are the odor nuisance and eye and respiratory tract irritation.

Exposure Analysis—Accidental Releases

The discussion of accidental releases begins with a description of examples of accidental releases of sour oil and gas in the United States that have impacted the public and wildlife. These examples are then supplemented by calculations of the consequences of a series of hypothetical accident scenarios using atmospheric dispersion models. The risk to the public from an accidental release of H_2S is a function of both the potential consequences and the likelihood of occurrence of an accidental release. Risks from a major accidental H_2S release will vary from facility to facility depending on site-specific factors such as the population density and distribution of nearby populations and the quality of process safety management and risk management practiced at the facility. Since risk is a product of both consequences and likelihood, risk reduction must take both into account. The accidental release discussion concludes with an assessment of accident prevention, mitigation, and emergency procedure measures that, if systematically implemented, could help to prevent or reduce the likelihood of accidental releases of H_2S from sour oil and gas, and mitigate the

consequences in the event that a release occurs. Supporting details for the atmospheric dispersion calculations may be found in Appendix C.

Accidental Release Records

A variety of sources were investigated to locate documentation of accidental sour gas releases. These sources include: Congressional testimony; literature searches; database searches; state regulatory authorities; emergency response organizations; and industry officials. No national statistics regarding sour oil or gas releases were identified. Data base sources were the Accidental Release Information Program (ARIP) database which is maintained by the EPA, the Acute Hazardous Events (AHE) database which was developed by EPA, and the Emergency Response Notification System (ERNS) database. ARIP has records of chemical accidental releases that have occurred since October 1986 with some detailed information on accident cause. AHE has incident records covering the time period 1982 to 1986 and was developed from various sources including press reports, spill reports to the National Response Center, and some state and EPA regional office records. ERNS contains records of releases reported to the National Response Center.

A review of available sources revealed several documented examples of incidents in oil and gas extraction operations in the United States where accidental releases of H₂S have impacted the public and/or the environment since 1974. There was also a very large sour gas release that caused some environmental damage in Alberta, Canada during this time period. Examples of some of these accidents are summarized in Table III-4. It should be noted that these incidents include two accidents related to carbon dioxide injection to improve recovery rather than from the accidental releases of sour natural gas. One of these accidents resulted in eight fatalities, and another accident resulted in two injuries. The other incident resulting in fatalities was the result of fire associated with a natural gas release. However, effects on the public that are directly related to oil and gas extraction activities have most often been limited to evacuation. Isolated incidents resulting in hospital treatment have also occurred. Evacuation may occur as a conservative measure whether or not a life-threatening situation exists. There have been several documented incidents involving livestock and wildlife fatalities. In addition to toxicity, the flammability of accidental releases of sour oil and gas may also present a significant hazard.

Information from the State of Texas shows that there were 145 incidents of sour oil and gas release during the years 1985 through 1992 (Hall, 1992). These accidents were generally related to sour oil and gas rather than specifically from extraction activities. In these incidents, there were 10 deaths (all occupational), and 109 injuries (100 occupational and 9 public). The Texas incidents may be illustrative of the relative hazard to operating personnel, the general public, and the environment. These statistics indicate that the major hazard from oil and gas operations involving H₂S would be to workers rather than the public or wildlife. Workers are more often in close proximity to the wells and associated equipment.

Table III-4. Examples of Accidental Releases of H₂S from Oil and Gas Extraction Operations with Impact on the Public or Environment

| Date and Location | Effects on Public | Effects on Environment | Comments | Source |
|-------------------------------|--------------------------------------------------------------------------|------------------------------------------------|-------------------------------------------------------------------------------------------------|---------------------------------------------------|
| 5/21/74 Meridian, MS | 5 deaths due to associated fire | 40 acres burned | Sour gas gathering pipeline rupture and subsequent fire | Texas Oil and Gas Pipeline Corporation, 1976 |
| 2/2/75 Denver City, TX | 8 occupants of house 200 ft from well were overcome by the gas and died. | None identified | Gas escaped from gas injection well. Gas was 93 v/o CO ₂ and 5 v/o H ₂ S. | Layton et al., 1983 |
| 6/21/81 Big Piney, WY | No impact on public | Deaths of some jackrabbits and blackbirds | Well blowout lasting 8 days. Nearest residence was 2 miles away | Layton et al., 1983 |
| 10/7/82 Calgary, Canada | No impact on public | A number of moose and other large animals died | Release of 10 million ft ³ H ₂ S per day of accident | Oil Daily, 1982 |
| 1/88 Lea County, NM | 1 person physically incapacitated | 1 horse died | An individual changing a tire was overcome with H ₂ S | Correspondence NM Oil Conservation Division, 1992 |
| 6/20/89 Scurry County, TX | Evacuation of nearby residents, 2 treated at hospital | None identified | CO ₂ injection line rupture | Texas Railroad Commission Hall, 93 |
| 1/20/90 Laplata County, CO | 2 mile radius evacuated | None identified | Well leak | ERNS, National Response Center Report #01425 |
| 5/29/90 Heidelberg, MS | No deaths but 2,000 local residents were evacuated | None identified | Well blowout and consequent fire | Platt's Oilgram News, 1990 |
| 5/16/91 Lambert, MT | 12 people were evacuated | None identified | Incident was caused by corrosion of gathering line. Evacuation due to smell. | National Response Center |
| 8/19/91 Yoakum County, TX | None identified | 7 cows, 1 coyote, and rabbits died | Sour gas gathering line rupture, 1.2% H ₂ S | Texas Railroad Commission Hall, 93 |
| 12/17/91 Gaines County, TX | None identified | Unspecified number of wildlife died | Sour gas gathering line rupture, approximately 6% H ₂ S | Texas Railroad Commission Hall, 93 |

Atmospheric Dispersion Analysis

Atmospheric dispersion analyses of sour oil and gas releases by computer model were both reviewed in the literature and conducted. The following issues are discussed prior to analyses of the consequences of sour gas release scenarios:

- Choice of scenarios;
- Sour gas composition and density;
- Behavior of sour gas upon release; and
- Choice of atmospheric dispersion models.

Choice of Scenarios. The objective in choosing scenarios was to investigate a representative range of potential accidental release situations including hypothetical worst case scenarios. Scenarios for atmospheric dispersion analysis were chosen from documented accidental releases, expressions of public concern, and literature analyses in which dispersion models were applied to sour gas release scenarios.

The accidental sour gas releases documented in the previous section show some common causes. Well blowouts and line releases are examples of accidents that have occurred and resulted in offsite impact. Therefore, these accident scenarios were included in the atmospheric dispersion analyses. Investigation of some public complaints resulted in concerns regarding sour gas releases from extinguished flares, collection of sour gas in low-lying areas, leakage from temporarily abandoned or idle wells, and line leakage (NDS DH&CL, 1989; U.S. EPA, 1992). These concerns were also investigated as accidental release scenarios.

Several literature sources provided descriptions of hazards associated with the operation of sour oil and gas wells in addition to sour gas dispersion analysis to support scenario development. Hazard/risk analyses and data on the composition of sour gas of wells in Alberta, Canada (Alp et al., 1990), southwest Wyoming and northern Utah (Quest, 1992), and western Wyoming and adjoining areas of Utah and Idaho (Layton et al., 1983) were considered in the choice of scenarios. Assessments of levels of concern (LOC), concentrations at which H_2S is of concern, for acute exposure to H_2S were also provided in these sources. Although H_2S alone is more dense than air, in general, the literature pertains to sour gas mixtures that are typically less dense than air and concludes that sour gas releases from well blowouts and line ruptures are of most concern as potential causes for levels of concern to extend significant distances from the point of release.

Sour Gas Composition and Density. The density of sour gas mixtures is of importance because it is one determinant of whether an accidental release will result in a plume that travels downwind at ground level or will result in a buoyant plume that rises and disperses. A dense plume may have a greater impact on humans and wildlife because it remains at ground level for a period of time. The density of sour gas mixtures at atmospheric pressure (to which accidental releases of sour gas are discharged) is dependent

on the temperature and composition of the mixture. The density of a given gas mixture increases as temperature decreases. Expansion of natural gas released from a pressurized system results in cooling of the gas. The colder a gas, the higher its density.

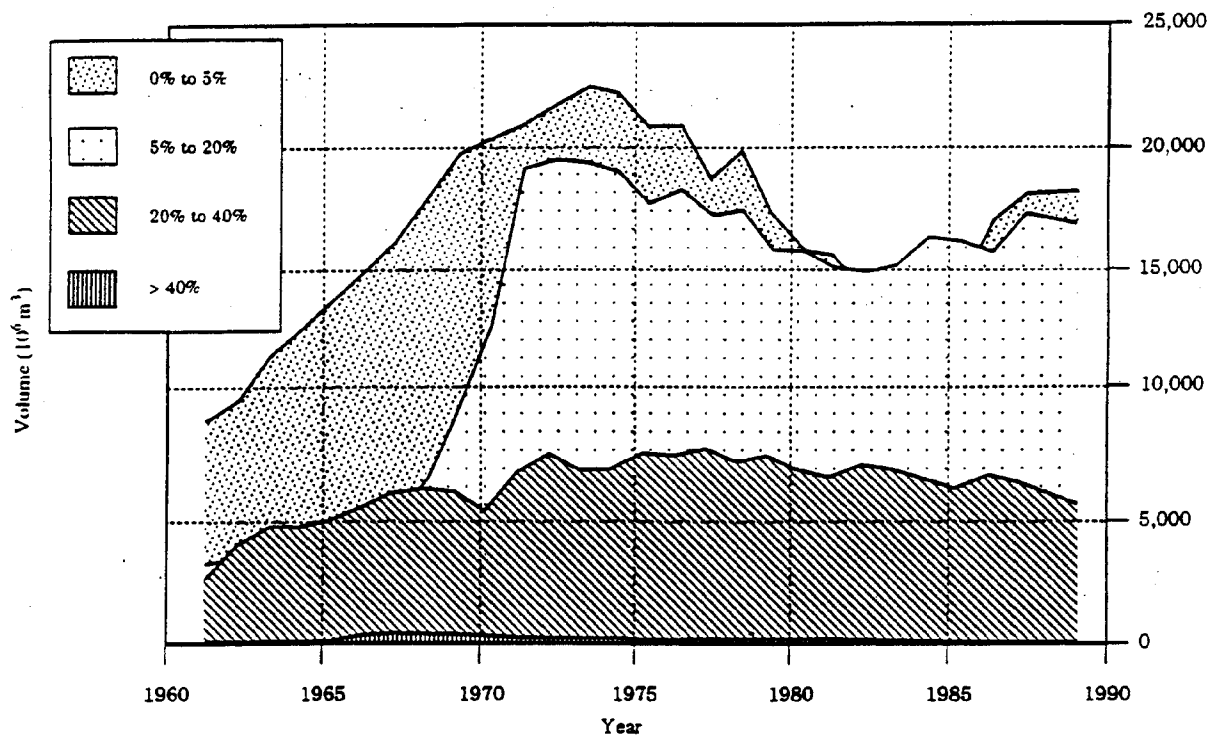
There is a wide variety of potential compositions of sour gas mixtures, depending on the reservoir. The density of these mixtures depends on their composition. In addition to hydrogen sulfide, natural gas can also contain some or all of the following: hydrogen, helium, carbon dioxide, nitrogen, methane, ethane, propane, isobutane, n-butane, isopentane, n-pentane, hexanes, heptanes, and higher molecular weight hydrocarbons. The largest component is typically methane, with hydrogen sulfide, ethane and possibly carbon dioxide (CO_2) likely to be present in significant proportions. Natural gas must contain some proportion of hydrogen sulfide in order to be considered sour.

Figure III-13 illustrates the variability of sour gas composition by showing the distribution of H_2S composition by number of sour gas wells in Alberta, Canada (Alp et al., 1990). Figure III-14 presents the same information as a function of the total number of tons of sulfur from natural gas produced each year. The H_2S composition can range from a small fraction of a percent to over 40 percent. A statistical analysis was performed of the sulfur composition of wells in the Overthrust Belt in western Wyoming and adjoining areas of Idaho and Utah (Layton et al., 1983). Volume percentages of sulfur were found similar to those in the Alberta wells. The sulfur composition ranged from less than 1 percent through 35 percent, with a mean of about 10 percent. Data on H_2S in California oil and gas fields shows fields with H_2S concentrations varying from less than 1×10^5 ppb (0.01 percent) to 20 - 30 percent (Dosch and Hodgson, 1986).

In addition to increasing the density of a sour gas mixture, carbon dioxide in sufficiently large concentrations can extinguish sour gas flares, resulting in uncombusted H_2S being released. CO_2 concentrations in various parts of the Overthrust Belt were found to vary from less than 5 percent by volume to more than 50 percent (Layton et al., 1983).

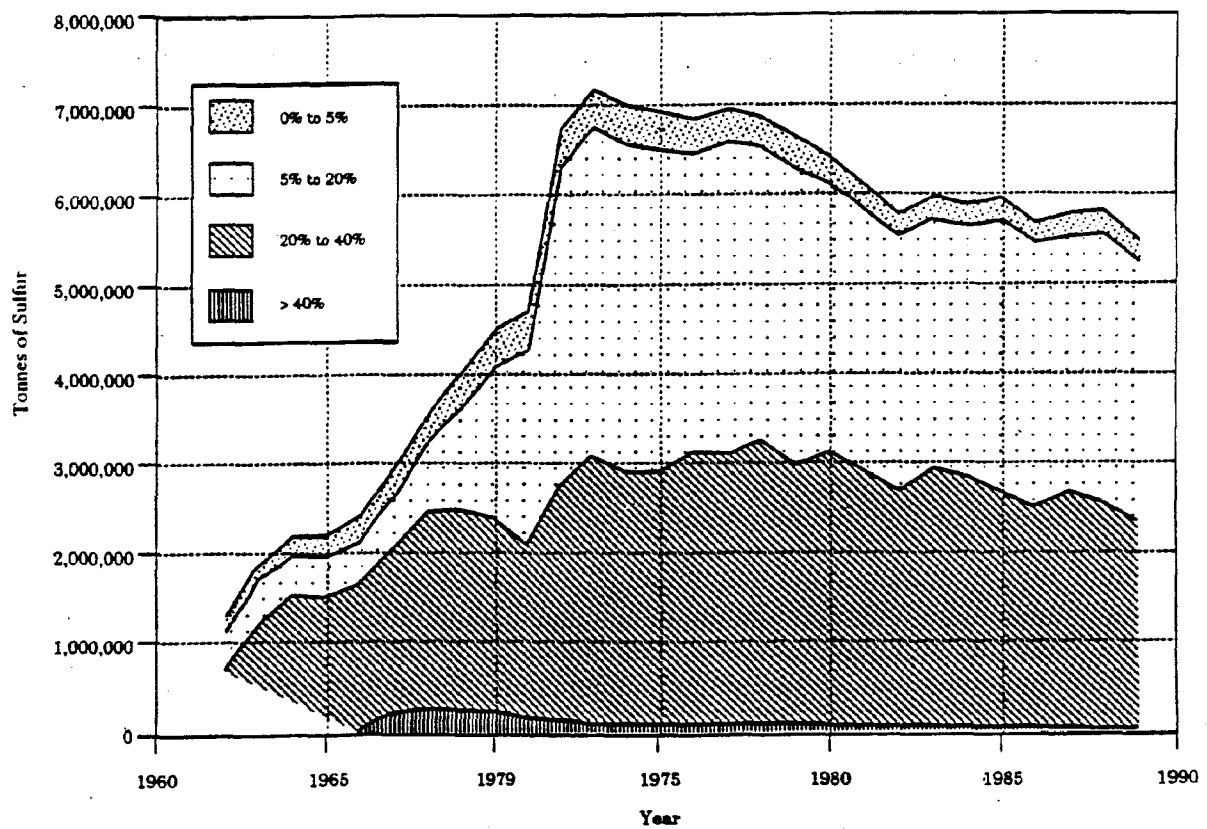
Some example sour gas compositions are presented in Table III-5. Composition D is the single composition considered representative of all the data on producing gas wells in Alberta, Canada. Composition C is a representative gas composition produced by wells in a southwestern Wyoming sour gas field (Quest, 1992). Data were collected for a producing well in western North Dakota (U.S. EPA correspondence, 26 October 1992), and the compositions of streams after processing to recover hydrocarbon condensate at that well are given by compositions A and B of Table III-5. Composition A shows the gas composition after high pressure separation, and Composition B shows the composition after low pressure separation. The low pressure stream has a significantly higher H_2S concentration than the high pressure stream although its flowrate is lower.

H_2S alone is more dense than air, while methane alone is less dense than air. Natural gas mixtures of H_2S and light hydrocarbons are typically less dense than air to the extent that methane predominates in the mixture. The approximate molecular weight of air is 29. The



Source: Alp et al., 1990.

Figure III-13. Distribution of producing sour gas wells in Alberta by H₂S content.



Source: Alp et al., 1990.

Figure III-14. Total sulfur generated from producing gas wells in Alberta by H_2S composition of well.

III-5. Example Gas Stream Compositions

| Component | Molecular Weight | Mole Fraction | | | |
|-------------------------------|------------------|----------------------------------|----------------------------------------------|----------------------------------------------------|------------------------------|
| | | Sample Well | | Composition Used in Cave Creek Risk Assessment (C) | Composition Used by ECRB (D) |
| | | High Pressure (A) (well flow) | Low Pressure (B) (vapor recovery systems) | | |
| Hydrogen Sulfide (H_2S) | 34 | 0.075 | 0.277 | 0.146 | 0.30 |
| Carbon Dioxide (CO_2) | 44 | 0.01 | 0.013 | 0.027 | 0.123 |
| Nitrogen (N_2) | 28 | 0.003 | - | 0.017 | 0.02 |
| Methane (CH_4) | 16 | 0.83 | 0.45 | 0.699 | 0.55 |
| Ethane (C_2H_6) | 30 | 0.047 | 0.10 | 0.058 | 0.005 |
| Propane (C_3H_8) | 44 | 0.012 | 0.064 | 0.018 | 0.001 |
| Isobutane (C_4H_{10}) | 58 | 0.0032 | 0.024 | 0.0042 | 0.001 |
| Normal butane (C_4H_{10}) | 58 | 0.0038 | 0.026 | 0.0050 | — |
| Pentane (C_5H_{12}) | 72 | 0.0016 | 0.011 | 0.0022 | — |
| Hexane (C_6H_{14}) | 86 | 0.0020 | 0.0086 | 0.0018 | — |
| Heptanes (C_7H_{16}) | 100+ } | 0.0034 | 0.019 | 0.0031 | |
| Octanes+ (C_8H_{18}) | | | | 0.0176 | |
| Average Molecular Weight | | 19.25 | 28.9 | 23.2 | 25.2 |

two composite compositions and the high pressure stream shown in Table III-5 have molecular weights less than 29. Thus, these streams are less dense than air at the same temperature and pressure. CO₂ is also more dense than air at similar conditions and may cause the density of a gas mixture to be higher than that of air if present in large concentrations. The low pressure stream has a molecular weight very close to that of air and with some modification in composition, such as more H₂S or CO₂ and less methane, could be more dense than air.

Gas mixtures which are denser than air due to high concentrations of CO₂ have caused fatalities as described in the discussion of release histories. A well blowout near Big Piney, Wyoming, on June 21, 1981, killed small animals up to about 0.8 km from the well (Alp et al., 1990). The gaseous emissions from the well were composed of 70 percent CO₂, 20 percent methane and 3 to 4 percent H₂S. It is not clear that H₂S caused the animal fatalities in this case. However, these emissions were clearly denser than air. The literature generally describes mixtures that are less dense than air; the studies of hazards/risks associated with sour gas (Alp et al., 1990; Quest, 1992) referred to in this report used gas compositions that are buoyant.

In conclusion, sour gas as produced is typically buoyant. There can be atypical cases where natural gas contains high concentrations of H₂S and/or CO₂ which results in a denser-than-air mixture. Also, gas processing such as separation for condensate (liquid hydrocarbon) recovery at the well site may affect the density of a gas stream.

Behavior of Sour Gas Upon Release. High pressure sour gas releases from well blowouts and line ruptures are initially high momentum jets which can vary directionally between the extremes of vertical and horizontal. The jet (high velocity) nature of such releases is caused by the differential pressure between the contained gas and the atmosphere and results in entrainment of the surrounding air into the released gas. Entrainment of air results in dilution of the released gas and causes its density to approach that of air. Thus, as air is entrained, both positively and negatively buoyant gas mixtures with air will tend to have densities approaching that of air. A high velocity jet (such as from a high pressure source) will entrain air more rapidly and to a greater extent than a low velocity jet from a low pressure source. Depending on the release conditions, it is possible for a gas mixture to retain its initial positive or negative buoyancy. Negative buoyancy releases are of greatest concern because of dense gas behavior and their tendency to travel to ground level where exposure is likely to occur.

As previously discussed, the effective molecular weight (and thus, the density) of sour gas mixtures as produced is generally less than that of air with isolated exceptions. Therefore, models for these cases should consider the various mechanisms that describe the near-field (near the point of release) and far-field (downwind) behavior of the plume of released gas and its interaction with the surrounding air. In particular, the models should contain mechanisms for simulation of the following sequence of effects occurring along a plume of released gas from the point of release: a) near-field momentum jet modeling; b)

subsequent positively-buoyant rise or negatively-buoyant sinking; c) potential for a nominally buoyant plume that is initially on the ground to rise or, if negatively-buoyant, to stay at ground level; and d) far-field transition to a subsequent Gaussian (passive modeling) phase. The Gaussian or passive phase assumes random mixing in the far-field due to the action of atmospheric turbulence; whereas, close to the source, entrainment of air is affected or sometimes dominated by the released material itself.

Choice of Atmospheric Dispersion Models. The models reviewed in the literature for analysis of the dispersion characteristics of sour gas were GASCON2, FOCUS, and a Gaussian dispersion model. Confirmatory, independent atmospheric dispersion analyses were conducted for most of the scenarios with the SAPLUME, SLAB, and DEGADIS models.

The computer model GASCON2 was specifically developed in Canada to model sour gas releases from well blowouts and line ruptures (Alp et al., 1990). The model incorporates high pressure gas jet releases, plume rise or sinking (depending on density) and subsequent passive atmospheric dispersion. GASCON2 was validated by comparison with experiment. The associated literature also contains extensive discussions on uncertainties and the work was reviewed by a science advisory board.

The proprietary model, FOCUS, contains a treatment of momentum and buoyancy effects and transition to subsequent passive atmospheric dispersion (Quest, 1992). The model has been available for several years and has been used in a number of risk assessments of toxic and flammable vapors.

The Gaussian dispersion model is suitable for passive releases (Layton et al., 1983). Therefore, jet momentum effects are neglected and the results are not expected to be reliable close to the emission source. However, at large distances where low concentrations of H_2S would result (e.g., in the low part per million range), all three of the above models should converge to similar results.

A well-established model developed by Ooms (1974, 1983) for jet releases of vapors can model the dispersion of both buoyant and heavier-than-air momentum jets. The EPA has sponsored the incorporation of the Ooms model into the well-known DEGADIS model (Spicer, 1988), which can only simulate vertical, but not horizontal releases. Another proprietary model, SAPLUME, is also based on the Ooms model and can simulate jets at any orientation (SAIC, 1990).

SLAB was developed by Lawrence Livermore National Laboratory (Ermak, 1989). This computer model also accepts jets of vertical or horizontal orientation. However, it was specifically developed for heavy vapors and has not been carefully validated for use with buoyant plumes, so results must be interpreted with care.

Consequence Analysis — Accidental Releases

In the following sections, the consequences of accidental releases for a variety of scenarios are presented.

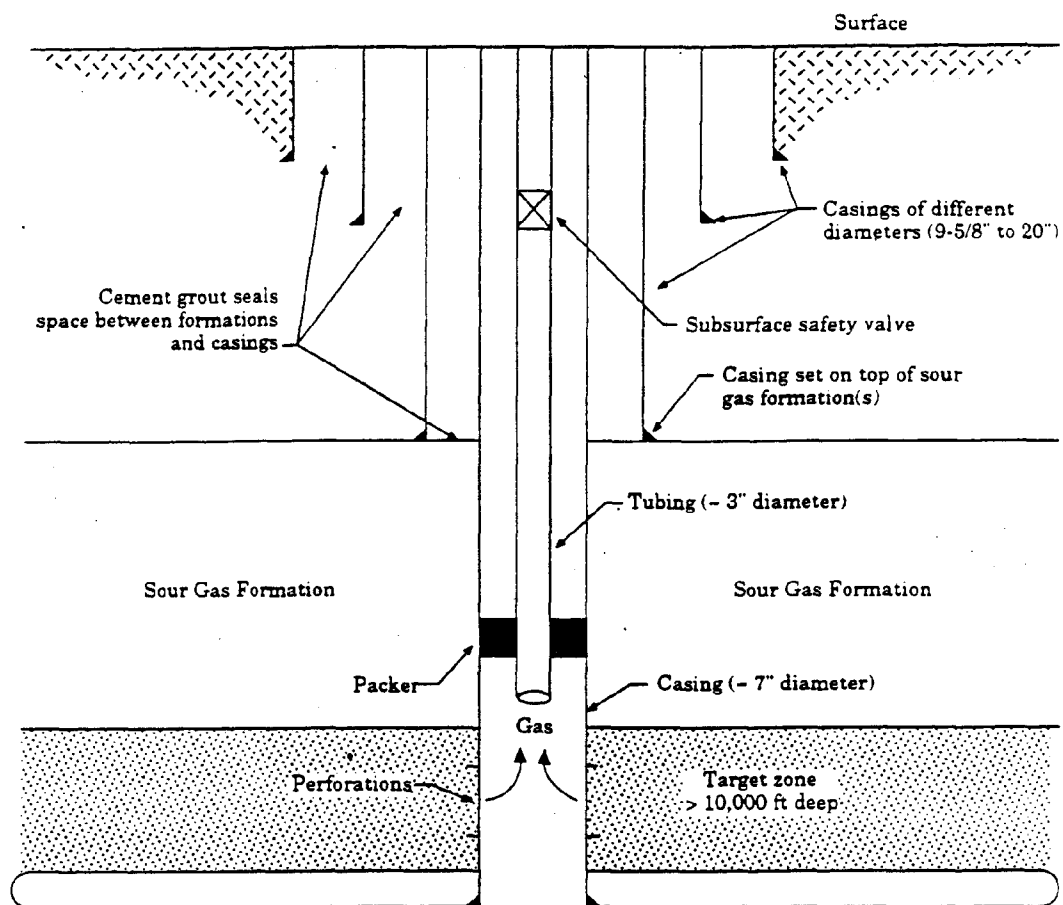
It should be noted that the calculated consequences of some of the modeled scenarios are based on very conservative assumptions in order to examine the worst case. The worst-case scenario is designed to generate the maximum impact off-site. It is considered to be extremely unlikely and does not take into account a variety of factors that can significantly reduce downwind impacts. However, the worst-case scenario is useful to facilities and communities surrounding facilities in gaining an understanding of the potential magnitude of severe situations. The potential for severe consequences should be taken into account along with more probable scenarios when setting priorities for community emergency planning.

Consequence Analysis of Jets from Well Blowouts

Figure III-15 shows the layout of a typical completed sour gas well. A well blowout is an uncontrolled release from a well during drilling, servicing, or production operations. Such an accident could occur if a blowout preventer failed during drilling or a subsurface safety valve fails to operate during production. The possible types of flow from a ruptured well are shown in Figure III-16. A useful simplification is that an accidental release into the casing is possible during drilling or servicing, while flow would likely be restricted to the production tube if there were a blowout during normal production operations. Potential flow orientations are shown on Figure III-17. Examples evaluated for the purposes of this study included the extremes of a vertical jet and a horizontal downwind jet.

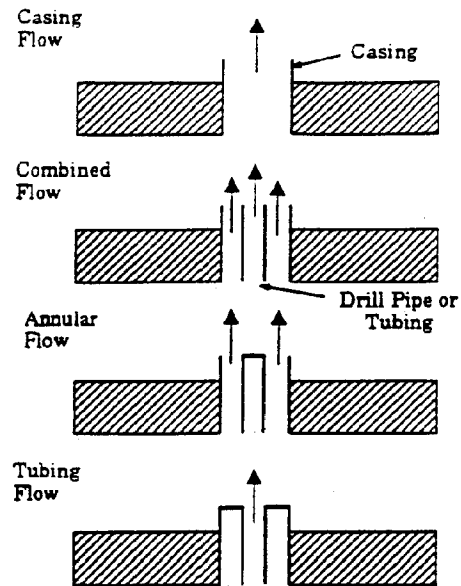
Flow rates for the scenarios identified in Figure III-16 are functions of such items as rock permeabilities, gas properties, depth, and tubing and casing diameters. Overall, there are large variabilities in these parameters. One measure of the potential rate of flow from a well is the Calculated Absolute Open Flow Rate (CAOF), which is the rate of flow of gas into the well bore when the pressure is atmospheric. This measure represents a maximum possible flow rate. The actual flow rates out of a ruptured well will be less than the CAOF because of frictional effects in the pipework. Thus, the use of CAOF for a release rate is conservative. Table III-6 gives some representative examples of how the CAOF is reduced for a specific set of well parameters. A flow rate of 2×10^7 standard cubic feet per day (scf/d) was chosen for representative calculations, with a flow rate of 10^8 scf/d being taken as an example of a very high flow rate. The bases for these assumptions are presented in Appendix C.

For the scenarios analyzed for this report, it was assumed that the gas emerges as a vapor. Since typical pressures are very high (e.g., in excess of 1,000 pounds per square inch gauge (psig)), the flow is choked (limited) at sonic velocity.



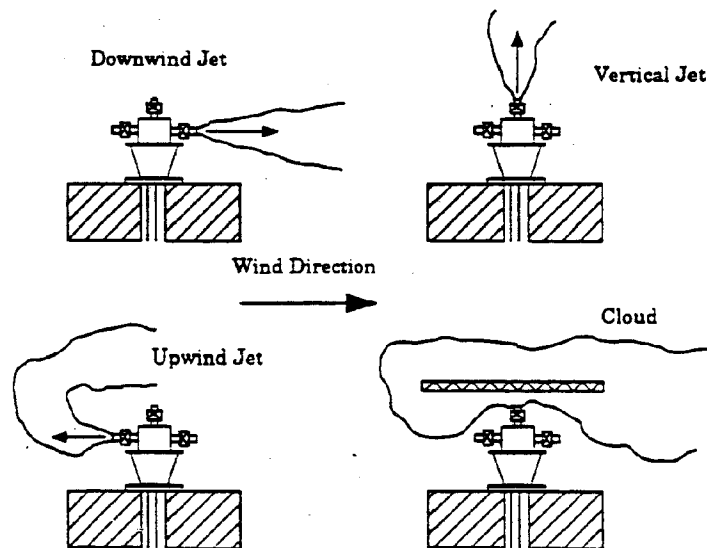
Source: Layton et al., 1983.

Figure III-15. Simplified representation of a completed sour-gas well.



Source: Alp et al., 1990.

Figure III-16. Possible well flow scenarios.



Source: Alp et al., 1990.

Figure III-17. Possible well accidental release geometries.

Table III-6. Surface Deliverability as a Function of Well CAOF

| CAOF (10³ m³/d)* | Casing Flow | Annulus and Tubing Flow | Annulus Flow | Tubing Flow |
|---------------------------------------------------|------------------------|------------------------------------|-------------------------|------------------------|
| 5000 | 57.4 % | 52.2% | 39.3% | 8.5% |
| 1000 | 95.0 | 82.5 | 76.0 | 26.0 |
| 500 | 98.0 | 96.0 | 92.0 | 46.0 |
| 100 | 99.0 | 98.0 | 97.0 | 90.0 |
| 50 | 99.2 | 99.2 | 99.2 | 98.6 |

Source: Alp et al., 1990.

* At 15°C and 101.3kPa.

The values in Table III-7 were based on the following well conditions:

- Well depth (m) 2660
- Casing inside diameter (mm) 156.3
- Tubing outside diameter (mm) 73.0
- Tubing inside diameter (mm) 62.0
- Reservoir pressure (kPa) 15,900
- Reservoir temperature (°C) 75

The temperature of the gas in the well prior to expansion to atmospheric pressure through the rupture depends on the depth of the gas reservoir. The amount of cooling depends on the initial pressure and the composition. For the purposes of this analysis, an expanded gas temperature of 0°C (32°F) was assumed. This assumption is further discussed in Appendix C.

For a well blowout, the release could continue indefinitely. For illustrative purposes, it was assumed that any nearby individuals could be evacuated within one hour. The calculations of distances of concern discussed below assume that the duration of release and possible duration of exposure is one hour.

For vertical releases of sour gas from well blowouts, the independent dispersion modeling (SLAB, DEGADIS, SAPLUME, and the Gaussian model) and results reported in the literature (Alp et al., 1990; Quest, 1992) indicate that there will be no concentrations above levels of concern at ground level, either at the emergency countermeasure (ERPG-2) or potential fatality (LC_{01}) level. The jet is oriented upwards and, for either buoyant or negatively buoyant sour gas, dilutes rapidly due to its high momentum.

For horizontal releases from well blowouts, results calculated using the SLAB and SAPLUME models are given in Table III-7 for low wind speed and stable conditions. Releases in the direction of the wind were assumed. Depending on composition, release rate, and the model used, distances to the LC_{01} range from 700 meters (approximately 0.4 miles) to greater than 10 kilometers (approximately 6 miles). Distances to the ERPG-2 range from 2.8 kilometers (approximately 1.7 miles) to greater than 10 kilometers (approximately 6 miles). The atmospheric conditions input into the models represent conditions of high stability and little atmospheric mixing. Thus, these conditions represent the "worst-case" because levels of concern will be exceeded for predicted distances from the point of release that will exceed those for other weather conditions. The results were calculated neglecting the possibility of slight buoyancy of the plume even after dilution. DEGADIS results are not quoted because the jet module of that computer model can only handle vertical releases. For all the models, results in the range greater than 10 km (6 miles) should be regarded as beyond the limit of validity and probably conservative (see below).

For comparison, the GASCON2 model calculates an estimated distance of 1.6 km (1 mile) to the LC_{01} for a composition D flow rate of 2.4×10^5 m³/d (cubic meters per day), or 8.5×10^6 scf/d, and an estimated distance of approximately 5 km (3 miles) for a composition D flow rate of 9.5×10^5 m³/d (3.4×10^7 scf/d) (Alp et al., 1990). From Table III-7, for composition D with a flowrate of 6×10^5 m³/d (2.1×10^7 scf/d), SLAB and SAPLUME predict a distance of 2.9 km and 3 km (both approximately 1.8 miles) to the LC_{01} , respectively. These distances and release rates are intermediate to those values in the GASCON2 model. Therefore, the results calculated with GASCON2 are consistent with the results generated by SLAB and SAPLUME (to within the uncertainties expected in such models).

**Table III-7. SLAB and SAPLUME Results - Horizontal Releases
from a Well Blowout**

| Composition (from Table III-6) and Flow Rates (m ³ /d) | Predicted Distance 1 h Exposure (SLAB) | | Predicted Distance 1 h Exposure (SAPLUME) | |
|-----------------------------------------------------------------------------------|----------------------------------------------|--------|-------------------------------------------------|--------|
| | LC ₀₁ | ERPG-2 | LC ₀₁ | ERPG-2 |
| A, 6 x 10 ⁵ m ³ /d (7.5% H ₂ S) | 700 m | 2.8 km | 1 km | 3.1 km |
| B, 6 x 10 ⁵ m ³ /d (27% H ₂ S) | 2.8 km | 7 km | 2.7 km | 10 km |
| C, 6 x 10 ⁵ m ³ /d (15% H ₂ S) | 1.5 km | 4.7 km | 1.5 km | 5.7 km |
| D, 6 x 10 ⁵ m ³ /d (30% H ₂ S) | 2.9 km | 7 km | 3 km | 10 km |
| D, 3 x 10 ⁶ m ³ /d (30% H ₂ S) (extreme case) | 7 km | >10 km | >10 km | >10 km |

By contrast, the FOCUS model calculates an estimated distance of 0.7 km to the LC_{01} for composition C with a flow rate of $6 \times 10^5 \text{ m}^3/\text{d}$ ($2.1 \times 10^7 \text{ scf/d}$) (Quest, 1992). This prediction is about half that given by the SLAB and SAPLUME calculations, which predict a distance of 1.5 km (0.9 miles) to the LC_{01} for composition C with a flowrate of $6 \times 10^5 \text{ m}^3/\text{d}$ (by implication, GASCON2 would predict similar distances). This difference in predictions may lie within the range of uncertainty of vapor dispersion models; the precise reason for the difference cannot be determined from the information available about the proprietary model FOCUS.

Figure III-18 shows the results of the comparison of observations from actual well blowouts in Alberta, Canada, with GASCON2 predictions. The actual blowouts were at Lodgepole (October 17 through December 23, 1982), Clovesholm (September 24-28, 1984) and Rainbow Lake (December 9-14, 1985). The air quality data associated with each blowout were collected with public safety interests in mind and not model verification or validation. As a consequence, most of the observations were poorly documented with respect to magnitude, location, averaging time and meteorological conditions. Screening of the data to select only measurements in which there could be reasonable confidence produced a data set of 50 (45 of which were from the Lodgepole blowout). For the Lodgepole case, seven stationary and five mobile units collected data within 50 km of the site.

As can be seen, GASCON2 significantly overpredicts, especially when its predicted concentrations are in the greater than $3 \times 10^4 \text{ ppb}$ range, where overpredictions are by as much as a factor of 10. This concentration is the range of interest for ERPG-2 and LC_{01} . These overpredictions tentatively (because of the poor quality of the data) suggest that the GASCON2 results are conservative and, by implication, that the results from the SLAB and SAPLUME calculations are also conservative.

Possible reasons for conservatism include underestimating the effect of the plume lifting off the ground. For distances in the several km to the greater than 10 km (6 mile) range, neglect of dry deposition (fallout, transfer from the air to other surfaces) of the highly reactive H_2S may also lead to overestimation of airborne concentrations. However, it is more likely that the poor quality of the observations is responsible for the apparent disagreements.

Standard text-book calculations indicate that flammable mixtures will not propagate more than 100 m from the point of release (Quest, 1992). If ignition occurs, potentially fatal thermal radiation loads could be received up to approximately 100 meters from the source. Although not pertinent to a discussion of hazards from H_2S releases, it should be noted that SO_2 will be emitted as a result of igniting a sour gas stream and may present a toxicity hazard.

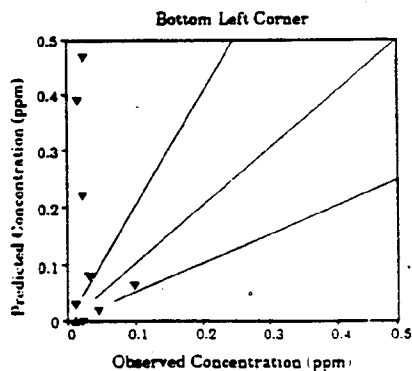
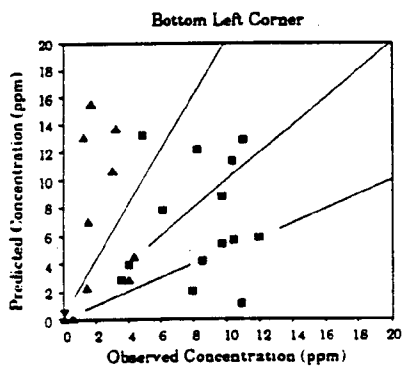
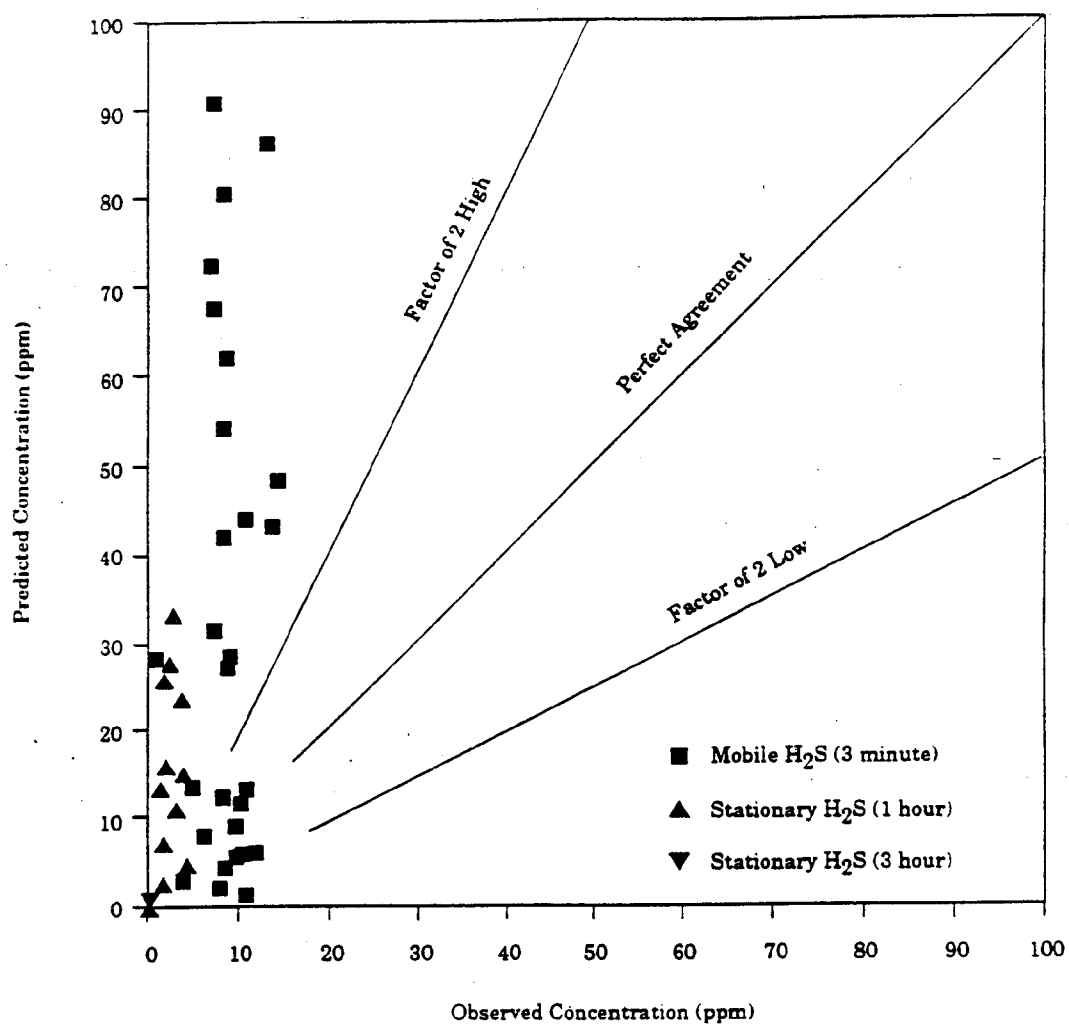


Figure III-18. Predicted H₂S and SO₂ concentrations for selected well blowout observations.

Consequence Analysis of Line Ruptures

Releases from line ruptures will behave much like well blowouts unless there is a means to isolate the rupture. Most gathering systems are not equipped with isolation systems, and aging pipework presents integrity concerns (particularly when not properly maintained). Advanced gathering line systems may have emergency shutdown valves (ESDs) that are remotely or locally operated. ESDs may be manually or automatically operated (e.g., by a signal from an H_2S detector). Figures III-19 and III-20 show some typical configurations for ruptures of lines that are equipped with ESDs. For such releases, the total mass released is limited by the quantity of gas between ESDs. The valves may be 1 km to 3 km apart (0.6 mile to 1.8 mile) (Alp et al., 1990).

Figure III-21 shows typical mass release rates for the rupture cases identified in Figure III-20, assuming a 6" diameter pipe at a pressure of approximately 5,000 kPa (725 psi). Rupture Scenario 4 (no ESD) follows Scenario 1 until a steady state of $2.4 \times 10^6 \text{ m}^3/\text{d}$ ($8.5 \times 10^6 \text{ scf/d}$) is reached after about a minute.

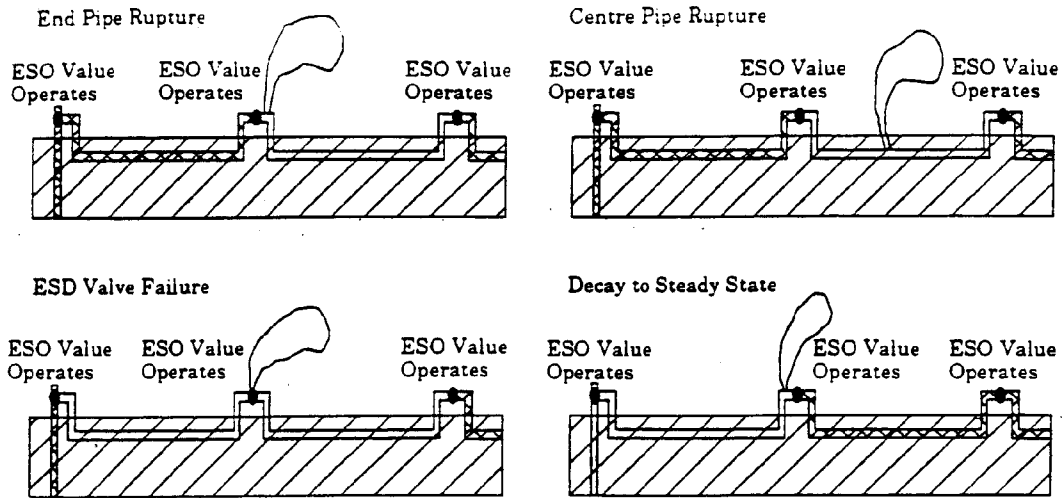
Figure III-22 shows mass release rates as a function of time for various pipe diameters and various ESD separations with an assumed line pressure of approximately 50 atmospheres (735 psi). The variable, t_d , listed on Figure III-22 is the time in seconds taken for 99 percent of the line contents to be depleted after closure of the ESD valves. M_d is the total mass released in kg. As can be seen, for many of the cases, a puff release (rather than a continuous release) is a reasonable approximation because of the short duration.

The predicted distances of concern for lines with ESD valves that close promptly are smaller than those for wellhead blowouts because the duration of release is shorter, the total mass released is smaller, and because shorter exposure times allow higher tolerable levels of concern.

Calculations from SADENZ, a companion model to SAPLUME for puff releases, predict that distances to the LC_{01} for compositions A-D in Table III-5 and released masses specified in Figure III-22 range from 600 m (0.4 miles) to 4.3 km (2.6 miles). Predicted distances to the ERPG-2 adjusted for shorter exposure time (method described by Gephart and Moses, 1989) range from 750 m (0.45 miles) to approximately 5.6 km (3.4 miles). This is consistent with the calculated results from the GASCON2 model (Alp et al., 1990) and, as before, somewhat higher than those calculated from the FOCUS model (Quest, 1992).

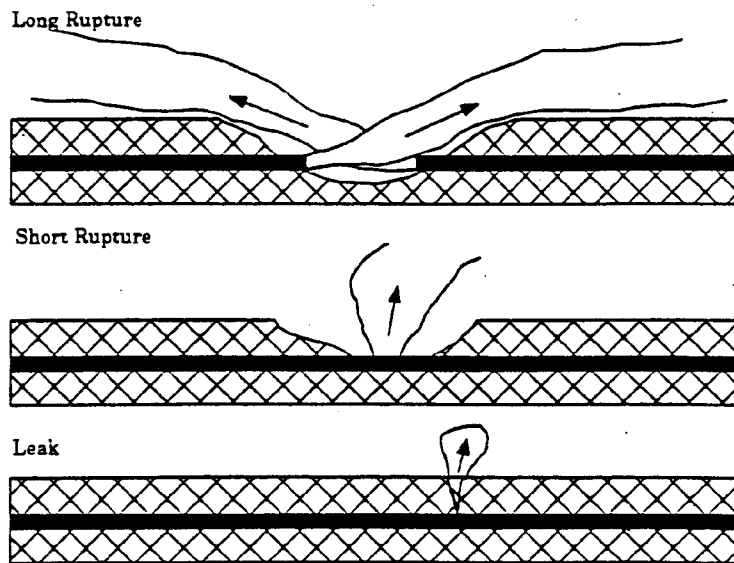
Consequence Analysis of Line Release Seepage

A survey of several gas pipeline incidents that were investigated by the National Transportation Safety Board (NTSB) indicated that, for buried gas pipelines operating above 600 psig, a 1" diameter hole will blow away the soil above the line (Quest, 1992). This will result in the formation of a crater from which the gas will escape as an unobstructed jet. For smaller holes (e.g., a 1/4" diameter hole caused by corrosion), the soil remains in place



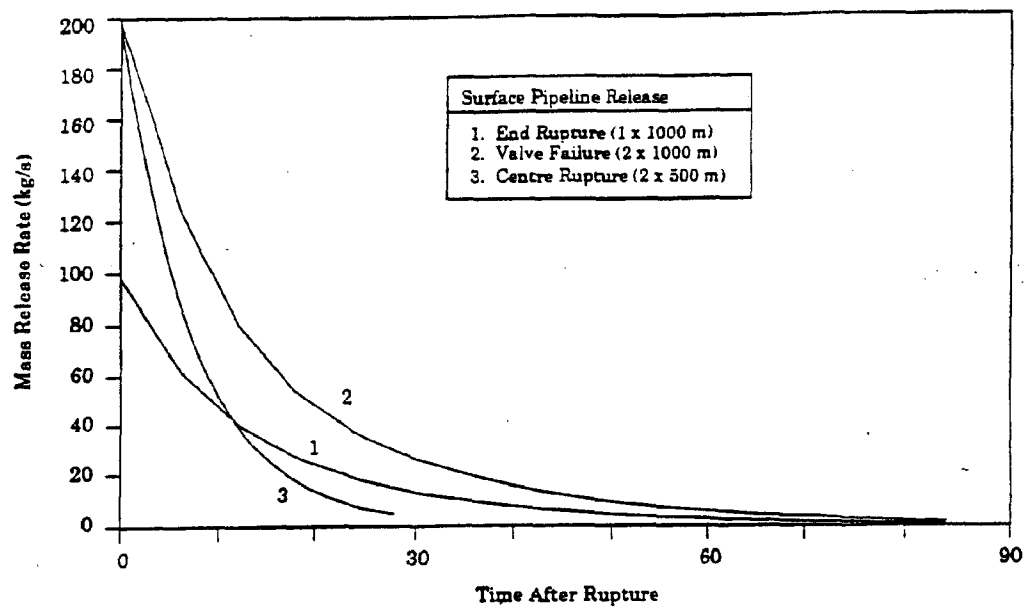
Source: Alp et al., 1990.

Figure III-19. Possible pipeline rupture scenarios.



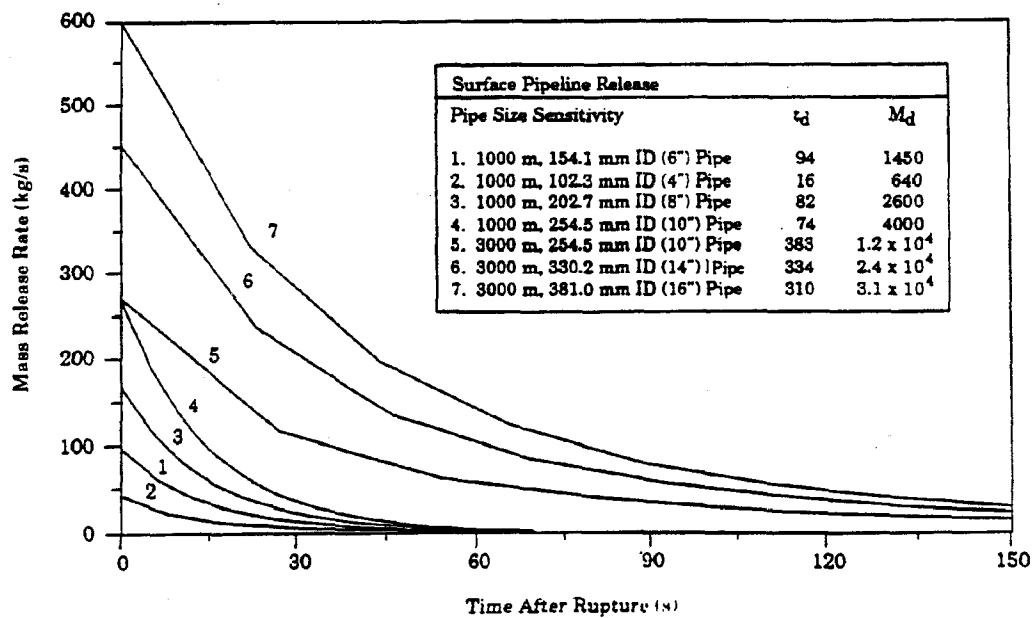
Source: Alp et al., 1990.

Figure III-20. Possible pipeline release geometries.



Source: Alp et al., 1990.

Figure III-21. Predicted mass release rates - rupture of 6" pipe.



Source: Alp et al., 1990.

Figure III-22. Predicted mass release rates - rupture of pipes of differing diameters.

and the vapors migrate to the surface where they are released without any momentum (although the resulting vapor cloud may still be buoyant enough to lift off).

For a 1/4" diameter hole in a line containing gas at a pressure of 1,000 psig, the calculated release rate (using standard text book formulae for choked flow) is about 1 lb/sec, assuming that the surrounding soil does not reduce the emission rate by physically impeding the flow. If this gas seeps to the surface, the predicted distance to which the ERPG-2 would be exceeded for a person who inadvertently enters the plume for five minutes is about 400 m (0.2 miles) and the predicted distance to the LC_{01} is about 250 m (0.15 miles) when the atmospheric stability category is F and the windspeed is 1.5 m/sec (4.9 feet per second), utilizing composition C from Table III-5. These results neglect the possibility that the plume might lift off the ground or exhibit dense gas behavior.

Consequence Analysis of Flare Stack Releases

Results calculated using the GASCON2 (Alp et al., 1990) and FOCUS (Quest, 1992) models and those carried out independently with the SAPLUME model show that, with or without sour gas ignition, the plume emitted from a flare stack is a momentum jet with dilution of the discharge and will rise sufficiently high to avoid concentrations above the ERPG-2 at ground level.

It is possible that a release of very dense gas from an unignited flare could exhibit dense gas behavior. For example, in 1950 in the town of Poza Rica, Mexico, 22 people died from exposure to hydrogen sulfide emitted from a malfunctioning flare at a gas purification plant (McCabe and Clayton, 1952). However, in this case, the gas from the well contained 3 percent by volume of H_2S and 15 percent by volume of CO_2 . During the startup period for the desulfurization units to which the gas was sent, partially processed gas containing 81 percent CO_2 and 16 percent H_2S was sent to a flare. It was this processed, heavy vapor and not the produced gas that, upon failure of the flare, descended to ground level. However, despite the limitations in applicability and the unlikelihood of occurrence, this incident is illustrative of the potential for severe consequences when managing a dense gas stream.

Consequence Analysis of Releases Collecting at Ground Level

The specific cases listed in Table III-5 are all less dense than air. This has been the case for all the gas streams investigated for this report for which detailed compositions were documented. Also, note that the most dense composition on Table III-5, stream B which has a density close to that of air, was obtained after some separation and processing for vapor recovery. It appears that the concern about heavy vapors containing H_2S settling or collecting in low-lying areas may be justified for only a fraction of wells such as the previously described Big Piney, Wyoming well blowout and Poza Rica, Mexico flare incident. It is pertinent to address other situations where this concern is justified.

Nine people were killed in an incident in Denver City, Texas, when they were exposed to gas escaping from a well injecting gas into an oil reservoir as part of an enhanced oil recovery project (Layton et al., 1983). The injected gas was composed of 93 percent by volume CO₂ and 5 percent by volume H₂S - clearly denser than air, but as before, gas that was previously processed and not of as-produced composition.

In general, it is possible that releases directly from wells with unusually dense sour gas compositions or associated lines could settle in low-lying areas at ground level. These releases would not be of typical composition. It is also possible that people entering areas of seepage such as those previously described for line releases could confuse these with settling on the ground. It is therefore reasonable to speculate that, in some cases, such concerns could possibly have arisen from seepage events.

The modeling described in the foregoing applies to plumes over flat terrain. In complex terrain, it is unlikely that released gas of typical composition will flow into lower elevations such as valleys because, as previously noted, it is generally not denser-than-air. However, it is very likely that a small or chronic release will follow the flow of the wind. Thus, for example, on cold, still nights there could be flows of air with relatively little turbulence from higher elevations into valleys (katabatic flows). This could carry slowly diluting H₂S with it and potentially cause odors within houses in valleys some distance from the well. This situation would likely not occur during the day when such air flows are uncommon. However, as previously discussed, it is possible for sour gas of unusually dense composition to remain at ground level. Therefore, for such releases, it is conceivable that flow could "channel" through terrain of low elevations such as valleys. This possibility is highly uncertain. The study of the behavior of dense gas flow around obstacles and through rough terrain is controversial and is an area where further research is needed.

Accidental Releases—Prevention, Mitigation, and Emergency Response

The design and operation of sour gas systems require special consideration as a result of the potential hazards presented by a release of H₂S. The hazards of exposure to H₂S can be significantly reduced by the implementation of process safety management principles. A primary emphasis on containment together with design features for the detection and mitigation of losses in containment are necessary for safe operations. The degree of sophistication of individual sour gas system designs will vary depending on site-specific circumstances and age. Older systems may incorporate relatively simple safety designs when compared with current state of the art. The presence of sour oil and gas operations in remote locations or near populated areas may both be justification for the use of advanced designs. Remote areas may be subject to extended releases if accessibility is limited. Process safety management and major safety considerations are discussed below.

Process Safety Management

Facilities that handle hazardous materials have a responsibility to understand the hazards present at their sites and to take steps to ensure that chemical accidents due to these hazards are prevented. Many organizations, including the American Institute of Chemical Engineers - Center for Chemical Process Safety (AIChE-CCPS) and the EPA, have found that major chemical accidents cannot be prevented by hardware or by technology alone. Prevention requires comprehensive management systems designed to identify and control hazards (AIChE, 1989; U.S. EPA, 1988). These management systems are known as Process Safety Management (PSM) and consist of "comprehensive sets of policies, procedures, and practices designed to ensure that barriers to major incidents are in place, in use, and effective. The management systems serve to integrate process safety concepts into the ongoing activities of everyone involved in the process - from the chemical process operator to the chief executive officer" (AIChE, 1989). The Occupational Safety and Health Administration (OSHA) has set standards for process safety management, which are discussed in Chapter IV.

PSM consists of several essential elements that work together to allow safe operation of a facility;

- **Management Commitment:** Management must adopt a philosophy that makes safety an integral part of operation from the top down; an attitude that all accidents can be prevented and that business must always be conducted safely.
- **Process Hazards Analysis or Hazard Evaluation:** The purpose of the process hazards analysis is to systematically examine the equipment, systems, and procedures for handling a hazardous substance; to identify the mishaps that could occur, analyze the likelihood that mishaps will occur, and evaluate the consequences of these mishaps; and to analyze the likelihood that safety systems, mitigation systems, and emergency alarms will function properly to eliminate or reduce the consequences of the incident. Thorough process hazards analysis is the foundation for the remaining elements of the PSM system.
- **Process Knowledge and Documentation:** Facilities document the details of the technology and design of the process, its standard conditions and consequences of deviation from these standards, the known hazards of the chemicals and processes involved and protective systems for protection of workers, the public, and the environment.
- **Standard Operating Procedures (SOPs):** These are procedures that describe the tasks to be performed by the operator or maintenance worker to ensure safety during operation and maintenance.

- **Training:** A program to teach those responsible for designing, operating, and maintaining the unit or plant. Elements in a management training system include development of training programs, training of instructors, measuring performance and determining the effectiveness of training. Training is typically carried out by facility managers and training staff.
- **Maintenance (Process and Equipment Integrity):** A formal program to ensure that equipment is constructed according to design, installed properly, and adequately maintained.
- **Prestartup Review:** The purpose of this review is to ensure that all elements of process safety, including hardware, procedures, and control software, are in place prior to startup, and that all prior issues of concern have been resolved.
- **Management of Change:** Management must instruct personnel to recognize change and to evaluate change with regard to process safety.
- **Safety Audits:** The purpose of safety audits is to measure facility performance, to verify compliance with a sound process safety program, and to determine that risks are being appropriately managed.
- **Accident Investigation:** Accident investigation is a management process by which the underlying causes of an incident are identified and steps are taken to prevent similar incidents.
- **Emergency Planning and Response:** Emergencies involving highly hazardous substances can have catastrophic results if not handled properly. Employees need to know and be trained in proper emergency procedures, evacuation requirements, and notification steps.

Major Safety Considerations

Siting. The magnitude of the potential consequences from human exposure to an H₂S release decreases with distance from the sour oil or gas source. Therefore, operations involving H₂S should be situated as far as possible from residential and commercial structures to minimize potential hazards to the public. Prevailing weather patterns (e.g., wind direction), terrain features, transportation routes, population centers, the potential for evacuation, and the potential for access control are some additional factors to be considered in siting decisions. These are site-specific factors that must be determined for each location.

At a minimum, well sites should be fenced to maintain some obstacle to approaching the wellhead.

Materials Selection and Corrosion Prevention. Materials must be chosen that are suitable for the service into which they are placed. Sour oil and gas operations are often conducted under high pressure and corrosive conditions. Therefore, in addition to temperature and pressure considerations, system designs for the wellhead, downhole equipment, and pipelines must incorporate features to minimize the effects of corrosion in order to prevent a breach of containment and accidental release of H_2S . Several national engineering standards governing the choice of materials are applicable. Standards include those by the American Petroleum Institute (API), American Society of Mechanical Engineers (ASME), and the National Association of Corrosion Engineers (NACE). One such standard is NACE Standard MR0175, "Material Requirements for Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment." Also applicable are the API 6A specifications for equipment in high H_2S concentrations in close proximity to occupied structures.

In addition to proper selection of materials, corrosion inhibiting fluids can be used to prevent internal corrosion and cathodic protection can be used to prevent external corrosion. Inhibitor applications include the filling of wells with inhibitor during extended periods of shut-in and injection into pipelines.

Corrosion monitoring programs should be a normal part of the operations and maintenance for sour oil and gas systems so that corrosion problems can be anticipated and repairs made before an accidental release occurs. The need for a corrosion control program and program monitoring was discussed in the first edition of API RP 55, "API Recommended Practices for Conducting Oil and Gas Production Operations Involving Hydrogen Sulfide" (API, 1983). This document has been withdrawn pending publication of an updated, second edition. Additional discussion of RP 55 can be found in Chapter IV. Corrosion monitoring systems can take a variety of forms including external monitoring (ultrasonic or X-ray inspection), corrosion coupons and spool pieces (test pieces), instrumented "pigs", or in-place instrumentation. Pigs are instruments that can be transmitted through lengths of larger diameter piping to take measurements of internal surfaces.

Leak Detection and Mitigation. While systems should be designed to meet the appropriate standards, there is still the potential for releases to occur as a result of human error or equipment failure (e.g., corrosion, impact, etc.). A possible design feature for oil and gas operations is the use of detection systems which monitor for evidence of system leaks and then isolation systems that can be used to shut off leaks. For H_2S -containing systems, detection systems can focus directly on measurement of H_2S , on measurement of pressure changes which could be indicative of a leak, or temperature indicators that can be indicative of a loss of containment and subsequent fire. Signals from such detection systems can be used in modern, sophisticated systems to automatically initiate additional containment measures such as well shut-in or isolation of sections of pipeline. There are national

standards for performance and use of H₂S monitoring equipment such as these set by the Instrument Society of America, ISA-S12.15 "Part I: Performance Requirements of Hydrogen Sulfide Detection Instrumentation" and "Part II: Installation, Operation, Maintenance of Hydrogen Sulfide Detection Instruments." Not all systems have leak detection or signalling devices associated with them. Such systems may present a greater hazard potential than those that have devices because detection would have to be by visual means or by smell. Any release would continue until detected.

Flares may malfunction resulting in extinguishment of the flame. This may occur due to several causes including flow of noncombustible compounds (e.g., nitrogen or carbon dioxide) and high winds. Flares can be equipped with automatic ignition devices to reignite extinguished flames and supplemental fuel systems to maintain ignition of the flare gas in the presence of inert gas. Flares should also be constructed at a height that provides for sufficient dispersion of the discharge.

The equipment used to mitigate releases depends on the operations. For well drilling and workover operations, a blowout preventer is used. This piece of equipment consists of high-pressure valves that allow the operator to shut in the well. For operating wells, there can be subsurface shutoff valves which are located in the well as well as above grade valves located at the wellhead and in the lines around surface equipment such as separators. Shut-in may be accomplished automatically via a signal (H₂S concentration, pressure change, temperature) that is received indicating a potential leak. For pipelines, there may also be isolation or shutdown valves located along the pipeline and these may be automatically activated if there is an indication of a leak in the pipeline or at the well. Not all systems will have automatic mitigation capability and isolation would have to be manual in these cases.

Inspection and Monitoring Practices. API RP 55 made recommendations for actions that were intended to monitor performance of the containment system for the sour oil and gas. API RP 55 specifically called for inspection of equipment and system performance to look for indications of corrosion that are indicators of degradation of the sour oil and gas containment equipment. Inspections were specifically recommended for changes in lift performance; changes in pressures associated with packed off annuli; and for the condition of valves, flanges, and connections. The document also recommended that any equipment failures be evaluated to determine the cause of the failure. Particular attention should be paid to the effectiveness of the corrosion control program at a site and corrective action should be considered if there is any indication that the program is inadequate.

API RP 55 also called for the monitoring, maintenance and recalibration of monitoring equipment (temperature, pressure, composition, etc) to make sure it is functioning as intended.

Emergency Procedures. In the event of loss of containment of the sour oil and gas, emergency procedures must be implemented to both restore containment and to protect the public. API RP 55 called for the preparation of a contingency plan for operations involving

sour oil and gas. The plans are to contain information that would be needed by personnel responding to the accident at the site. Among the information that should be in the plan according to the API recommended practices are:

1. Location of wells and details on the equipment including flow lines, isolation valves, processing facilities, and tank batteries;
2. Location of safety and life support equipment;
3. Location of telephones and other communication equipment;
4. Potential location of roadblocks for excluding unauthorized personnel for the areas associated with the accidental release;
5. Location of residences, businesses, parks, schools, roads, medical facilities;
6. Areas that could experience elevated H_2S concentrations (e.g. levels greater than 1×10^5 ppb);
7. Potential evacuation routes; and
8. Designated safe areas for operations personnel.

In addition to this information, the plan should have a list of emergency telephone numbers including company supervisors; residences, schools and businesses; nearby operators and service companies; local law enforcement agencies; officials responsible for public facilities that could be impacted; medical assistance personnel, facilities and equipment; and concerned local, state, and Federal agencies.

Beyond the information listed above, the contingency plan should have an immediate plan of action. Among the elements in an immediate action plan are the determination of the potential hazard to the public from the discharge and then an identification of actions to respond to the hazard (e.g. immediate measures to eliminate the discharge, notification of responsible supervisors, establishment of a restricted access zone, evacuation of personnel). API RP 55 also recommended consideration of advanced briefing of public and public officials so they understand the nature of the hazard, the necessity for emergency response plans, and the general steps that would be taken in the event of an emergency. Finally, API RP 55 called for the updating of the plan as necessary to keep the information in the plan current and conducting periodic drills so that personnel are familiar with the type of situations to which they may have to respond.

The Department of the Interior has promulgated regulations that are applicable to sour oil and gas operations on Bureau of Land Management (BLM) property (BLM, 43 CFR 3160). These regulations call for the preparation of public protection plans for drilling and production operations where (1) the 1×10^5 ppb H_2S radius is greater than 50 feet and the area includes locations where the public could reasonably be expected to be (e.g. occupied residences, schools, churches, parks); (2) the 5×10^5 ppb H_2S radius is greater than 50 feet and includes any part of Federal, State, or county or municipal road or highway; or (3) the 1×10^5 ppb H_2S radius is greater than 3,000 ft. where facilities and roads are principally maintained for public use. The requirements for the content of these public protection plans are very similar to those called for in API RP 55.

Abandonment Practices

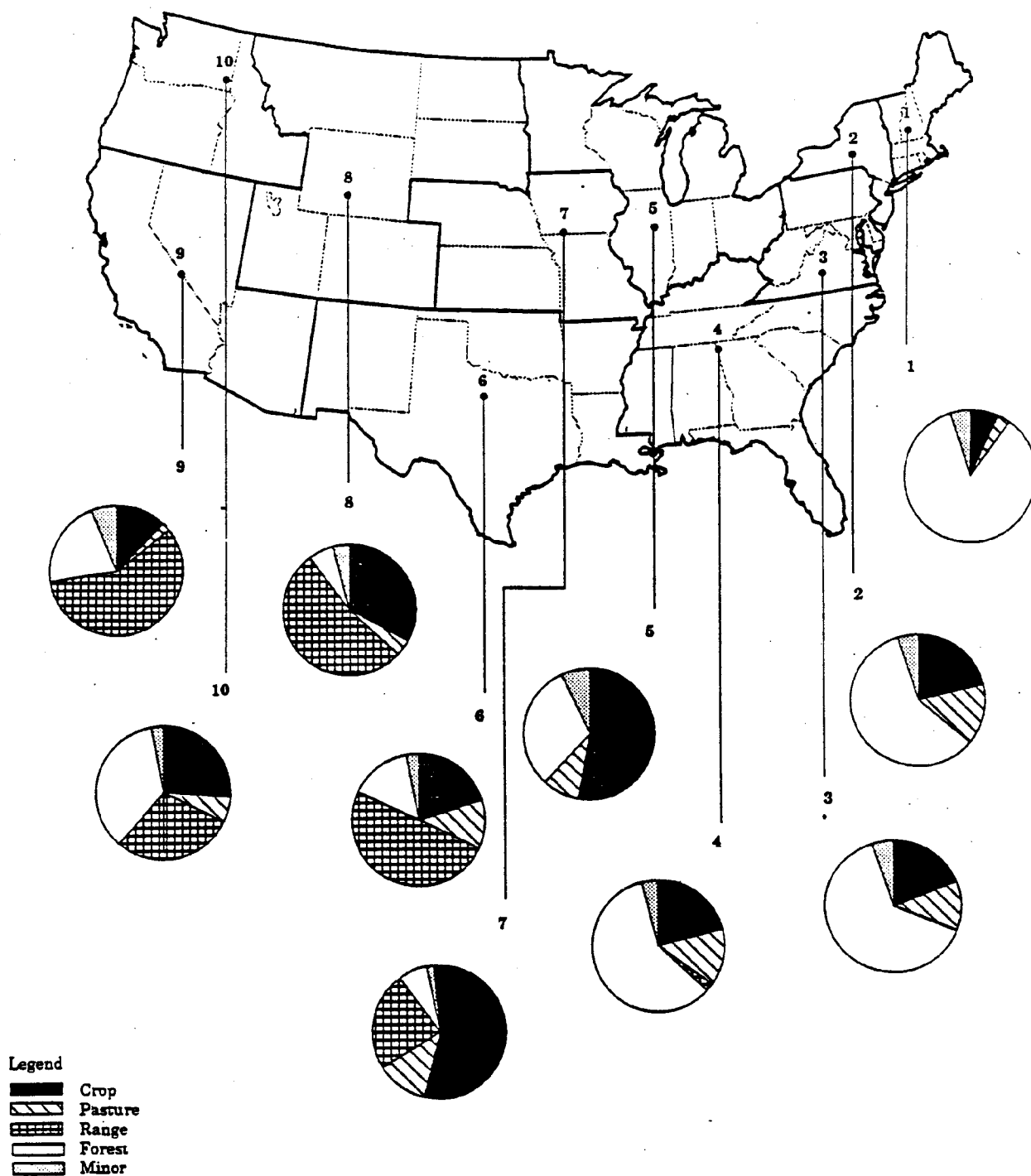
The termination of sour oil and gas production operations normally results in the plugging of the well with cement prior to abandonment by the operator. As a result, a potential exists for H₂S to be released from sour oil and gas from the well and associated equipment if proper precautions are not taken. API RP 55 identified actions that should be taken at the end of operations. The document specifically called for precautions to ensure that H₂S does not present a hazard to the public and the environment. The document called for either air purging or water flushing of equipment followed by opening to the atmosphere. Pipelines then were to be purged and capped. API RP 55 also called for the setting of cement across formations that could produce H₂S.

In some cases, wells may be temporarily abandoned. These wells may also be called "idle" or "inactive." In temporary abandonments, the well will not be plugged with cement but perforations may require isolation. Typically, application must be made and approval given by a state authority to temporarily abandon a well. Conditions justifying temporary abandonment to a State most often include economic conditions and future utility (IOGCC, 1992). Approval is temporary and of limited duration although extensions may be granted at the discretion of the state authority. Depending on the state, initial approval periods range from 6 months up to 10 years. Extensions may be granted for up to an unlimited number of time periods. In many states, but not all, periodic testing is required on idle wells. For example, mechanical integrity and pressure tests may be required. These practices are intended to prevent releases of oil and gas.

Of 215,000 oil and gas wells estimated to have been idle in 1992, approximately 68,000 were thought to have been idled without State approval (IOGCC, 1992). 50,000 of these wells, known as orphan wells, were believed to have been idled by operators who were unknown or insolvent. Although the fact that a temporarily abandoned well has not been reported to the State does not mean the well will be the source of an accidental release, the lack of control and supervision does represent an unsafe situation and may present a greater risk to the public and the environment. The majority of States have developed some funding mechanism and implemented programs to plug and abandon orphan and preregulatory wells although these activities vary widely from state to state (IOGCC, 1992).

Land Use Around Well Sites

Land use can vary enormously around oil and gas wells. The wells may be found in urban areas or open rangelands. Figure III-23 shows current land-use patterns by EPA region (Southerland, 1992). In Regions 6, 8, and 9, which contain the majority of wells in naturally occurring H₂S areas, between 50 and 60 percent of the land is used as range. The three regions represent about 60 percent of the oil and gas producing wells. In the Midwest's Region 5, which contains 12 percent of the nation's producing oil and gas wells, over 50 percent of the land is farmed (U.S. EIA, 1990; U.S. EIA, 1991).



Source: Southerland, 1992.

Figure III-23. Current land-use pattern by EPA region

Regarding urban areas, in California, for example, the Division of Oil and Gas reports that "one-third of California's 1.7 billion barrels of oil reserves are in urban areas or in areas where residential development is increasing. (The H₂S content of these reserves was not available.) The Los Angeles Basin both typifies the situation and is the most complex example. Here, a large metropolitan area lies over one of California's major petroleum-producing provinces. Because oil and gas are so fundamental to the U.S. economy, any recoverable amounts cannot be ignored. Ways have been developed to produce oil and gas safely in urban areas, with minimum negative effects. Urban planners, administrators, and California Division of Oil and Gas engineers work together to ensure a safe partnership between urban life and oil and gas development" (CDC, 1988).

Affected Human Populations

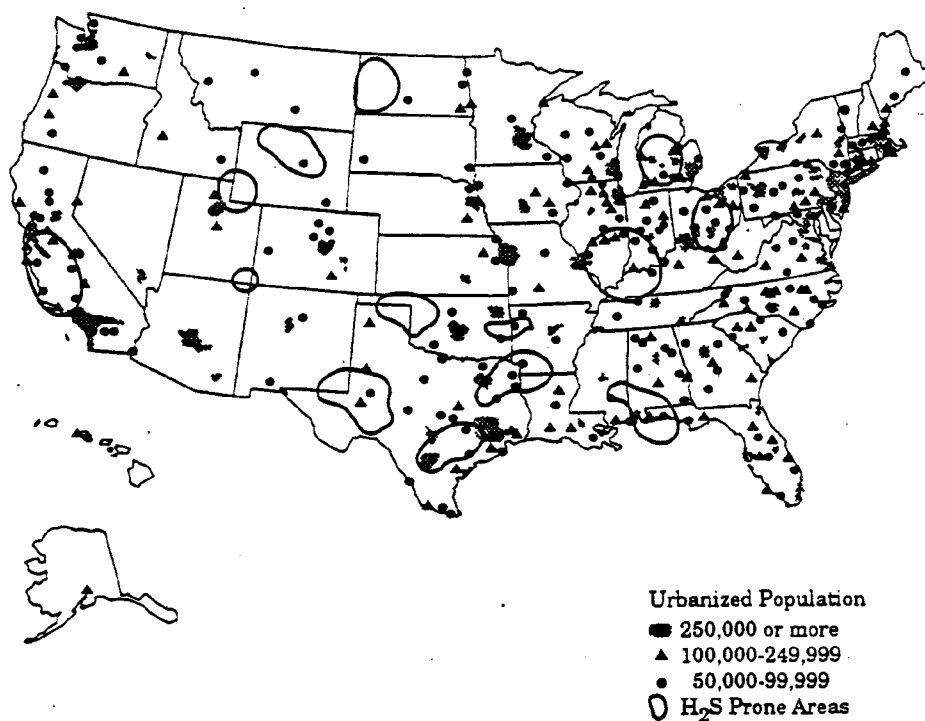
Figure III-24 overlays 1980 census data on the H₂S prone areas to show the proximity of major populations to H₂S deposits. The figure shows that a wide range in population density can be found in H₂S deposit areas. However, a look at the locations of well fields in the United States (Figure III-11) and the number of wells per State (Figure III-12) clarifies the potential exposure of large human populations to H₂S from oil and gas wells.

Data were not available to arrive at statistics on individuals exposed to H₂S emissions. Because the number of wells in the U.S. is so great and the diversity of population density around wells so large, it was not possible to arrive at an estimated affected population. The photographs in this report show that wells may be found in urban, suburban, and rural areas. Populations that could be exposed include adults in work settings (e.g., fire stations), children in schools, shoppers in downtown areas, and people in residential areas.

Affected Environmental Settings

A 1991 study in Wyoming found that, in two years, 237 animals had been killed by H₂S gas. In many oil fields this gas was vented through flare stacks. The researcher stated that when flare stacks are used, it is possible to install devices which would prevent raptors and other birds from using flares as perch sites. Also, wildlife mortality caused by H₂S would be reduced by ensuring that igniters were operating efficiently so that the gas would be properly flared and not accidentally vented directly into the environment (Esmoil, 1991). Based on other accident history, one impact on environmental settings has been the loss of livestock attributed to exposure to H₂S. Sixty percent of the U.S. wells are located in EPA Regions that contain more than 50 percent rangeland. However, many other species of animals and plants are potentially exposed to H₂S concentrations that could cause adverse effects. Testimony for the Clean Air Act Amendments included statements about episodes in the Great Plains that resulted in livestock dying and humans being hospitalized (Audubon Society, 1987).

Twelve percent of all wells are located in EPA Region 5, which is more than 50 percent cropland. As noted in a previous section of this report, soybeans have been



Source: Gas Research Institute, 1990, and Bureau of the Census, 1983.

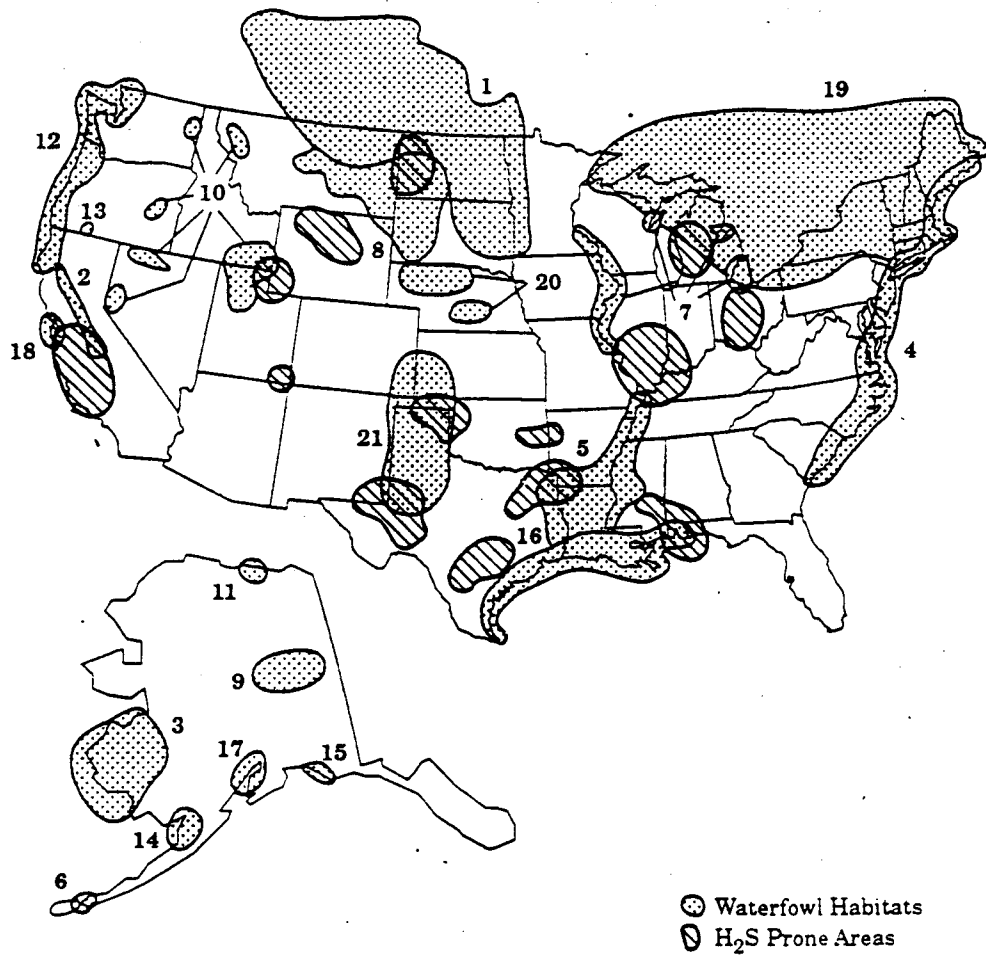
Figure III-24. Major H₂S prone areas shown in relation to 1980 census data.

determined to be sensitive to H₂S along with other crops. There has been evidence of scorching to young leaves and shoots but no effect on mature leaves (Heck et al., 1970).

Waterfowl habitats of major concern are located in some areas of oil deposits with H₂S, as shown in Figure III-25. Concern has also been expressed about the deterioration of air quality in Theodore Roosevelt National Park (Sierra Club, 1987). Figure III-26 shows the location of national parks and national forests in relation to H₂S deposits.

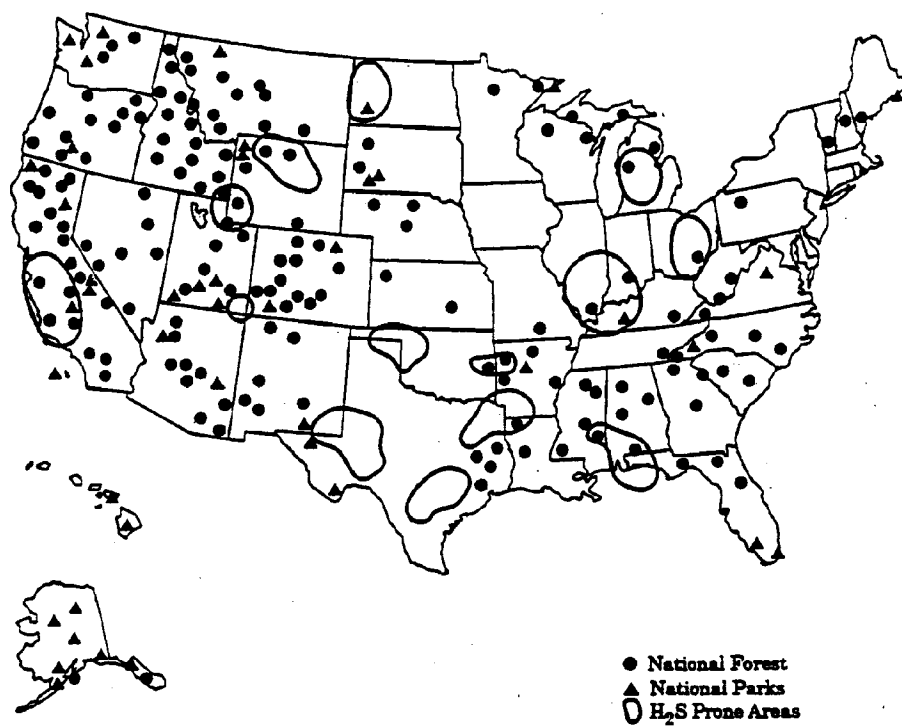
FINDINGS

1. Human exposure to H₂S may cause death, as well as symptoms including irritation, breathing disorders, nausea, vomiting, diarrhea, giddiness, headaches, dizziness, confusion, rapid heart rate, sweating, weakness, and profuse salivation. Levels greater than 1.5×10^5 ppb are life threatening.
2. No epidemiological studies were found on the effects of H₂S emissions from oil and gas extraction/production.
3. Human acute and chronic health effects data and ecological effects data are limited.
4. H₂S is classified as a Group D carcinogen, meaning not classifiable as a human carcinogen. The inhalation RfC is 9×10^{-4} mg/m³ (0.67 ppb) in chronic exposures scenarios. This RfC is not appropriate, however, for assessing concentration-response relationships in short-term or accidental exposure scenarios.
5. Few studies exist measuring natural or accidental exposure of wildlife to H₂S; however, wildlife deaths have been reported with blowouts.
6. High exposure studies have shown young, growing plants to be the most susceptible to H₂S injury (clover, soybean, tomatoes, tobacco, buckwheat).
7. Aquatic LC₅₀s show bluegill = 0.009-0.0478 mg/l.
NAOEL for mice = 42.5 mg/m³ (3.05×10^4 ppb).
LAOEL for mice = 100 mg/m³ (8×10^4 ppb).
8. Nationwide, vulnerability zones have been characterized as 14 major H₂S prone areas found in 20 states. Texas has 4 discrete H₂S prone areas.
9. North Dakota is the only State known to have routinely monitored ambient H₂S at well sites and surrounding areas.
10. Many oil and gas producing States require ambient air monitoring for H₂S at gas plants and refineries, but monitoring is not frequently required at oil and gas



Source: Gas Research Institute, 1990.
Coperrider, Boyd, and Stuart, 1986.

Figure III-25. Major H₂S prone areas in relation to waterfowl habitats of major concern (numbers indicate relative priority of concern).



Sources: Gas Research Institute, 1990. Rand McNally, 1992.

Figure III-26. Major H₂S prone areas shown in relation to National Forests and Parks.

extraction facilities, unless H₂S emission violations are suspected or complaints are filed.

11. North Dakota has three background and six special-purpose H₂S monitors. Monitoring periods vary in length from months to over a decade (32.75 years total).
12. At several locations, North Dakota monitoring data verified compliance with State H₂S standards. In two cases, data were from monitoring periods too short to support any conclusions; these were discontinued even though numerous NDAAQS violations were experienced their last year monitored.
13. North Dakota's database showed short-term H₂S concentrations ranging from 0 to 2734 ppb. The median value of all monitoring data was 0 ppb.
14. One North Dakota site had maximum short-term H₂S concentrations an order of magnitude higher than the other eight sites. At this site, more than 3,000 violations were recorded from 1984 to 1986. Concentrations improved greatly from 1986 to 1989, and only one violation occurred after the health-based standards went into effect.
15. Annual average H₂S concentrations at two sites in North Dakota approximated the RfC after introduction of a gas collection system with manifolded flares.
16. North Dakota flare operating efficiencies have been reported to range from 30 to 100 percent. (At 30 percent efficiency, H₂S can be routinely released in significant concentrations.)
17. The risk to the public of an accidental release of H₂S from the extraction of oil and gas is a function of both potential consequences and likelihood of occurrence. Judgements of risk should not be made solely on the basis of consequence analysis alone.
 - a. Risks may vary from facility to facility depending on site-specific factors such as the density and distribution of nearby populations and the quality of process safety management and risk management practiced at the facility.
 - b. Some facilities present greater risk than others.
 - c. Risk reduction must take both consequence and likelihood of occurrence into account.
18. In addition to being toxic, H₂S is corrosive to metals in the presence of moisture and is flammable.
 - a. Sour gas is flammable due to its composition of light hydrocarbons and H₂S. However, ignition of sour gas does not generally represent a thermal radiation hazard to the offsite public beyond a distance of about 100 meters.

- b. The corrosivity of H_2S in the presence of moisture can cause equipment leakage and other losses in containment.
19. If accidentally released to the air under certain circumstances, H_2S can present a threat to public health and the environment.
- a. Well blowouts, line ruptures, and equipment leakage have caused accidental releases of sour gas with documented impacts on public health and the environment.
 - b. The impacts on the public in the United States from sour natural gas releases from extraction activities documented in this study were limited to examples of hospital treatment and evacuation. A number of fatalities have occurred in the workplace. A single incident of the release of carbon dioxide containing H_2S from injection activities to enhance recovery resulted in the 1975 fatalities of eight members of the public.
 - c. In this study, several incidents were documented as examples of both livestock and wildlife fatalities resulting from exposure to H_2S from accidental releases of sour gas.
 - d. The concentration of H_2S in sour gas may vary from non-lethal levels to lethal levels above 30 percent. Unless there are high concentrations of carbon dioxide and/or hydrogen sulfide, an unprocessed sour gas mixture will usually be less dense than air and will not usually collect at ground level or in low-lying areas if accidentally released.
 - e. Releases of sour gas such as from an extinguished flare or from high-pressure equipment failures (e.g., well blowouts and line ruptures) will entrain surrounding air which can cause significant dilution of the hydrogen sulfide and other components in the gas, thereby reducing the potential magnitude of the consequences of its release.
 - f. A release of a sour gas mixture that is denser than air and is not significantly diluted through release phenomena (such as a jet from a high pressure source) could, under conservative atmospheric conditions, settle in low-lying areas and present a toxicity hazard. No documented incidents associated directly with oil and gas extraction were identified to support this scenario. Thus, this finding is based on theoretical premises.
20. Atmospheric dispersion modeling of worst-case scenarios shows that accidental releases of sour gas can have a range of impacts from no public impact to doses equivalent to the LC_{01} and AIHA ERPG-3 beyond 10 kilometers from the point of release.
- a. Modeling results indicate that, within a broad range of typical conditions for a vertical well blowout and emission from an extinguished flare, sour gas releases will not cause fatalities to the offsite public. This result would also apply to any similar vertical jet release at wellhead conditions resulting from equipment or line leakage.

- b. Modeling results estimate that, in the worst-case, a horizontal release of sour gas from a well blowout (or similar high release rate jet in a horizontal orientation from equipment or piping) could produce fatalities in one percent of the human population exposed at distances up to approximately 10 kilometers.
21. Results from modeling exercises are only gross approximations of what might occur during an actual accidental release. These results are extremely sensitive to factors such as the assumed release rates and assumed meteorological conditions. Precise prediction of downwind effects from an actual release is unlikely for reasons such as:
- a. An actual release may have a different release rate than that assumed for a hypothetical scenario.
 - b. The composition of an actual sour gas release may differ from that assumed in a modeling scenario.
 - c. The meteorological conditions existing during an actual release may differ from those assumed in a modeling scenario.
 - d. The effects of surface roughness (e.g., terrain and obstacles) are not fully understood. It is assumed in the models used that complex terrain and obstacles increase dispersion.
 - e. The levels used to predict the onset of toxic effects (i.e., LC₀₁ and ERPG-3) are highly uncertain.
22. While analysis of the worst-case scenario can be useful to help facilities and the community surrounding facilities to gain an understanding of the potential magnitude of severe situations, such an analysis does have its limitations. A worst-case scenario should be taken into account along with more probable scenarios when setting priorities for community emergency planning. Note, however, that the worst-case is designed to generate the maximum impact off-site and is considered to be extremely unlikely. The worst-case does not take into account a variety of factors that can significantly reduce downwind impacts.
- a. The worst-case scenario does not take into account the role of process safety management in reducing the probability of loss of containment.
 - b. The worst-case scenario does not take into account mitigation actions that can reduce the amount released into the air.
 - c. The worst-case scenario assumes terrain and topographical conditions that minimize dispersion of the plume. Actual conditions may result in greater dispersion.
 - d. Worst-case meteorological conditions may not exist during an actual release.
 - e. The dose that is actually received is uncertain and may be reduced or avoided by sheltering-in-place or evacuation.
23. Technologies have been developed to detect and reduce the amount of sour gas released as a result of breaches in containment. These technologies would serve to protect the public in inhabited areas and to protect wildlife in remote areas with

limited access by facilitating quicker mitigation. These technologies include:

- a. Subsurface safety valves;
- b. Remotely operated isolation valves;
- c. Automatically operated shutoff and isolation valves;
- e. Remotely monitored pressure and flow meters;
- f. Local and remote audible and visual warning signals; and
- g. Automatic flare ignitors and supplemental fuel sources.

In spite of the availability of detection and mitigation measures, all facilities have not uniformly adopted such measures. In addition, the reliability of such equipment and site-specific conditions must be considered before particular technologies are adopted or implemented.

- 24. Wells drilled in H₂S prone areas may or may not contact H₂S sources.
- 25. Eight States have a significant overlap of well fields and H₂S prone areas. Therefore, it is roughly estimated that as many as 280,000 oil wells and 54,000 gas wells have the potential to be located in an H₂S prone area. The actual number of sour wells in each State was not available.
- 26. Population densities in urban areas within ranges of 100,000-249,999 and 50,000-99,999 can be found in H₂S prone areas in California, Texas, Missouri, Florida, Illinois, Kentucky, Oklahoma, Arkansas, Ohio, Michigan, and Wyoming.
- 27. There have been several documented incidents of wildlife fatalities due to sour oil and gas releases. No incidents have been documented where large-scale wildlife fatalities have been caused by H₂S, and no national statistics on wildlife incidents were found. However, a Wyoming study found 237 animals killed by H₂S in two years.
- 28. H₂S-prone areas overlap 10 waterfowl habitats of major concern, 18 national forests and 3 national parks.
- 29. Land use and, therefore, potential human and ecological exposure scenarios can vary enormously around oil and gas wells:
 - a. In EPA Regions 6, 8, and 9 which contain the majority of wells in H₂S prone areas (which represent 60 percent of all wells nationwide), 50 to 60 percent of the land is used as range.
 - b. In Region 5 (12 percent of U.S. wells), 50 percent of land is farmed.
 - c. In California, 1.7 billion bbls of oil reserves are in urban or increasingly developed residential areas.

30. ACGIH's recommended TLV-TWA for H₂S is 1 x 10⁴ ppb (14 mg/m³) and TLV-STEL is 1.5 x 10⁴ ppb (21 mg/m³).
31. AIHA ERPGs for the general public for H₂S are --
ERPG 3 - 1 x 10⁵ ppb (1-hr exposure, not life threatening)
ERPG 2 - 3 x 10⁴ ppb (1-hr exposure, no irreversible or serious health effects)
ERPG 1 - 100 ppb (1-hr exposure, no mild, transient adverse effects or clearly defined odor).
32. NAS/NRC H₂S guidelines for protecting the general public from the effects of accidental releases are -
90-day continuous exposure guide level - 1 x 10³ ppb
24-hr emergency exposure guideline level - 1 x 10⁴ ppb
10-min emergency exposure guideline level - 5 x 10⁴ ppb.

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CHAPTER IV

REGULATORY PROGRAMS AND RECOMMENDED INDUSTRY PROCEDURES

INTRODUCTION

This chapter identifies and reviews the current State and Federal regulatory programs and industry-recommended procedures applicable to either reduce the potential for routine emissions and/or accidental hydrogen sulfide releases from oil and gas production or to mitigate the consequences of such emissions and releases.

STATE REGULATIONS

Currently, there are no national ambient air quality standards (NAAQS) for H₂S. Most oil- and gas-producing States have their own regulations pertaining to H₂S gas. Table IV-1 lists States that have set ambient air quality standards for H₂S emissions.

The EPA gathered and reviewed several States' regulations and related guidance documents and later contacted State agencies to obtain additional information on the unique aspects of the State regulations governing H₂S emissions in the oil and gas industry. EPA staff also met with officials from North Dakota during a trip to North Dakota oil and gas well sites. In addition, the Interstate Oil and Gas Compact Commission (IOGCC) was contacted to obtain information pertaining to regulatory programs (IOGCC, 1990).

This chapter contains a review of existing State regulations for nine States (California, Louisiana, Michigan, New Mexico, North Dakota, Oklahoma, Pennsylvania, Texas, and Wyoming).

These nine States were chosen for review because of their large production volumes, the potential presence of H₂S in their well fields, and their distribution across the United States. The nine States contain over 68 percent of the total oil wells (419,989 wells/613,810 total U.S. wells) and 54 percent of the gas wells (147,360 wells/272,541 total U.S. wells) producing in the United States in 1991 (Petroleum Independent, 1992). For these States, regulatory agencies are identified, H₂S regulations for routine emissions and accidental releases are described, enforcement programs are discussed, records and programs to track accidental H₂S release are included, and the effectiveness of each State program is assessed qualitatively. The qualitative evaluation identifies existing control standards and the populations or ecosystems the standard is intended to protect.

In addition, these States account for 67 percent of the total U.S. oil production and 87 percent of the total U.S. natural gas production (Petroleum Independent, 1992). State regulations for H₂S emissions from the oil and gas industry in Oklahoma, Texas, Michigan,

Table IV-1. Ambient Air Quality Standards for H₂S

| State | Concentration (ppb) | Average Time (hours) |
|---------------|--------------------------------|---------------------------------|
| California | 30 | 1 |
| Connecticut | 200 | 8 |
| Kentucky | 10 | 1 |
| Massachusetts | 14 | 24 |
| Minnesota | 50 ^a | 0.5 |
| | 30 ^b | 0.5 |
| Missouri | 500 ^a | 0.5 |
| | 30 ^b | 0.5 |
| Montana | 50 ^c | 1 |
| Nevada | 240 | 8 |
| New York | 10 | 1 |
| North Dakota | 200 ^d | 1 |
| | 100 ^c | 24 |
| Oklahoma | 100 | 0.5 |
| Pennsylvania | 100 | 1 |
| Rhode Island | 10 | 1 |
| Texas | 80 | 0.5 |
| Virginia | 160 | 24 |
| Hawaii | 40 | 1 |
| Delaware | 30 | 1 |
| Indiana | 50 | 1 |

^aNot to be exceeded more than two times/year.

^bNot to be exceeded more than two times/five consecutive days.

^cNot to be exceeded more than one time/year.

^dNot to be exceeded more than one time/month.

and California were reviewed in greatest detail because they are major oil and gas producing States. These states have extensive regulations dealing with H₂S in the oil and gas industry. California's air quality program is managed by 33 independent air pollution control districts and its Division of Oil and Gas is divided into 6 districts where District heads have great flexibility in enforcing rules. Therefore, California's program is discussed in the greatest detail.

Selected Oil and Gas Producing States

Oklahoma

The H₂S regulations for Oklahoma (10.3.16, "Operation of Hydrogen Sulfide Areas") were listed in *Guidelines for Petroleum Emergency Field Situations in the State of Oklahoma*, a guidance manual that expands on the regulations. The guidance manual contains sections on characteristics and effects of H₂S, recommended guidelines for safe drilling and production operations in an H₂S environment.

The following agencies regulate oil and gas activities in Oklahoma:

- Oklahoma Corporation Commission (OCC), Oil and Gas Conservation Division
- Oklahoma Air Quality Service
- Osage Indian Tribe (OIT)
- U.S. Bureau of Land Management
- U.S. Environmental Protection Agency.

The OCC has jurisdiction over laws and regulations "relating to the conservation of oil and gas and the prevention of pollution in connection with the exploration, drilling, producing, transporting, purchasing, processing and storage of oil and gas..." (OCC, 1986). The OIT has sole jurisdiction regarding oil and gas operations in Osage County. The U.S. Bureau of Land Management has responsibility for cases where both surface and mineral rights are owned by the Bureau or by an Indian tribe other than the Osage Tribe.

As noted earlier in this chapter, Oklahoma has an H₂S ambient air quality standard. This regulatory program (administered by the Air Quality Service) is used to control routine emissions (through permit) from oil and gas facilities.

The accidental release of H₂S from facilities is regulated by the OCC. Rule 165:10-3-16 of the OCC rules requires operators to assess their facilities for H₂S release potentials that would cause harm to the public. The rule is applicable to all facilities that handle natural gas containing 1 x 10⁵ ppb H₂S or more and have a significant radius of exposure to cause adverse effects on the public with the exception of storage tanks. The "radius of exposure" is that distance from a source where the ground level concentration of hydrogen sulfide resulting from a release of gas from a facility is 1 x 10⁵ ppb or 5 x 10⁵ ppb whichever is applicable in the Rule. The Rule applies as follows:

- Does the facility (drilling, producing, injection, storage, etc.) handle hydrocarbon fluids containing 1×10^5 ppb H_2S or more? If yes;
- Determine the 1×10^5 ppb radius of exposure using an equation required in the Rule or other methods approved by the Commission. The H_2S escape rate from the facility must be determined as required by the Rule.
- If the 1×10^5 ppb radius of exposure is in excess of 50 feet, warning, marker and security provisions must be provided at the facility.
- If the 1×10^5 ppb radius of exposure is in excess of 50 feet and includes a public area or if the 5×10^5 ppb radius of exposure is in excess of 50 feet and includes a public road or if the 1×10^5 ppb radius of exposure is in excess of 3000 feet, control and safety equipment and a contingency plan must be provided for the facility.
- Facility storage tanks near atmospheric pressure containing 5×10^5 ppb or greater H_2S must have warning signs, wind indicators and possible fencing. Radius of exposure calculations are not applicable to storage tanks.
- H_2S training, injection or flaring provisions, accident notification and other requirements are addressed in the Rule (personal communication, W. Freeman, Shell Oil, 6/23/93).

The OCC does not keep an emissions inventory of accidental H_2S releases, but it does keep an inventory of wells with actual or potential H_2S problems. Furthermore, an inventory of inspection data is kept by individual inspectors in the State and the local field offices. Any emissions of H_2S exceeding the OCC standard of 2.5×10^4 ppb must be reported to the OCC by the emitting facility. Rule 3-2032, H_2S Operation, is intended to provide for the protection of the public's safety in areas where H_2S concentrations greater than 1×10^5 ppb may be encountered.

Drilling facilities are not required to submit data periodically to show that they are in compliance with regulations. Facilities report release of H_2S on an "honor system" once permits are granted. When noncompliance is discovered, the OCC can use administrative proceedings to shut down or fine the operation. However, in recent years, there has been no evidence of noncompliance with the H_2S regulations.

The OCC lists training requirements for employees who will work in areas of potential H_2S exposure. The training must cover hazards and characteristics of H_2S , operation of safety and life support systems, and emergency response procedures. OCC safety inspectors attend annual industry-sponsored training programs in order to stay current on safety developments and to check the safety of their breathing equipment. Each H_2S inspector is required to have an H_2S monitor, a manual, H_2S gas monitoring test tubes, and a

self-contained air breathing apparatus. Specific H₂S provisions also exist regarding H₂S detection and alarm equipment, accident notification, injection, and flaring. In 1991, the OCC and the industry jointly sponsored an H₂S safety seminar. A film about H₂S safety was presented to regulatory and industry personnel, and questions about H₂S safety were answered. Safety training has also been provided to local police, fire, sheriff and ambulance services, and to interested oil and gas operators, as requested.

The enforcement, field monitoring, and inspection departments of the OCC employ 69 people. The State currently has two H₂S inspectors and a third is anticipated. In 1991, one emergency involving the accidental release of H₂S was reported to the OCC. However, the accident, which resulted in the death of one worker, was not related to the extraction of oil and gas resources.

Texas

Six agencies regulate oil and gas activities in Texas:

- Railroad Commission of Texas
- Texas Water Commission
- Texas Air Control Board
- Texas Parks and Wildlife Department
- U.S. Army Corps of Engineers
- U.S. Environmental Protection Agency.

The Railroad Commission regulates most of the operations of the oil and gas industry but has no authority over the Clean Air Act Amendments. The Railroad Commission is responsible for the well spacing, construction requirements (casing etc.), and most aspects of environmental protection and works with other State Agencies to ensure that their concerns are addressed. The Texas Water Commission works with the Railroad Commission on water quality issues. The Texas Air Control Board has jurisdiction over the regulation of oil field activities that generate air emissions. The Texas Parks and Wildlife Department investigates fish kills and water pollution complaints and evaluates the effects of discharged wastes on fish and wildlife. The Railroad Commission has jurisdiction over all oil and gas activities on Federal lands in Texas, regardless of who owns the mineral rights. The U.S. Army Corps of Engineers has permitting responsibility for activities that would affect statutory wetlands.

The Texas Air Control Board (TACB) is responsible for enforcing the Texas ambient air quality standard for H₂S (discussed previously). Certain allowances are made from the air standard if the hydrogen sulfide affects only property used for other than residential, recreational, business, or commercial purposes, such as industrial property and vacant tracts and range lands not normally occupied by people (i.e., the emission limit is raised to 120 ppb/30 min). If an operator violates these ambient air levels, corrective action must be taken such as flaring, installation of vapor recovery, etc. Consequently, the unauthorized emission of H₂S that exceeds the time weighted averages for the land use discussed above is a

violation of regulation and must be addressed by the operator. In addition, the TACB requires permits for facilities that handle sour gas emissions from crude oil storage which also address emergency releases from these type facilities.

Texas regulations on H₂S for drilling, extraction, and abandonment are listed under Statewide Rule 36 - Hydrogen Sulfide Safety, Section 3.36 (051.02.02.036, "Oil, Gas, or Geothermal Resource Operation in Hydrogen Sulfide Areas," as amended September 1, 1976). The Hydrogen Sulfide Safety Rule in Texas—issued to address accidental releases—applies to facilities that could expose the public to concentrations of H₂S in excess of 1×10^5 ppb as a result of an accidental release. Operators handling hydrocarbon fluids containing 1×10^5 ppb or more H₂S must determine if the Rule applies to their facility. If it does, they must calculate the radius of exposure; determine if the public will be impacted; and, if so, install warning signs, ensure security measures, address storage tank requirements, install appropriate safety equipment, develop contingency plans, provide training and implement other requirements as necessary. In addition, all operators subject to Rule 36 must submit a Certificate of Compliance to the Railroad Commission to demonstrate that they have complied with these requirements. This rule requires that employees working in H₂S areas be trained in the characteristics and effects of the gas. The Railroad Commission of Texas publishes a training manual containing this information. The Texas and Oklahoma regulations are virtually identical. Most of the Texas regulations were discussed in the previous section on Oklahoma regulations. The Hydrogen Sulfide Safety Rule in Texas does require safety equipment, alarm equipment, monitors, etc., but does not specify exact types in an attempt to remain flexible and allow for new technology. It was designed for the protection of the general public rather than industry, since OSHA rules are designed to protect industry workers (personal communication, W. Freeman, Shell Oil, 6/23/93).

In Texas, the Railroad Commission does keep an emissions inventory on accidental H₂S releases. Any emissions of H₂S that are found to be of sufficient volume to present a hazard and/or any H₂S-related accidents must be reported to the Railroad Commission by the emitting facility. Operator certificates are required by the Railroad Commission to demonstrate that prevention and response measures have been taken to address accidental releases of H₂S.

There was one case of noncompliance during 1991, which involved natural gas leaking from a pipeline. The Railroad Commission canceled the Certificate of Compliance for the operators of the well, which prevented the facility from producing or selling the product until the leak was fixed. In 1991, there were emergencies involving the accidental releases of H₂S. Those accidents were discussed in Chapter III.

The enforcement, field monitoring, and inspection departments of the Railroad Commission employ 215 people. Ground testing for traces of H₂S is performed near the wells. Emission data on each well are submitted to the Railroad Commission using the Form of Compliance. When noncompliance is discovered, the Commission uses administrative

proceedings to implement the following enforcement actions: enforcement letter, pipeline severance, zero allowable emissions, sealing, permit revocation and/or administrative penalties. The Railroad Commission may also seek civil penalties through the Attorney General's Office.

Michigan

The Michigan regulatory program is published in *Michigan's Oil and Gas Regulations - Act 61* (P.A. 1939 as amended and promulgated rules - Circular No. 15, revised in 1987, MDNR). Most of the regulations in the Michigan guidance were covered in the sections on Texas and Oklahoma regulations.

A review of *Michigan's Oil and Gas Regulations* reveals that the State has a comprehensive set of regulations dealing with H₂S. The Michigan rules require extensive training for all employees and contractors involved in drilling, completing, testing, producing, repair, workover or service operations. Employees must receive training in the following areas: physical properties and physiological effects of H₂S, effects of H₂S on metals and elastomers, emergency escape procedures, location and use of safety equipment, the location and operation of detection and warning systems and the location of primary and secondary briefing areas. Briefing areas are defined in *Michigan's Oil and Gas Regulations* as the areas "nearby where personnel can assemble in case of an emergency." Michigan defines safety equipment as including items such as first aid kits, dry chemical fire extinguisher, ropes, flare guns, portable H₂S detectors and warning signs.

In addition to training requirements, the Michigan oil and gas regulations contain comprehensive rules for the preparation of a contingency drilling plan in order to provide a plan for alerting and protecting personnel and the public in case of an emergency.

Five agencies regulate oil and gas activities in Michigan:

- Michigan Department of Natural Resources (MDNR)
- Michigan Department of Commerce, Public Service Commission
- U.S. Forest Services
- U.S. Bureau of Land Management
- U.S. Environmental Protection Agency.

The Department of Natural Resources is responsible for the well spacing, construction requirements (casing, etc.), and most aspects of environmental protection. The Michigan Public Service Commission regulates the production of gas from dry natural gas reservoirs and the safety of gas pipeline construction. When dealing with split estate situations, the U.S. Forest Service will issue a Special Use Permit which allows an operator to drill within the forest boundary. When both the forest surface and corresponding mineral rights are Federally owned, the U.S. Bureau of Land Management (BLM) issues drilling permits and the U.S. Forest Service issues Surface Use Plans. The BLM issues drilling permits in all

cases related to onshore Federal mineral estates (personal communication, T. Alexander, DOE, 2/22/93).

Worker safety issues are the responsibility of the Michigan Department of Labor. Part 57 of the General Industry Safety Standards Commission Safety Standards deals with oil and gas drilling operations safety standards. Under Rule 5717(1), the drilling and servicing of wells containing H₂S shall be conducted as prescribed in the American Petroleum Institute's Recommended Practice No. 49 (API, 1987).

The MDNR's Air Quality Division regulates H₂S emissions from all sources in the oil and gas industry. Rule 336.1403 states: "It is unlawful for a person to cause or allow the emission of sour gas from an oil or natural gas producing or transporting facility or a natural gas processing facility without burning or equivalent control of hydrogen sulfide and mercaptans." The Rule does allow operators with stripper wells to emit small quantities of H₂S unless one complaint is received from the public which would require some type of abatement technique to be imposed. All facilities handling H₂S are subject to these regulations.

The Geological Survey Division (GSD) of the Department of Natural Resources regulates accidental releases of H₂S in the oil and gas industry. In addition, it overlaps with the Air Quality Division on emission controls at production facilities. It appears that two agencies in the MDNR regulate H₂S handling facilities. Under Rule 299.1911-1939, operators handling hydrocarbon fluids containing more than 3×10^5 ppb H₂S must define a Well Class (defined by the radius of exposure in Rule 299.1912) to determine the applicability of the Rule. The radius of exposure is defined using the same dispersion equation as Texas Rule 36. The Rule addresses equipment standards, location standards for drilling and production equipment, contingency planning, training, drilling, testing, production operations, servicing operations and nuisance odor requirements (personal communication, W. Freeman, Shell Oil, 6/23/93).

The enforcement, field monitoring, and inspection departments for oil and gas regulation by the Geological Survey Division (GSD) of the MDNR employ 47 people. Wells are retested one year after the initial well test was performed, to check for compliance with laws. Further periodic tests are required only at the request of the MDNR. When a well is not in compliance, the MDNR can use administrative proceedings to shut down drilling processes and production, stop issuing permits to drill, stop well ownership transfers, and issue fines. Fines are also issued for falsifying records required by the GSD enabling legislation (Act 61, P.A. of 1939, amended). Violation of the Act or a rule or order under the Act carries a penalty of not more than \$1,000.00 per day that the violation continues. In 1991, there was no evidence of noncompliance for the release of H₂S.

The MDNR does not keep an emissions inventory of the accidental releases of H₂S from well blowouts and flare gas releases. Emissions of H₂S are reported by industry personnel to MDNR field personnel, who may keep records on the releases. One incident

was reported to the MDNR in 1990, which involved a pumper who was working on a storage tank. The exact date and nature of the incident were not available.

California

The following agencies regulate oil and gas activity in California:

- California Department of Conservation, Division of Oil and Gas
- California Water Resources Control Board and the nine Regional Water Quality Control Boards
- California Department of Health Services
- California Department of Fish and Game, Office of Spill Prevention and Response
- California/EPA Department of Toxic Substances Control
- California State Fire Marshall's Office
- California Public Utilities Commission
- California OSHA
- California Air Resources Board and the county or multi-county regional Air Pollution Control Districts
- California Governor's Office of Emergency Services
- State Lands Commission
- California Coastal Commission
- Local government agencies
- U.S. Bureau of Land Management
- U.S. Department of Energy
- U.S. Environmental Protection Agency.

The Division of Oil and Gas of the California Department of Conservation is responsible for the management and conservation of oil and gas resources. The Division issues permits for and inspects the drilling, reworking, and abandonment of oil and gas wells. Under delegated authority from the EPA, the division also issues underground injection control well permits for Class II injection wells.

Division 3 - Oil and Gas, part of the California Code of Civil Procedure, contains the California laws for conservation of petroleum and gas (CDC, 1991). Table IV-2 highlights key sections of the law applicable to H₂S releases. Although, there is no quantitative limit to H₂S emissions, the law grants the supervisor of the Oil and Gas Division, discretionary authority to control H₂S releases to ensure protection of human health and the environment.

California's Code of Regulations contains the oil and gas regulatory program enforced by the Division of Oil and Gas. These regulations are highlighted in Table IV-3. These rules include the definition of the term "critical well," requirements for contingency plans,

Table IV-2. Highlights of California Laws for Conservation of Petroleum and Gas Pertaining to H₂S Emissions

| Ch., Art., Section | Subject | Description |
|--------------------|--------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| 1, 4, 3219 | Blowout prevention | Where high-pressure gas exists, use adequate casing and safety devices |
| 1, 4, 3224 | Order for repair | Authorizes supervisor to order tests or repairs needed to prevent damage to life, health, natural resources, etc. |
| 1, 4, 3228 | Abandonment of wells | Protects ground and surface water from gas-bearing strata |
| 1, 4, 3235 | Complaint | Authority to investigate complaints |
| 1, 4, 3236 | Penalty | For obstructing enforcement, \$100 - \$1,000 or up to 6 months imprisonment per offense |
| 1, 4.1, 3241 | Strategy to extract gas in high risk areas | Develop strategy to extract hazardous gases from abandoned wells to protect public health and safety |
| 1, 4.2, 3251 | Define "hazardous well" | Poses danger to life, health, or natural resources |
| 3, , 3600 | Spacing wells | Well must be at least 100 feet from parcel's boundary or public road |

rules include the definition of the term "critical well," requirements for contingency plans, and environmental protection.

The Division of Oil and Gas has also published a guidance document on H_2S , *Drilling and Operating Oil, Gas, and Geothermal Wells in an H_2S Environment* (Dosch and Hodgson, 1986). This guidance document reflects the American Petroleum Institute's publication RP 49, *Safe Drilling of Wells Containing Hydrogen Sulfide* (API, 1987) and recommends safety procedures for H_2S release scenarios. The California Division of Oil and Gas (CDOG) is divided into six districts. Figure IV-1 shows the six districts and the distribution of H_2S in California, presenting parts per million of H_2S gas in some California oil and geothermal fields. Table IV-4 shows the documented concentration by oil field in each district. Three of the districts are discussed here.

District 1 of the Division of Oil and Gas has three oil and gas inspectors and seven energy engineers who inspect well drilling and rework operations. The inspectors wear tri-gas monitors (H_2S , oxygen, and combustibles). The well-permitting program does not specify H_2S limits. All wells are inspected at least once a year. Idle wells must be pressure-tested periodically to minimize casing leaks. Steam flooding, an enhancement process that often creates H_2S , is used frequently in the district. District 1 authorities know of past H_2S incidents leading to human injuries; however, because records are not computerized, exact data are not available (personal communication, K. Carlson, CDOG, 8/27/92).

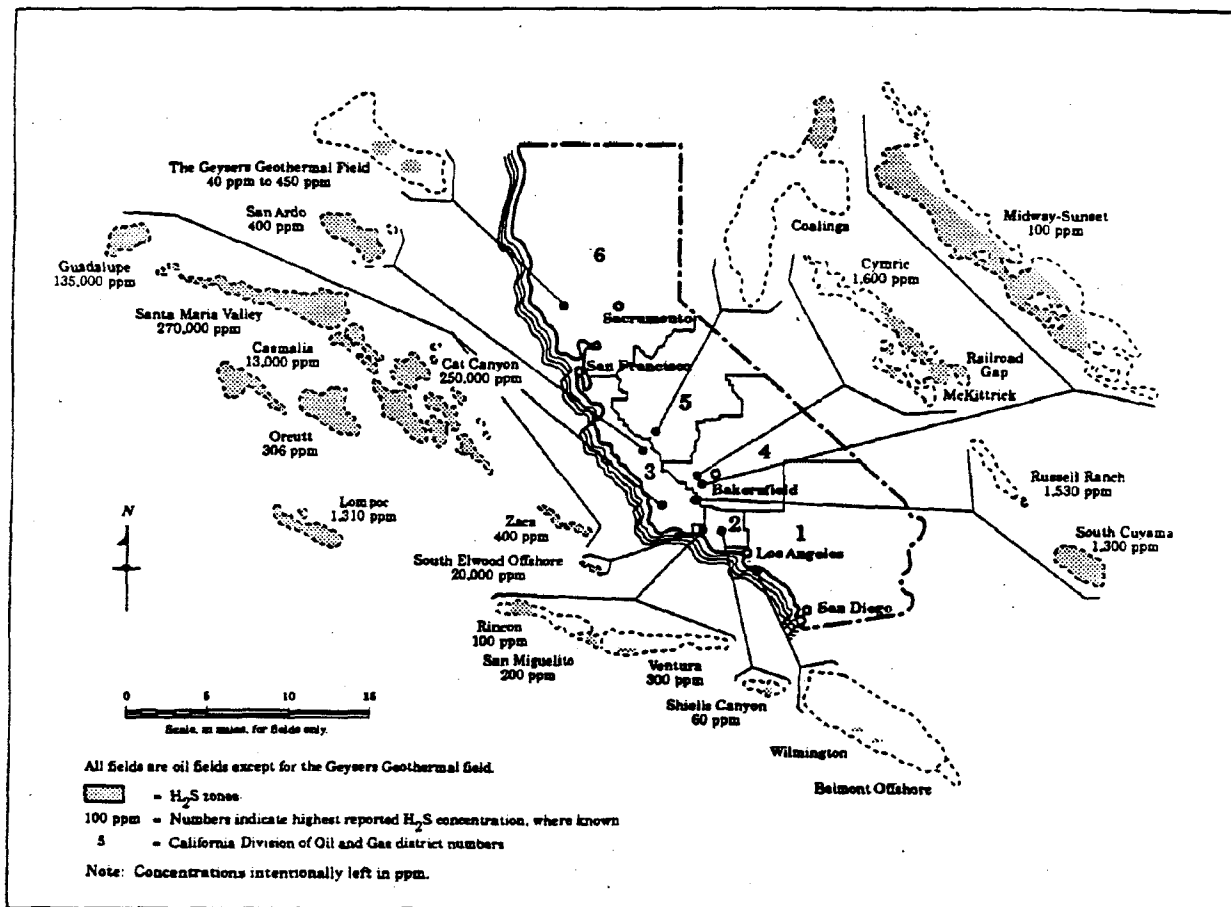
District 3 has 1,929 producing wells and 2,845 shut-in wells (i.e., no production is made on the well; its pump is turned off, the stuffing box is closed, and it is inspected to ensure no leakage). Three field inspectors cover District 3 (personal communication, A. Kollar, CDOG, 8/28/92).

District 4, which includes Kern County, has nine field inspectors, each equipped with an "escape pack" for H_2S protection. An environmental inspection is performed for every lease on every well. The inspection covers the surface area, well condition, tank condition, and operation. There are more than 40,000 wells in Kern County alone. District 4 had no records of H_2S incidents. However, inspectors in Kern County/San Joaquin Air District (described below) have documented incidents of H_2S releases (personal communication, R. Bowles, CDOG, 8/27/92).

The California Air Resources Board is authorized to enforce a statewide ambient air quality limit for H_2S emissions of 30 ppb over one hour's averaging time. However, California's air quality program is managed on a smaller scale by the 33 county or multi-county air pollution control districts (APCDs) shown in Figure IV-2 (CA Air Resources Board, 1991). Each district acts as an independent regulatory agency, establishing and

Table IV-3. Highlights of Title 14, Chapter 4 of the California Code of Regulations - Development, Regulation, and Conservation of Oil and Gas Resources

| Article, Section | Subject | Description |
|-------------------------|-----------------------------------|------------------------------------------------------------------------------------------------------------|
| Subchapter 1 | | |
| 1, 1712 | Scope | Onshore drilling and production; grants Oil and Gas Division Supervisor authority to establish field rules |
| 2, 1720 | Critical well | Addresses distances to public areas and navigable waters |
| 2.1, 1721 | Well spacing | Objectives include protecting public health, safety, welfare and the environment |
| 3, 1722 | General | Good oilfield practices, blowout prevention and control plan, prompt reporting of significant gas leaks |
| 3, 1724.3 | Well Safety Devices | Required of certain critical wells |
| 3, 1724.4 | Testing/inspecting Safety Devices | Test at least every 6 months |
| Subchapter 2 | | |
| | Environmental Protection | Requires covers on well cellars, no excessive leakage including wellheads and pipelines |



Source: Dosch and Hodgson, 1986.

Figure IV-1. Parts per million of H₂S gas in some California oil and geothermal fields. Data compiled in 1976.

Table IV-4. H₂S in California Oil, Gas, and Geothermal Fields

| Oil and Gas District | Fields with H ₂ S Concentrations 1×10^5 ppb or Above | Fields with H ₂ S Concentrations Under 100 ppm | Fields with H ₂ S Odor, But With Concentrations Unknown |
|----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | — | — | Wilmington, Huntington Beach, Newport, Torrance, Brea Olinda |
| 2 | Rincon, 1×10^5 ppb San Miguelito, 2×10^5 ppb Ventura, 3×10^5 ppb | Shiells Canyon 60 ppm | Aliso Canyon, Bardsdale, Big Mountain, Del Valle, Las Lajas, Oak Park, Oakridge, Ojai, Piru, Santa Paula, Santa Susana, Simi, South Mountain, Tapo Canyon So., Temescal, Torrey Canyon, and West Mountain |
| 3 | Casmalia, 1.3×10^7 ppb Cat Canyon, 2.5×10^8 ppb Cuyama So., 1.3×10^6 ppb Elwood So., Offshore, 2×10^7 ppb Guadalupe, 1.35×10^8 ppb Lompoc, 1.31×10^6 ppb Orcutt, 3.06×10^5 ppb Russell Ranch, 1.53×10^6 ppb San Ardo, 4×10^5 ppb Santa Maria Valley, 2.7×10^8 ppb Zaca, 4×10^5 ppb | — | Capitan Onshore, King City Four Deer |
| 4 | Midway Sunset, 1×10^5 ppb Cymric, 1.6×10^6 ppb | — | North Belridge, South Belridge, Blackwells Corner, Edison, Northeast Edison, Kern River, Lost Hills, McKittrick, Mount Poso, Poso Creek, Railroad Gap, and Wheeler Ridge |
| 5 | — | — | Coalinga |
| 6 | — | — | — |
| Geothermal District | | | |
| G3 | The Geysers, 4×10^4 - 4.5×10^6 ppb | — | — |

H₂S in some California oil and geothermal fields. Data compiled in September 1976. (Data in the first two columns are on Figure IV-1).

Source: Dosch and Hodgson, 1986.

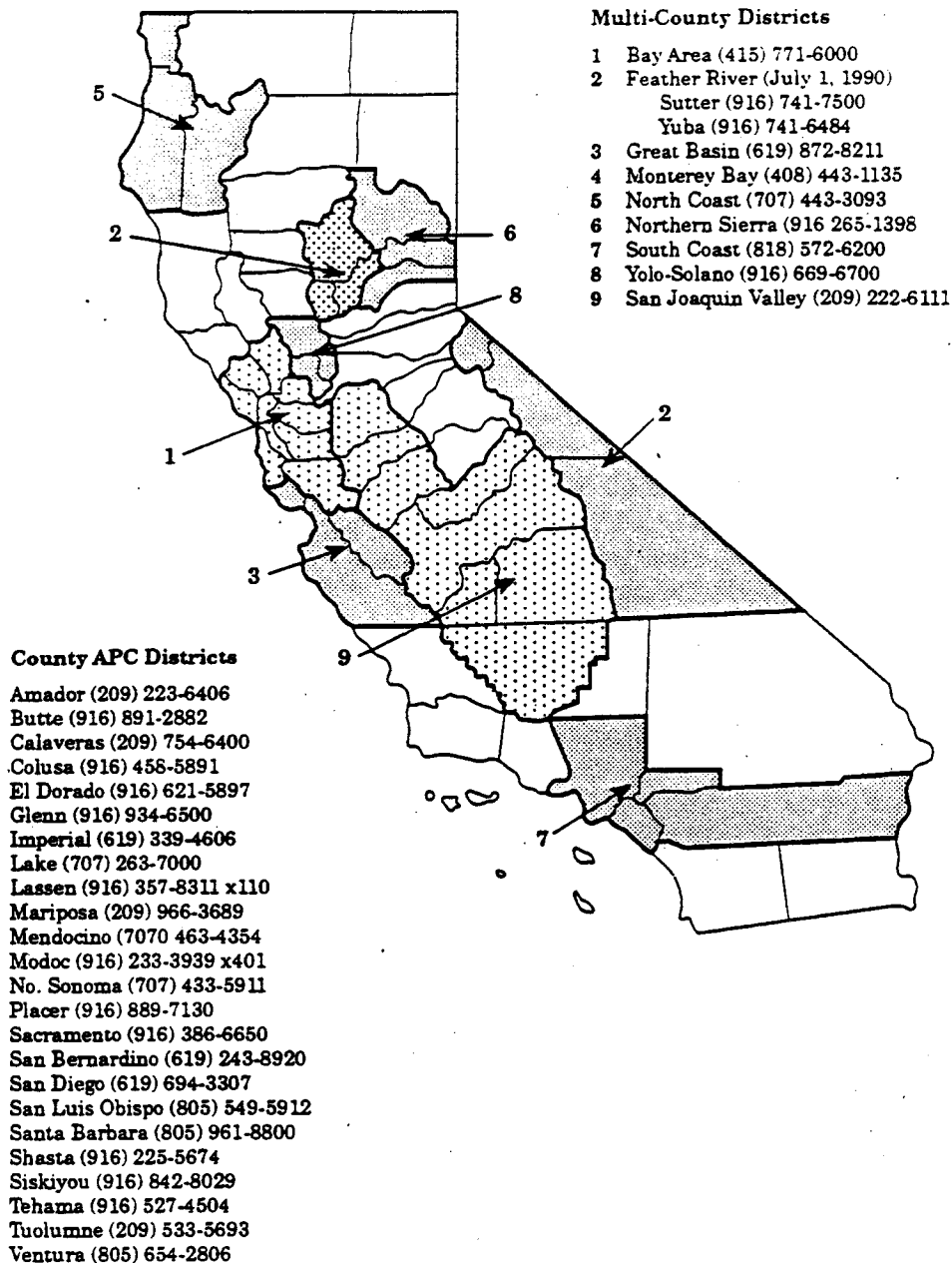
enforcing air quality rules tailored to the district's needs. Districts with significant oil production are:

Ventura County
Santa Barbara County
San Joaquin Unified Air District
South Coast Air Quality Management District
Monterey Bay Unified Air District
Bay Area Air Quality Management District.

This report highlights H₂S emissions programs in four districts: Ventura County, Santa Barbara County, San Joaquin Unified Air District, and the South Coast District.

Ventura County has Rule 54, "Sulfur Compounds," in place for air emissions containing sulfur compounds. This rule, adopted in 1968 and most recently revised in 1983, includes a limit for H₂S not to exceed 1×10^4 ppb by volume at the point of discharge. The point of discharge includes any distinguishable emission point such as valves, flanges, or process vents. There are no control technology regulations for H₂S in Ventura County other than these equipment standards. Another H₂S rule requires that the aboveground average concentration at or beyond the property boundary shall not be in excess of 60 ppb for over 3 minutes. The Ventura County limits were adopted in 1968 when the APCD was formed. Natural emissions of H₂S are low in the county's oil well fields, and H₂S monitoring is only performed when a problem is suspected (i.e., when the odor is detected). The APCD uses hand-held monitoring devices to inspect problem areas. No routine monitoring records are kept on file in Ventura County, but wells are inspected at least once a year, with large wells inspected more frequently (personal communication, K. Duval, Ventura APCD, 8/29/92). Ventura County has an enforcement staff of about 20 people, including 8 field inspectors (personal communication, K. Duval, Ventura APCD, 11/23/92).

Emission standards in Santa Barbara County are basically the same as in Ventura County. However, tighter emission limits are applied in parts of the county with SO₂ (an oxidation product of H₂S) nonattainment areas. Rule 309, "Specific Contaminants," for Santa Barbara County states that sulfur recovery units shall not emit more than 5×10^5 ppb as SO₂ or 1×10^4 ppb as H₂S. Rule 310 for odorous organic sulfides states that concentrations of organic sulfides beyond the property boundary shall not exceed 60 ppb/3 minutes or 30 ppb/hr. For gas produced and used as fuel in equipment on a well site, the sulfur content limit in the county's northern air shed is 7.96×10^5 ppb sulfur; in the southern county air shed, the limit is 2.5×10^5 ppb. Control technologies are not used on well heads for H₂S emissions. However, controls do exist for volatile organic compound (VOC) emissions from well fittings, stuffing boxes, well cellars, sumps and pits. Rules are being developed to require these controls, primarily in the surface area of the well cellar to control the release of VOC. This technology will also control H₂S emissions indirectly. The county's 10 field inspectors inspect wells for all types of emission sources at least once a year. H₂S violations via the total sulfur emission limit are not a problem because by the time



Source: California Air Resources Board, 1991.

Figure IV-2. Multi-county districts.

the ambient air quality standard is exceeded, the operator has already been alerted to a safety problem and is responding. The county has seven currently active H₂S ambient monitoring stations; however, these are at oil and gas processing facilities, rather than at well fields (personal communication, J. Top, St. Barbara APCD, 8/20/92).

The San Joaquin Unified Air District enforces Rule 407, "Sulfur Compounds," which limits the emission concentration of sulfur compounds at the point of discharge to 0.2 percent volume calculated as SO₂ (or 2×10^6 ppb SO₂). This rule, adopted in 1972 and renumbered in 1989, applies to any gas line or vapor control line from a well. Rule 220.1, "New and Modified Stationary Source Review Rules," has a trigger value for H₂S or total reduced sulfur or sulfur compounds other than SO_x of 54.79 lb/day. If this value is exceeded, the responsible party must use Best Available Control Technology (BACT) on the emission source. Rule 220.1 was adopted in September 1991 and revised March of 1992.

The San Joaquin District does not look at or enforce H₂S regulations until the 2×10^6 ppb SO₂ emission limit is exceeded, because the rule is based on the impact of SO₂ on human health and the environment, not on the health effects of H₂S. No ambient monitoring of H₂S is required by the district. However, the oil companies are required to keep their own records of SO₂ monitoring for two years. Companies also have H₂S monitoring data, and the State has the authority to request these data at any time (personal communication, M. Amundsen, San Joaquin, 8/21/92).

Kern County, part of the San Joaquin Unified Air District, has three of the largest producing wells in the United States. The county's production volume is exceeded only by Alaska, Texas, and Louisiana. The wells in Kern County produce a unique heavy crude and some use steam injection to enhance pumping. H₂S is a problem in well fields in the county, where numerous stripper wells (defined in Chapter II) are operating. The county has a ten-person enforcement team that performs inspections at least once a year. Steam casing collection systems, valves, fittings, etc., are inspected by staff wearing H₂S monitors. Inspectors in Kern County have been exposed to H₂S in the field. In one case, an inspector was exposed to greater than 1×10^6 ppb. The case involved a report from a fire department station downwind of a well and complaints of odor and illness. H₂S was measured at the station at 5×10^4 ppb. The source was a leaking underground gas recovery line. Companies are required to keep records of such incidents and report them to CAL OSHA (personal communication, M. Amundsen, San Joaquin Unified Air District, 8/21/92).

During conversations with Kern County representatives, it was noted that an important control technology for H₂S at wells is a casing collection system, which can be added to collect natural gas containing H₂S that has built up in the casing over time. If the natural gas pressure is not relieved, well production is hindered. Companies tend to release this gas to the atmosphere, but a casing collection system can treat the gas by vapor incineration (98 to 99 percent hydrocarbon destruction efficiency). However, the economic incentive to put casing collection systems on stripper wells is normally low due to the low

volume of oil produced (personal communication, M. Amundsen, A. Phillips, San Joaquin, 8/21/92).

The South Coast Air Quality Management District has no specific regulations pertaining to H₂S or oil production. Rules in place that indirectly control H₂S emissions include Rule 431.1, "Sulfur Content of Gaseous Fuels," which states that, effective May 1994, natural gas cannot be burned or sold for burning if it contains greater than 4×10^4 ppb total sulfur. This rule also requires organic vapor recovery systems, which would recover any H₂S gas along with the volatile organics. Rule 402 could also apply to H₂S, particularly for stripper wells that are too small for permitting. This rule is a nuisance rule that could be used to close wells if, for example, neighbors complained about H₂S odors or other health effects (personal communication, C. Bhatti, South Coast AQMD, 8/25/92). The South Coast District's enforcement program is managed as part of the Stationary Source Compliance Office, which has a staff of 500 (personal communication, C. Bhatti, South Coast AQMD, 11/23/92).

California's Occupational Safety and Health Administration is authorized to administer the Federal OSHA program. There are two OSHA standards that apply to H₂S. One focuses on the maintenance and use of valves. The second is the Permissible Exposure Limit for H₂S. It is difficult to monitor compliance with this limit because operations are outdoors. CAL OSHA maintains a database of occupational accidents. No accidents were found in the database related to H₂S releases at California oil wells dating back to 1982 (personal communication, R. Hayes, CAOSHA, 9/11/92). However, H₂S incidents were recorded in some of the Air Pollution Control Districts and Division of Oil and Gas Districts (personal communication, M. Amundsen, San Joaquin Unified Air District, 8/21/92).

The California Water Resources Control Board is generally responsible for the protection of the State's waters and for preserving all present and anticipated beneficial uses of these waters. The California Department of Health Services is responsible for the regulation of hazardous wastes. It determines which waste streams and constituents are hazardous under California's laws. The State Land Commission has joint responsibility with the Division of Oil and Gas for wells on State-owned, onshore lands.

The Office of Emergency Services administers Chapter 6.95 of the California Health and Safety Code which states that every business handling any hazardous material greater than 55 gal., 500 lb. or 200 cubic feet (gaseous material) must register and develop an emergency response plan and business plan. If the business handles extremely hazardous substances onsite exceeding threshold planning quantities (500 lb for H₂S), a preliminary analysis of the facility must be made to determine if a significant risk potential exists for accidental release of the extremely hazardous substance. If the potential does exist, the facility must develop and submit a "risk management and prevention program" that addresses how to reduce or eliminate the potential for accidental release (personal communication, Dr. F. Lercari, Office of Emergency Services, 9/13/93).

A Comparison of H₂S Regulatory Programs in Four States

Table IV-5 presents a summary of regulatory programs for H₂S across California, Michigan, Oklahoma, and Texas. This summary addresses the area of "state ... control standards, techniques, and enforcement" designated for evaluation in Section 112(n)(5) of the Clean Air Act Amendments. Appendix B tabulates components of the States' regulatory programs in greater detail.

Texas, Oklahoma, and California have H₂S ambient air quality standards in place. The California standard (30 ppb over 1-hr averaging time) is more stringent than the Texas standard (80 ppb over 0.5-hr averaging time) and the Oklahoma standard (100 ppb over 0.5-hr averaging time). Michigan does not have ambient air quality standards for H₂S.

The number of agencies in each State regulating oil and gas operations ranges from two in Oklahoma and Michigan to eleven in California. The enforcement staff, which includes inspectors and field monitoring staff, numbers 69 in Oklahoma, 215 in Texas, and 47 in Michigan. California's air emissions program is regulated by districts. The Santa Barbara District, an area with high concentrations of H₂S in its oil fields, has 10 field inspectors who are also responsible for inspecting other commercial operations. Kern County, California, has a staff of 10 field inspectors who also have other inspection responsibilities.

Michigan, Oklahoma, and Texas each have H₂S-specific regulations related to public safety. In California, State law grants the Director of the Division of Oil and Gas discretion to require additional controls (for areas such as H₂S emissions) on a case-by-case basis. However, none of the four States has specific H₂S standards in place to protect the environment, i.e., ecological protection.

Of the four States reviewed, only Texas maintains an inventory of accidental releases of H₂S from drilling and production operations. However, all four states require notification when threatening accidental releases occur. None of the four States requires reporting of H₂S routine emissions. "Routine" excludes such incidents as vapor recovery unit failures and other equipment upsets.

Texas, Oklahoma, and Michigan require worker safety training for H₂S. California's Division of Oil and Gas, however, provides guidance on worker safety in the form of a publication (Dosch and Hodgson, 1986).

Other Large Producing States

The EPA gathered initial information on several State regulations and later contacted selected State agencies to obtain additional information on the unique aspects of the State regulations governing H₂S emissions in the oil and gas industry. The results of each State review are summarized in the following sections.

Table IV-5. A Comparison of Four States' H₂S Regulatory Programs

| H ₂ S Area | Oklahoma | Texas | Michigan | California |
|-----------------------------------------------------------------|---------------|---------------|-----------|-------------|
| Ambient air quality standard? | 0.10 (0.5 hr) | 0.08 (0.5 hr) | No | 0.03 (1 hr) |
| Number of State agencies regulating oil/gas | 3 | 4 | 2 | 6 |
| Size of enforcement / inspection staff | 69 | 215 | 47 | * |
| Specific H ₂ S regulations for: | | | | |
| Public Safety | Yes | Yes | Yes | No |
| Ecological Protection (administered by environmental agency) | No | No | Not clear | No |
| Inventory of accidental releases kept by State? | No | Yes | No | No |
| Routine reporting of emissions required? | No | No | No | No |
| Notification of a threatening accidental release? | Yes | Yes | Yes | Yes |
| H ₂ S training required? | Yes | Yes | Yes | Guidance |

*Enforcement staff in California (example counties)

| | |
|------------------------------------------------------|----|
| Santa Barbara County Air Pollution Control District: | 10 |
| Kern County (in San Joaquin Unified Air District): | 10 |
| California Division of Oil and Gas - District 7: | 10 |
| California Division of Oil and Gas - District 4: | 9 |

Louisiana

Five agencies regulate oil and gas activity in Louisiana:

- Louisiana Department of Natural Resources, Office of Conservation
- Louisiana Department of Environmental Quality
- U.S. Bureau of Land Management
- U.S. Army Corps of Engineers
- U.S. Environmental Protection Agency.

The Louisiana Department of Natural Resources, Office of Conservation, regulates all subsurface and surface disposal of oil- and gas-associated wastes (*Statewide Order Governing the Drilling for the Producing of Oil and Gas in the State of Louisiana*). The office has primary responsibility for all classes of underground injection control wells. The Office of Conservation coordinates with the Louisiana Department of Environmental Quality, Office of Water Resources, on any problem dealing with discharges in the oil and gas industry. The U.S. Bureau of Land Management has jurisdiction over lease arrangements and post-lease activity on Federal lands where the mineral rights are Federally held. The Office of Conservation does not keep an emissions inventory for accidental H₂S releases. Any emissions of H₂S that exceed the Office of Conservation standard must be reported to the Office by the emitting facility.

The enforcement, field monitoring, and inspection departments of the Office of Conservation employ 34 inspectors. Emission data are sent to the Office of Conservation when an accidental release has occurred at the well site. The Office of Conservation, through administrative proceedings, can respond with the following enforcement actions when compliance is not met: compliance letters, compliance orders, civil penalty assessments, suspension/revocation of permits and pipeline severance.

In recent years, there has been no evidence of noncompliance and no emergencies involving the release of H₂S from oil or gas wells. The drilling process is not a significant threat because underground sources of H₂S are much deeper than the wells being drilled.

New Mexico

Five agencies have responsibilities for regulating oil and gas activities in New Mexico:

- New Mexico Oil Conservation Division of the Energy, Minerals and Natural Resources Department (OCD)
- New Mexico Oil Conservation Commission
- New Mexico Water Quality Control Commission
- U.S. Environmental Protection Agency

- U.S. Bureau of Land Management.

The Oil Conservation Division of the Energy, Minerals and Natural Resources Department is responsible for regulating oil and gas industry exploration and drilling, production, and refining. Its duties include regulating "nonhazardous" liquid and solid wastes from these operations to protect water quality, public health, and the environment. The Oil Conservation Commission works in conjunction with the Oil Conservation Division. The Commission initiates rules and orders to be administered by the Division. The Water Quality Control Commission develops water quality control standards and water pollution regulations. The U.S. Bureau of Land Management has jurisdiction over all Federally owned land, with the exception of Indian lands.

The Oil Conservation Division of Energy Resources (OCD) keeps emissions inventories at the district level. There are four districts in the State of New Mexico; any accidental release of H_2S must be reported to the district division of the OCD. The enforcement, field monitoring and inspection departments of the OCD employ 18 people. Inspections are made by each district OCD office. In recent years, there has been no evidence of noncompliance with the H_2S regulations set forth by the OCD, and no emergencies involving H_2S have been reported.

New Mexico's Oil Conservation Commission Rule 118 is intended to provide for the protection of the public safety in areas where H_2S concentrations greater than 1×10^5 ppb may be encountered. This rule adopts the guidance of the American Petroleum Institute publications RP 49 and RP 55 (discussed later in this chapter) and covers drilling, extraction, and abandonment.

North Dakota

Five agencies regulate oil and gas activities in North Dakota:

- North Dakota Industrial Commission, Oil and Gas Division
- North Dakota State Department of Health and Consolidated Laboratories
- U.S. Department of Agriculture, Forest Service
- U.S. Bureau of Land Management
- U.S. Environmental Protection Agency.

The North Dakota Industrial Commission, Oil and Gas Division, has regulatory authority over the drilling and production of oil, and is responsible for protecting the correlative rights of the mineral owners, preventing waste, and protecting all sources of drinking water. The Bureau of Land Management has jurisdiction over drilling and production on Federal lands, but the operator must obtain a permit from the Division of Oil and Gas. Drilling on forest land must comply with the rules of the U.S. Forest Service.

Any well completed or recompleted on or after July 1, 1987 must be registered with the State Department of Health and Consolidated Laboratories (NDSDH&CL). The registration process includes completion and submittal of a form which provides information about the well operator, well equipment (such as size and number of storage tanks, existence of a heater treater and type of fuel on which it is fired, flare stack height, etc.), surface equipment location, and disposition of produced gas. This form, submitted along with an analysis showing the H_2S concentration of any produced gas, constitutes registration. Information derived from the registration is entered into a shared database, which is used by the North Dakota Industrial Commission's Oil and Gas Division, for storing production data; thus, an emissions inventory which represents actual emissions can be generated from the database for all registered wells. H_2S concentrations in wellhead gas are field-pool specific; for example, within the Little Knife Oil Field, gas produced from the Madison Pool will have an H_2S concentration of approximately 9.56 percent, gas produced from the Red River Pool will be approximately 7.91 percent H_2S , and gas produced from the Duperow and Bakken pools is likely to contain only negligible amounts of H_2S . H_2S data from the registrations are, therefore, entered into the database as field-pool specific data (personal communication, D. Harman, NDSDH&CL, 5/19/93).

The enforcement, field monitoring, and inspection departments of the Division of Oil and Gas employ 14 people. The NDSDH&CL handles most of these complaint-related inspections. The Division of Oil and Gas can shut down an operation and fine up to \$12,500 per day when compliance is not met. The NDSDH&CL can impose a fine and/or imprisonment.

H_2S typically constitutes between 4 and 10 percent of the oil and gas found in North Dakota. Because of this prevalence, the State has established an ambient air quality standard (shown in Table IV-1).

The NDSDH&CL typically becomes more involved in situations where routine emissions (as opposed to catastrophic/episodic releases) from a production facility result in excessive ambient concentrations. This scenario typically manifests itself in the form of citizen complaints. In these situations, it has been the Department's experience that an equipment problem, such as flare stack ignitor malfunction (i.e., low efficiency flare), storage tank gasket degradation and leakage, etc., has been the primary cause. Correction of the immediate problem and implementation of a more rigorous maintenance schedule will typically resolve these cases (personal communication, D. Harman, NDSDH&CL, 5/19/93). Acute, unpredictable releases of H_2S , such as natural gas pipeline rupture, etc., are typically handled by the North Dakota Industrial Commission; however, the Industrial Commission has had no reports of emergencies involving accidental releases of H_2S in the past two years.

Pennsylvania

Six agencies regulate oil and gas activities in Pennsylvania:

- Department of Environmental Resources,
- Bureau of Oil and Gas Management (BOGM)
- U.S. Environmental Protection Agency, Region III
- Pennsylvania Fish Commission
- U.S. Forest Service
- U.S. Bureau of Land Management.

The Bureau of Oil and Gas Management (BOGM) was created to coordinate and combine all regulatory activities of the oil and gas industry (*Oil and Gas Operators' Manual*). The U.S. Environmental Protection Agency issues permits for underground injection and secondary recovery. The Pennsylvania Fish Commission identifies pollution of surface waters and takes appropriate action under the Pennsylvania Fish and Boat Code.

The BOGM does keep records of any accidental releases; however, routine emission rates are not reported. Nearly all of Pennsylvania's H₂S problems have occurred in the northern part of the State, around Lake Erie.

The enforcement, field monitoring, and inspection departments of the BOGM employ 38 people. The Department of Environmental Resources has the following enforcement options available when compliance is not met: notice of violation, citation for summary offense, misdemeanor, civil penalty, injunction, administrative order, consent order and agreement, permit suspension and/or revocation, and bond forfeiture.

Six wells near Lake Erie have significant concentrations of H₂S that could be a threat to the surrounding environment and people. One incident in 1990 involved discharges of H₂S from a well blowout. Local authorities evacuated a neighboring town until the H₂S could be contained and the well plugged. The blowout did not cause any negative health effects or other types of injury.

In the past, Pennsylvania explored the possibility of establishing a committee that would include consultants, gubernatorial appointees, and citizens to examine H₂S in relation to the oil and gas industry and determine if a serious problem exists. It is understood that this project is currently inactive due to budget limitations.

Wyoming

There are four agencies that regulate oil and gas activities in Wyoming:

- Wyoming Oil and Gas Conservation Commission
- Wyoming Department of Environmental Quality
- U.S. Bureau of Land Management
- U.S. Environmental Protection Agency.

The Oil and Gas Conservation Commission has the general authority over oil and gas production in the State. The Department of Environmental Quality is responsible for land applications of all types of exploration and production wastes. The Bureau of Land Management is responsible for all drilling and production on Federal lands.

The Wyoming Oil and Gas Conservation Commission does keep emissions inventories on accidental releases of H₂S. Any accidental release of the gas must be reported to the Commission immediately.

The enforcement, field monitoring, and inspection departments of the Oil and Gas Conservation Commission employ ten people. The Commission has the following enforcement options when compliance is not met: civil assessments, permits denial and revocations, and bond forfeiture.

In 1989, approximately 2,982 stripper wells in Wyoming produced over 5 million barrels of oil. In recent years, there have been no signs of noncompliance; however, there have been emergencies involving accidental H₂S releases.

FEDERAL REGULATORY PROGRAMS

Current Federal regulations potentially applicable to the oil and gas production industry's handling of hydrogen sulfide are summarized below. These include regulations of the Occupational Safety and Health Administration (OSHA), Bureau of Land Management, (BLM), U.S. Geological Survey, (USGS), Superfund Amendments and Reauthorization Act (SARA) Title III, the Clean Air Act, and others. Although the OSHA standards are applicable only to workers, they are analyzed as guidelines for reducing exposure to H₂S from both accidental releases and routine emissions.

OSHA Regulations

Currently, hydrogen sulfide emissions from oil and gas exploration and drilling are not directly addressed by OSHA regulations. The regulations that are in effect to protect workers are: OSHA Standards for General Industry (29 CFR Part 1910.1000), and the respirator standards (29 CFR Part 1910.134) and the OSHA Process Safety Management Standards (listed in Chapter III). Industries in which hydrogen sulfide occurs in quantities in excess of 1500 pounds are covered in the Process Safety Management of Highly Hazardous

Chemicals Standard (29 CFR 1910.119), but retail facilities and remote, unmanned operations are exempted. Oil and gas well drilling or servicing operations are also exempted. The potential exists that oil and gas operations that are the focus of this Report to Congress may be exempt from this OSHA standard if the facility is remotely located or if servicing operations include those studied in this Report. Table IV-6 lists current and proposed regulations pertaining to hydrogen sulfide.

Current Regulations

General Industry Standards (29 CFR 1910.1000). Acceptable concentrations for chemical exposure are listed in Section 1910 under Table Z-1-A., Limits for Air Contaminants, of the General Industry Standard (1910.1000). Effective December 31, 1992, the permissible exposure limit (PEL) time weighted average (TWA) for H_2S is 1×10^4 ppb (14 mg/m^3). That is, an 8-hour time weighted average, such that an employee's exposure to hydrogen sulfide in any 8-hour workshift of a 40-hour workweek, shall not exceed 1×10^4 ppb. Also for hydrogen sulfide, the short-term exposure limit (STEL) is 1.5×10^4 ppb (21 mg/m^3). The 1.5×10^4 ppb STEL is the employee's 15-minute (time weighted average) exposure, which shall not be exceeded at any time during the workday. The basis for the STEL is eye irritation.

The transitional OSHA standard, whose levels have been in effect since 1966, are ceiling limits and are listed in Table Z-2 of the OSHA standard. The acceptable ceiling concentration for hydrogen sulfide is 2×10^4 ppb, with an acceptable maximum peak above the ceiling concentration of 5×10^4 ppb lasting no more than 10 minutes, and occurring only once in an 8-hour shift, if no other measurable exposure occurs. The definition of a ceiling is the employee's exposure that shall not be exceeded during any part of the workday. If instantaneous monitoring is not feasible, then the ceiling shall be assessed as a 15-minute time weighted average exposure that shall not be exceeded at any time over a working day.

Respirator Standards (29 CFR 1910.134). The OSHA Personal Protective Equipment Standard (29 CFR 1910.134) outlines the types of personal protective devices (respirators) that should be worn when the ambient concentration exceeds the standards. Specific rules pertaining to hydrogen sulfide are not included in the standard. Covered in the standard are rules requiring written standard operating procedures, and employee training and screening for ability to use the equipment. Respirator selection, use, inspection and maintenance, storage, and cleaning are covered in the standard, as is air quality in supplied air respirators.

Process Safety Management of Highly Hazardous Chemicals (29 CFR 1910.119). The CAAA instructed OSHA (in section 304), in coordination with EPA, to promulgate a chemical process safety standard to prevent accidental releases of chemicals that could pose a threat to employees. This standard was finalized in February 1992 (57 *Federal Register* 6356).

The OSHA requirements for employers include standards to:

Table IV-6. Summary of Occupational Exposure Standards for H₂S

| Agency/Association | Background | Standard or Guideline |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Occupational Safety and Health Administration (OSHA) ^a General Industry Standards 29 CFR 1910.1000 | Current: Lists acceptable concentrations for chemical exposure in the work environment. H ₂ S – listed under Table Z-1-A. | TWA 10 ppm 8-hour Time Weighted Average (TWA) STEL 15 ppm 15-minute Short Term Exposure Limit (STEL) |
| OSHA Respirator Standards 29 CFR 1910.134 | Current: Covers respirator selection, use, inspection and maintenance, storage and cleaning. Requires standard operating procedures; employee screening and training. | No specific rules pertaining to H ₂ S |
| OSHA Process Safety Management of Highly Hazardous Chemicals Standards 29 CFR 1910.119 | Current: Remote unmanned facilities and drilling and servicing exempted. Purpose: To prevent or minimize the consequences of catastrophic releases of highly hazardous chemicals. Some elements specified by the 1990 Clean Air Act Amendments. | Threshold quantity for H ₂ S: 1500 pounds; meaning that the potential exists for a catastrophic accident at facilities with more than 1500 pounds on site. |
| OSHA Oil and Gas Well Drilling and Servicing Standards 29 CFR 1910.270 | Proposed: 1983 proposal; OSHA still supports a specific standard for oil and gas production, thus their exemption from 29 CFR 1910.119 above. | Specifics pertaining to H ₂ S include: monitoring programs, personal protective devices, automatic flare ignitors, spark arrestors, drilling mud programs. |
| National Institute for Occupational Safety and Health (NIOSH) ^b Criteria Document for a Recommended Standard for Occupational Safety and Health | Recommendations for safe levels of worker exposure to H ₂ S. Standards developed for healthy workers, not for the public at large. | H ₂ S ceiling conc.: 15 mg/m ³ (approx. 1 x 10 ⁴ ppb), 10-minute sampling, 10-hour workday, 40-hour workweek. Evacuation: 70 mg/m ³ (approx. 5 x 10 ⁴ ppb) |
| American Conference of Governmental Industrial Hygienists (ACGIH) ^b Threshold Limit Values for Chemical Substances in the Work Environment | Professional organization of industrial hygienists which publishes annually updated Threshold Limit Values (TLVs) as guidelines in the control of occupational health standards. | TLV-TWA: 1 x 10 ⁴ ppb, for an 8-hour workday, 40-hour workweek. TLV-STEL: 1.5 x 10 ⁴ ppb, 15-minute weighted average, not more than 4 times/dayday. |

^aFederal regulatory agency with enforceable standards; 25 of the States and territories run their own occupational safety programs.

^bRecommended standard.

- 1) Develop and maintain written safety information identifying workplace chemical and process hazards, equipment, and process technology;
- 2) Perform a process hazard analysis which shall include an estimate of workplace effects of a range of releases and their health and safety effects on employees;
- 3) Consult with employees and their representatives on the conduct and development of the process safety management program.
- 4) Develop and implement written operating procedures for the chemical process;
- 5) Provide training to employees;
- 6) Evaluate and monitor contractor safety standards and performance;
- 7) Perform pre-startup safety reviews for new and modified facilities;
- 8) Establish maintenance systems for critical process related equipment;
- 9) Establish and implement written procedures to manage changes to the process;
- 10) Investigate every incident that has resulted or could result in a major accident;
- 11) Establish and implement a plant emergency action plan.

OSHA issued its final process safety standard on February 24, 1992.

Appendix A to the process safety standard (1910.119), lists the chemicals that present a potential for a catastrophic event with respective threshold quantities. For H_2S , the threshold quantity is 1500 pounds. This means that facilities with 1500 lbs or greater of H_2S on-site would be subject to the process safety management standard. OSHA further requires that the 25 States and territories with their own occupational safety organizations adopt similar rules within 6 months.

Although hydrogen sulfide is covered in this standard, oil and gas drilling or servicing operations are exempted, along with retail facilities and normally unoccupied remote facilities. OSHA explains the reason for the drilling and servicing exemptions in its preamble to the final rulemaking (57 FR 6369), stating that "OSHA continues to believe that oil and gas well drilling and servicing operations should be covered in a standard designed to address the uniqueness of the industry." This exclusion is retained in the final standard since OSHA continues to believe that a separate standard dealing with such operation is necessary. The potential exists that oil and gas operations that are the focus of this Report to Congress may be exempt from this OSHA standard if the facility is remotely located or if servicing

operations include those studied in this Report. Table IV-6 lists current and proposed regulations pertaining to hydrogen sulfide.

Proposed Regulations

In 1983, OSHA proposed an Oil and Gas Well Drilling and Servicing Standard (48 FR 57202). The proposed standard would supplement the general standards already in effect and address the operation's unique hazards, such as those related to the unusual equipment, special situations dictated by the locations of operations, and hazards resulting from well pressures. According to the Bureau of Labor Statistics, the oil and gas well drilling and servicing industry was ranked among the most hazardous industries in the United States. OSHA estimated that 95,000 workers at approximately 5,400 rigs were employed in various occupations relating to oil and gas well drilling and servicing operations. The National Institute for Occupational Safety and Health (NIOSH) conducted a study of the oil and gas industry and provided OSHA with recommendations for developing a standard. In addition to a discussion of the Bureau of Labor Statistics injury data, NIOSH's "Comprehensive Safety Recommendation - Land Based Oil and Gas Well Drilling" also referenced in an early draft a study of data NIOSH received on fatalities and injuries occurring between 1973 and 1978 in Texas and California drilling operations. NIOSH applied these statistics for the entire drilling industry and concluded that the injury incidence and severity rates for the oil and gas drilling industry were more than six times the rate of general industry. However, these statistics include hazards other than H₂S.

In 1973 OSHA decided to regulate this industry under its Construction Safety Standards (29 CFR 1926); however, the applicability of this rule was contested by the industry. As a result of the industry contention, the Occupational Safety and Health Review Commission (OSHRC) ruled several times that the construction standards were not applicable. According to OSHRC, employers engaged in oil and gas well drilling and servicing should be subject to the general industry standards found in 29 CFR 1910. New enforcement problems emerged as a result of applying general industry standards. At the time of the issuance of the proposed standard, OSHA data showed that the oil and gas industry received a higher percentage of citations than any other industry. These citations are issued only when a standard does not exist to address the hazard, but the hazard is well recognized as a potential source of serious injury. OSHA felt that the high number of citations indicated the need for standards directed to these hazards in order to assist employers in meeting their obligations under the Occupational Safety and Health Act. They stated that it was apparent that the general industry standards either did not address or inadequately addressed hazards unique to oil and gas production, possibly even contributing to the higher injury and illness rate experienced by this industry. With the help of data from numerous studies of injury and illness in the oil and gas production industry, and input from numerous states, trade associations, labor unions and industry representatives, the draft oil and gas standards were proposed in 1983. No known action on this proposal has occurred since then. Currently, the proposed oil and gas well drilling and servicing rule has not been withdrawn, but it is also not on the regulatory agenda for finalizing.

OSHA proposed specific requirements for drilling, servicing, and special services operations performed in areas where a potential for exposure to H_2S gas exists. The requirements proposed establishing and implementing a monitoring program in specified areas of the rig. The monitoring program would be applicable where the potential exists for H_2S exposure, including areas where data are unavailable or inconclusive with respect to the potential H_2S exposure. The program would use automatic environmental monitoring systems connected to an employee alarm system. Details of the program and its procedures would be required from the regulated community in written form. Testing and maintenance of the monitoring system would also be regulated under the proposal, because improperly maintained or untested systems may lead to a false sense of security for employees who rely on them for warning.

Specific respiratory protection equipment requirements were also included in the proposed regulation. All employees working in an area of potential hydrogen sulfide exposure would be required to wear or carry an approved escape-type, self-contained breathing apparatus. An approved positive-pressure respirator would be required for employees who remain in or return to the danger area.

In Appendix A to the proposed rule, OSHA also suggested the following practices to control or limit hydrogen sulfide exposure:

- automatic ignitors on the flare from the degasser, choke manifold, and mud-gas separator to burn off hydrogen sulfide;
- spark arrestors for all internal combustion engines to lessen the chance of the engine serving as a source of ignition in the event of a blowout;
- regular checking of drilling mud to assure it has the right constituents and pH to counteract H_2S ;
- addition of hydrogen sulfide neutralizer to the drilling mud to prevent the gas from reaching the surface;
- installation of H_2S monitoring systems on all rigs working within 1000 feet of known or suspected H_2S zones.

Although the oil and gas well drilling and servicing rule (1910.270) was proposed in 1983 and has not been enacted, OSHA has continued to express a preference for a specific regulation pertaining to the oil and gas drilling and servicing operation in 1992, by exempting these industries from the Process Safety Management of Highly Hazardous Chemicals; Explosives and Blasting Agents Final Rule (29 CFR 1910.109 and 1910.119; 57 FR 6356).

Impact of OSHA Regulations on Occupational and Human Health

OSHA regulations are designed to protect the worker rather than the general public or the environment. In this respect, they set levels that protect the health of workers exposed for a 40-hour workweek, rather than residents who may be exposed continuously. The OSHA permissible exposure limit (PEL) for H_2S is 10 ppb. Levels set to protect human health in general are often much more conservative since they are often based on models which assume exposure scenarios in which the person is exposed 24-hours a day for a lifetime. Non-occupational health effects levels may also account for possible developmental effects on young children and the effects of pollutants on those whose health is already compromised due to age or a chronic condition.

Four OSHA standards have the potential to protect workers exposed to H_2S . Two of these OSHA standards could apply to both workers and the public, while the other two apply specifically to workers. The OSHA general industry air contaminants and respirator standards protect the worker from H_2S exposures above certain levels. These standards address the protection of the worker from an exposure in excess of a set level through the use of personal protective equipment. The public is not protected through these two standards, since they aim to protect workers from contact with H_2S rather than prevent the release of the H_2S into the atmosphere. The process safety management standard and the proposed oil and gas well drilling and servicing standard have the potential to protect both the worker and the general public by preventing the release of H_2S .

National Institute for Occupational Safety and Health

Recommendations for safe levels of worker environmental exposure to H_2S are presented in the May 1977, *National Institute for Occupational Safety and Health (NIOSH) Criteria Document for a Recommended Standard for Occupational Exposure to Hydrogen Sulfide* (NIOSH, 1977). Hydrogen sulfide was cited as the leading cause of sudden death in the workplace (Ellenhorn and Barceloux, 1988). It was recognized as a serious hazard to the health of workers employed in energy production from hydrocarbon or geothermal sources, in the production of fibers or sheets from viscous syrup, in the production of deuterium oxide (heavy water), in tanneries, sewers, sewage treatment and animal waste disposal, in work below ground, fishing boats, and in chemical operations. Table IV-6 presents specific work practices recommended by NIOSH for the gas and oil industry.

A ceiling concentration was proposed to prevent eye effects and other adverse effects, including anorexia, nausea, weight loss, insomnia, fatigue, and headache, from prolonged exposure to hydrogen sulfide at low concentrations. The proposed ceiling concentration would also prevent acute eye effects, unconsciousness, and death, which can rapidly follow exposure to hydrogen sulfide at high concentrations. NIOSH suggests no employee be exposed to hydrogen sulfide at a ceiling concentration greater than 15 mg/m^3 (approximately 1×10^4 ppb), as determined with a sampling period of 10 minutes, for up to a 10-hour work shift in a 40-hour workweek. Evacuation of the area shall be required if the concentration of

hydrogen sulfide equals or exceeds 70 mg/m^3 (approximately 5×10^4 ppb). NIOSH warns that the standard was not developed for the population-at-large, and any extrapolation beyond occupational exposures is not warranted.

The document includes monitoring requirements for all areas where there is occupational exposure to H_2S . First, there should be personal monitoring to detect each employee's ceiling exposure, with source and area monitoring as a supplement. The monitoring should be done quarterly, or as recommended by an industrial hygienist. Recording automatic monitors would be permitted to show short-term (less than 1-minute) peaks of up to 5×10^4 ppb, as long as no more than one occurs in any 30-minute period. These recording automatic monitors should be set up to signal spark-proof audible or visual alarms. They should have different alarms to signal concentrations of 1×10^4 ppb as an alert level to employees and 5×10^4 ppb as the level for employee evacuation.

The Secretary of Labor weighs NIOSH's recommendations, along with other considerations such as feasibility and means of implementation, in developing regulatory standards. The criteria document also contains sections on medical screening and followup of exposed employees, labeling and posting of H_2S hazards, personal protective equipment, hazard information for employees, work practices, sanitation, and monitoring and recordkeeping.

Bureau of Land Management

If a sour oil and gas well is located on Federal or Indian land, the facility operator or owner is subject to the requirements imposed by the Onshore Oil and Gas Order No. 6 developed by the Bureau of Land Management. This order requires submittal of a public protection plan by operators of sour oil and gas facilities upon detection of the potential to release a hazardous volume of H_2S (defined as concentrations of H_2S that exceed 1×10^5 parts per billion in the gas stream). Site-specific conditions are also criteria for determining whether or not a facility needs to submit a public protection plan. These conditions include (1) proximity to public buildings, public gathering centers, and roadways used for public use; and (2) radius and concentration of exposure. The order also has requirements for danger signs, fencing and gates, and wind direction indicators. Additional requirements include well control equipment, corrosion protection, and automatic safety valves or shutdowns for accidental release prevention.

The Bureau of Land Management does have procedures for enforcing Onshore Oil and Gas Order No. 6. Penalties for failure to comply with are cited in 43 C.F.R. 3163.1 (1992).

Minerals Management Service

The Minerals Management Service (Department of the Interior) Outer Continental Shelf Standard, MMS-OCS-1, Safety Requirements for Drilling Operations in a H_2S

Environment is the name for the former U.S. Geological Survey Outer Continental Shelf (OCS) Standard No.1. In February of 1976, the Conservation Division of the U. S. Geological Survey (USGS) released offshore rules for safety and pollution prevention in Standard No. 1, Safety Requirements for Drilling Operations in a Hydrogen Sulfide Environment (USGS, 1976). Required details of a contingency plan for emergency hydrogen sulfide situations are listed in the standard, and each platform is required to have the plan developed prior to drilling. The standard also specifies details of the personnel training program, and type, storage location and use of personnel protective equipment. Finally, the standard requires state-of-the-art equipment for blowout prevention, and specifies details of the mud program, well-testing procedures and flare system.

The standard requires H₂S monitoring equipment at all wells, except when drilling in areas known to be free of hydrogen sulfide. Upon encountering hydrogen sulfide, the safety requirements of the rules go into effect, and when concentrations reach 2×10^4 ppb the remainder of the rules dealing with hydrogen sulfide's corrosive effects must be observed. The precautions in the American Petroleum Institute Recommended Practice for Safe Drilling of Wells Containing Hydrogen Sulfide, (API RP 49) are considered supplemental to the requirements of the standard (API, 1987).

Two separate operational conditions are outlined with requirements for warning flags and notification of authorities. Moderate danger, when the threshold limit value of 10 ppm is reached, requires the display of signs and flags reading "DANGER - HYDROGEN SULFIDE - H₂S." If the concentration reaches 2×10^4 ppb, protective-breathing apparatus is required to be worn by all working personnel, and non-working personnel are required to evacuate to safe briefing areas. Extreme danger, when H₂S reaches the injurious level (5×10^4 ppb), is the point when all personnel (or all non-working personnel as appropriate) are required to evacuate. Radio communications are required to alert all known air and water craft in the immediate vicinity of the danger.

The Minerals Management Service is in the process of reproposing its standards for hydrogen sulfide.

CERCLA and EPCRA

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 establishes broad Federal authority to deal with releases or threatened releases of hazardous substances from vessels and facilities. The Act defines a set of hazardous substances chiefly by reference to other environmental statutes; currently there are over 700 CERCLA hazardous substances. Commonly known as "Superfund," CERCLA requires that the person in charge of a vessel or facility notify the National Response Center as soon as that person has knowledge of a release of a hazardous substance in an amount equal to or greater than the reportable quantity (RQ) for that substance. Currently, hydrogen sulfide is listed as a CERCLA hazardous substance with a reportable quantity of 100 pounds.

On October 17, 1986, the President signed into law the Superfund Amendments and Reauthorization Act of 1986 (SARA), which revises and extends the authorities established under CERCLA and other laws. The Emergency Planning and Community Right-to-Know Act (EPCRA), enacted in 1986 as Title III of SARA, establishes new authorities for emergency planning and preparedness, community right-to-know reporting, and toxic chemical release reporting. It is intended to encourage and support emergency planning efforts at the State and local levels and to provide citizens and local governments with information concerning potential chemical hazards present in their communities. EPCRA is organized into three subtitles (A-C), each containing a number of subsections.

Subtitle A establishes the framework for State and local emergency planning. Section 301 requires each State to establish an emergency response commission and local emergency planning committees. Section 303 governs the development of comprehensive emergency response plans by local emergency planning committees and provision of facility information to the committee. Section 302 requires EPA to publish a list of extremely hazardous substances and threshold planning quantities (TPQs) for such substances. This list was established by EPA to identify chemical substances that could cause serious irreversible health effects from accidental releases. The list includes hydrogen sulfide, with a threshold planning quantity of 500 pounds. Any facility where an extremely hazardous substance is present in an amount in excess of the threshold planning quantity is required to notify the State commission and be included in local planning efforts. Section 304 establishes requirements for immediate reporting of certain releases of reportable quantities of extremely hazardous substances, and CERCLA Hazardous Substances, to the local planning committees and State emergency response commissions. These requirements are similar to the release reporting provisions under Section 103 of CERCLA. Section 304 also requires follow-up reports on each release, its effects, and response actions taken.

Only those sour oil and gas wells and well-site facilities that have 500 pounds or more of H_2S present at the well facility are subject to the planning requirements. The reportable quantity of H_2S is 100 pounds. Therefore, releases into the environment at or above 100 pounds must be reported in accordance with CERCLA 103 and EPCRA 304.

Subtitle B provides the mechanism for community awareness of hazardous chemicals present in the locality. This information is critical for effective local contingency planning. If the owner or operator of a facility is required to prepare or have available a Material Safety Data Sheet (MSDS) for a hazardous chemical under the Occupational Safety and Health Act of 1970 and regulations promulgated under that Act, Section 311 requires that owner or operator to submit MSDSs, or a list of the chemicals for which the facility is required to have an MSDS, to the local emergency planning committees, State emergency response commissions, and local fire departments. Under Section 312, owners and operators of facilities that must submit an MSDS under Section 311 are also required to submit chemical inventory information on the hazardous chemicals present at the facility. The threshold for reporting for H_2S under sections 311 and 312 is 500 pounds. Only facilities that have more than the threshold quantity need to report under sections 311 and 312, unless

MSDS or inventory information is specifically requested by the State Emergency Response Commission (SERC) or Local Emergency Planning Committee (LEPC). The owner or operator must submit an inventory form containing an estimate of the maximum amount of hazardous chemicals present at the facility during the preceding year, an estimate of the average daily amount of hazardous chemicals at the facility, and the location of these chemicals at the facility. Section 313 requires that certain facilities with ten or more employees that manufacture, process, or use a "toxic chemical" in excess of a statutorily-prescribed quantity submit annual information on the chemical and releases of the chemical into the environment. This information must be submitted to EPA and to the appropriate State offices annually. Hydrogen sulfide is not listed as a toxic chemical for which annual release information is required.

Subtitle C contains general provisions concerning trade secret protection, enforcement, citizen suits, and public availability of information.

Clean Air Act Section 112(r) - Accident Prevention

The Clean Air Act Amendments of 1990 established programs to prevent accidental releases of extremely hazardous substances and to assure that mitigation and response measures are in place in the event that a release does occur. Section 112(r) of the Clean Air Act establishes the responsibility for prevention of releases of extremely hazardous substances as the general duty of owners and operators of facilities that produce, process, handle or store such substances. Section 112(r) also requires that EPA promulgate a list of at least 100 substances that could cause death, injury or serious adverse effects to human health or the environment. Facilities with threshold quantities of the listed substances will be required to establish risk management programs and to prepare risk management plans. The statute requires EPA to promulgate regulations concerning risk management plans and other aspects of accident prevention. H₂S is one substance to which these requirements will apply as mandated in the statute.

The general duty clause is intended to establish as a responsibility of the facility owner the prevention of accidental releases and minimization of the consequences of accidental releases which do occur. Responsibilities include the conduct of appropriate hazard assessments and the design, operation, and maintenance of a safe facility. This means that facilities must be equipped for release mitigation and community protection should a release occur. The clause in the Clean Air Act Amendments refers to and is correlated with the general duty clause contained in the Occupational Safety and Health Act administered by OSHA. The OSHA clause was designed for situations for which there is no specific OSHA regulation or standard. Recognition of the hazard by the owner or operator, or within an industry, of the industry has been one standard under the OSHA general duty clause (U.S. Senate 1989). Therefore, the general duty clause places on the owners and operators of facilities the responsibility to adhere to applicable industry codes and standards for safety, accident prevention, and response.

The accidental release prevention list criteria include severity of acute adverse health effects, likelihood of accidental release, and potential magnitude of human exposure. A threshold quantity is to be established for each regulated substance to account for toxicity, dispersibility, reactivity, volatility, combustibility, or flammability of the substance and the amount anticipated to cause adverse health effects in an accidental release. The list and threshold quantities were proposed on January 19, 1993 (58 FR 5102). H_2S is listed as a toxic, and other substances present at oil and gas sites, such as methane, ethane, propane, and other hydrocarbons, are listed as flammables. Facilities with threshold quantities of the regulated substances will be required to prepare risk management plans (RMPs) and implement risk management programs. The RMPs will include a summary of assessments of offsite consequences for a range of accidental releases (including worst-case accidental releases) and a history of accidental releases. Facilities must also describe release prevention and emergency response programs developed under the risk management regulations as part of the RMP process.

Clean Air Act - PSD Program

There is no NAAQS which addresses hydrogen sulfide; however, emissions of H_2S are regulated under the Prevention of Significant Air Quality Deterioration (PSD) Program. PSD is designed to allow for industrial growth within specific air quality goals. The basic goals of the PSD regulations are (1) to ensure that economic growth will occur in harmony with the preservation of existing clean air resources to prevent any new nonattainment problems; (2) to protect the public health and welfare from any adverse effect which might occur even at air pollution levels better than the national ambient air quality standards; and (3) to preserve, protect and enhance the air quality in areas of special national or regional natural, recreational, scenic, or historic value, such as national parks and wilderness areas.

PSD permits are required for stationary sources located in areas designated, pursuant to section 107 of the CAA, as attainment or unclassifiable for a criteria pollutant. Major sources or modifications are those emitting either at least 100 tons per year or 250 tons per year of any pollutant regulated under the CAA, depending on the source category of the PSD listed pollutants. Major sources in nonattainment areas would be regulated under permit requirements pursuant to Part D under title I of the CAA.

The CAA has set significance levels, below which a PSD permit is not required. Two tables set the significance values, one for defining significant emissions changes, in tons per year; and the other for defining significant air quality changes, in $\mu g/m^3$. For hydrogen sulfide, the applicable emissions threshold is the significant emission rate of 10 tons per year. An exemption from the monitoring provision of the permitting regulations for hydrogen sulfide is set as a 1-hour average concentration of $0.02 \mu g/m^3$. Hydrogen sulfide emissions are also counted as part of the Total Reduced Sulfur and Reduced Sulfur, both having significance values set at 10 tons per year. These pollutant classes are regulated primarily to avoid nuisance (odor) problems.

The applicability of the PSD permit program to oil and gas extraction wells would be dependent on the amount of emissions and the grouping of the wells (i.e., whether several wells would be combined for calculation of emissions). In general, it appears that most oil and gas extraction wells would not likely be subject to PSD regulations based on the applicability criteria.

INDUSTRY-RECOMMENDED SAFETY AND ENVIRONMENTAL PROTECTION PROCEDURES

This section summarizes selected industry standards and practices for managing H₂S releases to the atmosphere. The American Petroleum Institute (API) has developed and published design, construction, and operating standards. Certain aspects of these standards pertaining to accidental release prevention were discussed in the previous chapter.

API Recommended Practices

The American Petroleum Institute (API), an industry-wide technical organization, has published several recommended practices (RP) pertaining to hydrogen sulfide in the oil and gas production industry. These voluntary guidelines are intended to maintain worker and public safety and health. Table IV-7 lists API Recommended Practices pertinent to production and operations in formations containing H₂S.

Control Standards

API RP 49, Recommended Practices for Safe Drilling of Wells Containing Hydrogen Sulfide (April 15, 1987) and API RP 55, Recommended Practices for Conducting Oil and Gas Production Operations Involving Hydrogen Sulfide (October 1981; reissued March, 1983; and preparation of a second edition began in 1990) are the two main documents dealing with H₂S in oil and gas production. It is expected that the revised RP 55 will provide information similar in scope to that in the document currently under revision, but with additional detail and more current references. These recommended practices do not set a control level for H₂S emissions; rather they identify situations to which the practices apply. They are applicable in oil and gas operations where the potential exists for atmospheric concentrations of H₂S to reach 2×10^4 ppb. They also apply "where the fluids handled contain sufficient H₂S to produce a partial pressure above 0.05 pounds per square inch absolute (psia) and the total pressure is 65 psia or greater, or where internal or external stresses are present which could result in pipe or equipment failure due to sulfide stress cracking and/or hydrogen embrittlement" (API, 1987). In these cases, materials must meet National Association of Corrosion Engineers (NACE) standards.

Control Techniques

The control techniques discussed in the API Recommended Practices take two approaches to worker and public safety. First, when hydrogen sulfide has already been

Table IV-7. Reviewed American Petroleum Institute* Documents Pertaining to H₂S in Oil and Gas Production

| Document | Date | Title | Topics Covered |
|--------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Recommended Practice 49 (RP49) | 2nd Edition April 15, 1987 | Recommended Practices for Safe Drilling of Wells Containing Hydrogen Sulfide | Personnel training and protective equipment. Locations. Rig and well equipment. Rig operations in H ₂ S environments. Contingency planning and emergency procedures. Properties and effects of H ₂ S and SO ₂ . Sour environment definition. |
| Recommended Practice 51 (RP51) | 1st Edition October 1974 Reissued May 1982 | API Recommended Onshore Production Operating Practices for Protection of the Environment | Producing wells. Lease roads, gathering systems and pipelines. Production and water handling facilities. Oil discharge – prevention and cleanup. |
| Recommended Practice 53 (RP53) | 2nd Edition May 25, 1984 | Recommended Practice for Blowout Prevention Equipment Systems for Drilling Wells | Arrangement (surface and subsea) and/or installation of: blowout preventers, choke and kill units and lines, closing units, auxiliary equipment, pipe stripping, marine riser systems. Inspection and testing. Sealing components. Blowout modifications for H ₂ S environments. |
| Recommended Practice 54 (RP54) | 2nd Edition May 1, 1992 | Recommended Practices for Occupational Safety for Oil and Gas Well Drilling and Servicing Operations | Injuries and first aid. Protective equipment. Fire prevention. Drilling and well servicing rig equipment and electrical systems. Wireline service. Stripping and snubbing. Drill stem testing. Operations (including H ₂ S environment). |
| Recommended Practice 55 (RP55) | 1st Edition October 1981 Reissued March 1983 (revision in progress) | Recommended Practices for Conducting Oil and Gas Production Operations Involving Hydrogen Sulfide | Personnel training and protective equipment. Contingency plans and emergency procedures. Design, construction, and operating procedures. Surveillance and maintenance. Continuous H ₂ S monitoring equipment. Supplementary guidance and reference material for H ₂ S operations. |
| Specification 6A (SPEC 6A) | 16th Edition October 1, 1989 | Specification for Wellhead and Christmas Tree Equipment, Supplement 1 and 2 | Design and performance. Materials. Welding. Quality control. Equipment marking, shipping, storing, and specific requirements. |

*American Petroleum Institute; 1220 L Street, Northwest; Washington, DC 20005.

released, worker and public safety is protected through the use of monitoring programs, personal protective devices and contingency plans for evacuations. Second, the engineering approach uses design, construction, and operating procedures to prevent the release of hydrogen sulfide to the atmosphere. The prevention of equipment damage due to corrosion (sulfide stress cracking) and the techniques for prevention of blowouts in API RP 53, Recommended Practice for Blowout Prevention Equipment Systems for Drilling Wells, are two main considerations in this more site-specific engineering control technique.

API RP 49, which deals with drilling in a hydrogen sulfide environment, contains the following recommendations for well siting in order to protect workers from the effects of hydrogen sulfide accumulation at the well site: "Rig components should be arranged on a location such that prevailing winds blow across the rig in a direction that will disperse any vented gas from the areas of the wellhead, choke manifold, flare stack or line, mud/gas separator, drilling fluid tanks, reserve pits, shale shaker, and degasser away from any potential ignition source (i.e., engines, generators, compressors, crew quarters, etc.) and areas used for personnel assembly. All equipment should be located and spaced to take advantage of prevailing winds and to provide for good air movement to eliminate as many sources of potential gas accumulation as possible" (API, 1987).

Other siting recommendations in API RP 49, shown in Figure III-4, are the use of caution signs at entrance and exit roads to warn of hydrogen sulfide concentrations above 2×10^4 ppb and danger flags to warn of extreme danger when the concentration exceeds 5×10^4 ppb. These signs are required to stay in place when flaring of the hydrogen sulfide could produce sulfur dioxide concentrations in excess of 5×10^3 ppb. Protection or briefing centers should be placed upwind or perpendicular to the prevailing wind, with wind direction indicators easily visible from the briefing location and all work locations. Mechanical ventilation, large fans or bug blowers, should be available for use during light wind conditions to prevent the hydrogen sulfide from accumulating in low lying locations. The locations of drilling fluid systems, power plants, burn pits, and flare stacks are also discussed from the vantage point of worker safety after the release of hydrogen sulfide.

Both API RP 49 (pertaining to drilling in a hydrogen sulfide environment) and API RP 55 (dealing with production operations) contain recommendations for personnel training. RP 55 training program topics include: the effects upon humans of various concentrations of hydrogen sulfide; protective equipment, including the use of self contained breathing apparatus rather than canister type gas masks (a filtering type mask is not appropriate for protection from hydrogen sulfide); monitoring devices; emergency procedures; material selection; and the importance of ventilation. Monitoring equipment that would set off a visual alarm at 1×10^4 ppb and an audible one at 2×10^4 ppb is recommended. Breathing equipment requirements are also discussed, including selection and storage (where they are readily available in an emergency).

Contingency plans are outlined in Section 4 of API RP 55 (API, 1983). They are recommended for each operation that has the potential for an accidental release capable of

exposing the public to hazardous concentrations of hydrogen sulfide. Contingency plans should include the locations of: equipment that contains hydrogen sulfide, residences and other public facilities, evacuation routes, safety equipment, telephones, and designated briefing areas for employees. The contingency plan should also include procedures for calculating the dispersion of releases and lists of emergency telephone numbers. Finally, it is suggested that public and local officials should be briefed about the potential hazard prior to an incident, and that periodic tests of the contingency plan should be conducted.

RP 55 also covers protection of workers from the toxic effects of hydrogen sulfide due to build-up of gas concentration in confined areas. Protective equipment or purging is recommended for vessels that have previously held hydrogen sulfide. Extreme caution should be used when entering buildings containing equipment used to handle fluids containing hazardous concentrations of hydrogen sulfide. Routine use of personal protective devices is suggested in these instances.

API RP 54, Recommended Practices for Occupational Safety for Oil and Gas Well Drilling and Servicing Operations (May 1, 1992) also addresses some aspects of personal protection from the toxic effects of hydrogen sulfide (API, 1992). This document was released after OSHA's implementation of the 1×10^4 ppb time-weighted average standard. RP 54 does not mention any specific standard or level, rather it refers the reader back to API RP 49 and API RP 55, which state that they apply to oil and gas operations where the potential exists for atmospheric concentrations to reach 2×10^4 ppb (the old OSHA ceiling standard), or where the gas could cause corrosion of the equipment. API does caution throughout their documents that the latest local, State and Federal regulations should be consulted.

Engineering controls used to prevent the production of, or the release of, hydrogen sulfide to the atmosphere are covered in the recommended practices for drilling and production (RP 49 and RP 55). API RP 55, pertaining to production, warns of the potential for introducing sulfur-reducing bacteria, which produce hydrogen sulfide, into a formation during pressure maintenance or water flooding operations (i.e., enhanced oil recovery). Operators are warned to be aware of the possibility and to act quickly if introduction occurs. If care is taken to prevent the bacteria from being introduced into formations that do not contain hydrogen sulfide, the danger of hydrogen sulfide pollution will be prevented.

Other engineering controls such as those used in design, construction, and operating practices are covered in Section 5 of RP 55. API recommends that construction materials meet specifications of the National Association of Corrosion Engineers (NACE) Standard MR-01-75: Material Requirements for Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment. These materials include all those that are exposed to fluids containing hydrogen sulfide and critical to its containment. Process factors for consideration are discussed, including the concentration of hydrogen sulfide, the maximum atmospheric temperatures expected, pressure, pH, water content of fluids, mechanical stresses, corrosional or scale effects on the system, and any others unique to each situation. Finally,

piping design should eliminate dead or slow-flow areas where fluids containing hydrogen sulfide gas can collect.

Drilling fluids are important to the control of the drilling environment. According to API RP 49 (Recommended Practices for Safe Drilling of Wells Containing Hydrogen Sulfide), the following practices help to maintain environmental control: maintenance of a pH of 10 or higher to neutralize hydrogen sulfide (failing to maintain proper pH can cause release of hydrogen sulfide from the drilling fluid system), the use of chemical sulfide scavengers, and the use of oil-based drilling fluids. When hydrogen sulfide gas is breaking out of drilling fluids, the fluids should be routed through a mud-gas separator until the level is reduced to a safe one. Corrosion inhibitors that create a film which protects the equipment from pitting and eventual sulfide stress cracking are also recommended. Finally, extreme caution is urged in storing fluids that have been exposed to hydrogen sulfide, and in entering enclosed areas where drilling fluids have been stored.

Drill stem, casing, tubing, and wellhead selection must meet specifications of API, NACE, the American Society of Mechanical Engineers, and the American National Standards Institute, detailed in Section 5 of RP 49. Section 5 also covers procedures for limited entry tests and equipment considerations for blowout preventer units, closing units, remote choke control lines, and kill lines. Hydrogen sulfide considerations in mud/gas separators, degassers and flare system are also discussed.

Abandonment procedures are included in API RP 55, with the disclaimer that the suggested procedures do not supersede local, State or Federal regulations. Section 6.5 discusses spontaneous combustion of iron sulfide, which is produced by the reaction of H_2S with steel. Because spontaneous combustion is possible when iron sulfide is exposed to air, RP 55 suggests that iron sulfide be kept wet until it can be burned or buried. Iron sulfide also poses a hazard during well servicing operations. Acids react with the iron sulfide to produce H_2S . Damage may also occur in pipes exposed alternately to hydrogen sulfide and air. API stresses the use of monitoring equipment when well servicing operations are performed on wells where a hydrogen sulfide hazard exists.

Hydrogen sulfide in oil and gas production is also mentioned in API RP 51, API Recommended Onshore Production Operating Practices for Protection of the Environment (October 1974, reissued May 1982). General information on the protection of personnel and equipment are presented in this document (API, 1982).

FINDINGS

1. Eighteen States have short-term H_2S ambient air quality standards. Four of the nine major oil and gas producing States reviewed in this report do not have ambient air standards.

2. Ambient air quality standards range from 160 ppb per 24 hr average time to 50 ppb per 0.5 hr average time.
3. The number of State agencies involved in controlling oil and gas operations varies widely.
4. The size of enforcement staffs at the State level varies greatly, with some staff having inspection responsibility beyond oil and gas operations.
5. No specific H₂S environmental (i.e., ecological) protection standards were found for Texas, Michigan, Oklahoma and California.
6. Not all States maintain notification requirements for accidental releases of H₂S from oil and gas wells. Some do require notification when a threatening accidental release occur.
7. Reporting of routine H₂S emissions is not required in Texas, Oklahoma, Michigan, or California. "Routine" excludes such incidents as vapor recovery unit failures and other equipment upsets.
8. NIOSH suggests no employee be exposed to H₂S at a ceiling concentration greater than 15 mg/m³ (about 1 x 10⁴ ppb) for up to a 10 hr work shift in a 40 hr work week. Evacuation is required if the concentration equals or exceeds 70 mg/m³ (5 x 10⁴ ppb).
9. NIOSH requires monitoring in work areas with alarms sounding at 1 x 10⁴ ppb and 5 x 10⁴ ppb.
10. The Minerals Management Service requires for offshore rigs drilling in an H₂S environment: contingency plan, personnel training, state-of-the-art blowout prevention equipment, monitoring equipment and response procedures at 1 x 10⁴, 2 x 10⁴, and 5 x 10⁴ ppb. Special mud programs, well-testing procedures, and flare systems are also required. This Federal regulatory program does not have an equivalent onshore program.
11. The PSD permit program applies to significant emissions of H₂S from new sources emitting greater than 250 tons per year (or 100 tons per year for certain source categories) of any regulated pollutant, i.e., major PSD sources. It also applies to modifications of existing facilities if the net emissions increase of H₂S from the modification is significant. In either case, the significant emission rate for H₂S is 10 tons per year. Also, permits do not require monitoring if the 1-hr average concentration is below 0.014 ppb (0.02 µg/m³). H₂S is also regulated under the PSD program for its nuisance odor as part of a larger group of Total Reduced Sulfur and Reduced Sulfur (significant ≥ 10 tons/yr).

12. Accidental releases of H₂S can be prevented by application of process safety management principles. The following are among the ways that these principles are adopted:
- a. Under the Clean Air Act, as amended, industry has a responsibility to identify hazards, take the actions necessary to prevent chemical accidents, and to take action to mitigate accidents in the event that they do occur.
 - b. OSHA has promulgated a process safety management standard that requires facilities to implement process safety management programs for chemicals including H₂S to protect workers from accidents. These same measures can also prevent chemical accidents that might affect the public. However, the OSHA requirements do not apply to remote or unstaffed facilities such as most oil and gas well sites.
 - c. Under the Clean Air Act, as amended, EPA must promulgate rules that require facilities handling H₂S to implement a risk management plan designed to prevent chemical accidents that adversely affect the public.
 - d. The Bureau of Land Management's Onshore Oil and Gas Order No. 6 addresses the prevention of accidental releases of H₂S on Federal or Indian lands.
 - e. Several State programs address the prevention of accidental releases of H₂S. States with such programs include Oklahoma, Texas, Michigan, California, and New Mexico.
 - f. Voluntary industry initiatives (e.g., codes, standards, recommended practices) such as the API RP 55, Recommended Practices for Conducting Oil and Gas Operations Involving H₂S, which is currently being revised, have been implemented by many facilities.
13. A number of Federal and State requirements exist for emergency planning in the event that an accidental release of H₂S occurs.
- a. Facilities handling quantities of H₂S greater than threshold amounts are subject to the emergency planning requirements of the Emergency Planning and Community Right-to-Know Act (EPCRA).
 - b. The accidental release prevention provisions of the Clean Air Act Amendments will require facilities handling amounts of H₂S above threshold quantities to implement an emergency response program.
 - c. For Federal and Indian lands, the Bureau of Land Management requires public protection plans for sour oil and gas production operations that meet certain criteria.
 - d. Several States require contingency plans in the event of accidental H₂S releases. State requirements include those of Oklahoma, Texas, Michigan, California, and New Mexico.

- e. API RP 55 recommends that contingency plans be developed for oil and gas extraction facilities where an accidental release of H₂S could be immediately hazardous to life or health.

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CHAPTER V RECOMMENDATIONS

ROUTINE EMISSIONS

From the limited data available, there appears to be no evidence that a significant threat to public health or the environment exists from routine H₂S emissions from sour oil and gas extraction. States and industry are encouraged to evaluate existing design, construction, and operation principles within the framework of process safety management. EPA recommends no further legislation pertaining to routine H₂S emissions from oil and gas extraction at this time.

ACCIDENTAL RELEASES

General

The EPA recommends no further legislative action pertaining to accidental H₂S releases from oil and gas extraction activities at this time. The regulations already promulgated, and being developed, under the authorities provided to EPA in CERCLA, EPCRA, and the accidental release prevention provisions of the CAA, provide a good framework for the prevention of accidental releases and preparedness in the event that they occur.

- EPA should track implementation of current and future industry standards and recommended practices at sour oil and gas extraction facilities. An example of such industry standards is the American Petroleum Institute Recommended Practices for Conducting Oil and Gas Production Operations Involving Hydrogen Sulfide (API RP55). EPA should consider outreach specifically directed at non-participating sectors.
- The EPA should participate in the investigation of any accidental releases associated with H₂S that cause or have the potential to cause public impacts in order to determine the root cause of such accidents. Such investigations should be coordinated with the Occupational Safety and Health Administration (OSHA) in order to encompass worker safety issues.
- The EPA should continue to investigate the need for additional rulemaking under the accidental release prevention provisions of the Clean Air Act to require implementation of certain prevention, detection, monitoring and mitigation efforts at facilities where extremely hazardous substances (such as H₂S) could generate dense gas clouds and impact the public. The level of voluntary industry initiatives and degree of participation, and accident history should be taken into account.

Facility and Local Emergency Planning Committee (LEPC)

Facilities that handle hazardous substances that could form dense vapor clouds if accidentally released, such as H₂S, should work closely with their LEPC to prevent accidents and to be prepared to respond to such accidents.

- Facilities should identify and thoroughly understand the hazards and conditions that can lead to accidental releases and the potential impacts on the public. These hazards and potential impacts should be communicated to the LEPC.
- All sour oil and gas extraction facilities and the LEPC for that area should conduct drills and exercises with workers, the community, first responders and others to test mitigation, response, and medical treatment for a simulated major H₂S accident. All such facilities should have training programs in place for H₂S emergencies.

Preparedness and Response

All sour oil and gas extraction facilities should actively conduct outreach efforts to ensure that the community is aware of the hazards of H₂S, that protective measures are in place to prevent public health impacts, and that proper actions will be taken during an emergency. Such outreach should be conducted through the LEPCs.

- All sour oil and gas extraction facilities should be able to rapidly detect, mitigate, and respond to accidental releases in order to minimize the consequences. Site-specific risk factors should be taken into account.
- Because a general duty exists to design, operate, and maintain a safe facility, owners and operators of sour oil and gas facilities should use appropriate equipment for the facility to provide public safety and should implement a program to remedy the effects of wear and tear and corrosion on equipment.
- In addition to regular inspection of all equipment, owners and operators should pay particular attention to corrosion monitoring of existing flow and gathering lines and to the condition of temporarily abandoned equipment. Remedial action should be taken before accidental releases occur.
- EPA should foster the development and continued refinement of release detection and mitigation systems for hazardous substances, such as H₂S, in order to improve their reliability and effectiveness.
- All facilities that handle oil and gas with potentially harmful levels of H₂S should have proper medical treatment supplies and trained personnel available and should ensure that first responders, hospitals, and clinics in the area are prepared to treat H₂S exposure.

Research and Further Studies

- Further study on the acute exposure levels of H₂S that result in irreversible health effects or lethality in humans should be continued in order to improve emergency planning tools such as atmospheric dispersion models.
- Further research on the effects of surface roughness and obstacles on dense-gas dispersion behavior should be continued to determine their influences on toxic substance concentrations in a dispersing vapor cloud. The Liquefied Gaseous Fuels Spill Test Facility could be used for spill tests to assist in this research.
- EPA should continue to study the issues surrounding worst-case releases, their consequences, and the likelihood of worst-case or other significant releases for extremely hazardous substances and the role and relationship of these issues to prevention, preparedness, and response.

GLOSSARY

Abandon: To cease producing oil or gas from a well when it becomes unprofitable. A wildcat may be abandoned after it has been proven nonproductive. Usually, before a well is abandoned, some of the casing is removed and salvaged and one or more cement plugs are placed in the borehole to prevent migration of fluids between the various formations. In many States, wells may not be abandoned unless approved by an official regulatory agency.

Accidental Release: The unanticipated emissions of a regulated substance or other extremely hazardous substance into the air from a stationary source.

Acid: Any chemical compound, one element of which is hydrogen, that dissociates in solution to produce free-hydrogen ions. For example, hydrochloric acid, HCl, dissociates in water to produce hydrogen ions, H^+ , and chloride ions, Cl^- .

Additive: A substance or compound added in small amounts to a larger volume of another substance to change some characteristic of the latter. In the oil industry, additives are used in lubricating oil, fuel, drilling mud, and cement for cementing casing.

Air drilling: A method of rotary drilling that uses compressed air as its circulation medium. This method of removing cuttings from the wellbore is as efficient or more efficient than the traditional methods using water or drilling mud; in addition, the rate of penetration is increased considerably when air drilling is used. However, a principal problem in air drilling is the penetration of formations containing water, since the entry of water into the system reduces its efficiency.

Alkalinity: The combining power of a base, or alkali, as measured by the number of equivalents of an acid with which it reacts to form a salt.

Annular injection: Long-term disposal of wastes between the outer wall of the drill stem or tubing and the inner wall of the casing or open hole.

Annulus or annular space: The space around a pipe in a wellbore, the outer wall of which may be the wall of either the borehole or the casing.

API: The American Petroleum Institute. Founded in 1920, this national oil trade organization is the leading standardizing organization on oil-field drilling and production equipment. It maintains departments of transportation, refining, and marketing in Washington, D.C., and a department of production in Dallas.

Artificial lift: Any method used to raise oil to the surface through a well after reservoir pressure has declined to the point at which the well no longer produces by means of natural energy. Artificial lift may also be used during primary recovery if the initial reservoir pressure is inadequate to bring the hydrocarbons to the surface. Sucker-rod pumps, hydraulic pumps, submersible pumps, and gas lift are the most common methods of artificial lift.

Barrel (bbl): A measure of volume for petroleum products. One barrel (1 bbl) is equivalent to 42 U.S. gallons or 158.97 liters. One cubic meter (1 m^3) equals 6.2897 bbl.

Basin: A synclinal structure in the subsurface, formerly the bed of an ancient sea. Because it is composed of sedimentary rock and its contours provide traps for petroleum, a basin is a good prospect for exploration. For example, the Permian Basin in West Texas is a major oil producing area.

Bit: The cutting or boring element used in drilling oil and gas wells. Most bits used in rotary drilling are roller-cone bits. The bit consists of the cutting element and the circulating element. The circulating element permits the passage of drilling fluid and uses the hydraulic force of the fluid stream to improve drilling rates. In rotary drilling, several drill collars are joined to the bottom end of the drill-pipe column for added weight. The bit is attached to the end of the drill collar.

Blowdown: The emptying or depressurizing of a material from a vessel. The material thus discarded.

Blowout preventer (BOP): Equipment installed at the wellhead, at surface level on land rigs and on the seafloor of floating offshore rigs, to prevent the escape of pressure either in the annular space between the casing and drill pipe or in an open hole during drilling and completion operations.

Blow out: To suddenly expel oil-well fluids from the borehole with great velocity. To expel a portion of water and steam from a boiler to limit its concentration of minerals.

Borehole: The wellbore; the hole made by drilling or boring.

Casing: Steel pipe placed in an oil or gas well as drilling progresses to prevent the wall of the well from caving in during drilling and to provide a means of extracting petroleum if the well is productive.

Casing string: Casing is manufactured in lengths of about 30 ft, each length or joint being joined to another as casing is run in a well. The entire length of all the joints of casing is called the casing string.

Cement: A powder consisting of alumina, silica, lime, and other substances which hardens when mixed with water. Extensively used in the oil industry to bond casing to the walls of the wellbore.

Cement plug: A portion of cement placed at some point in the wellbore to seal it.

Christmas tree: Assembly of fittings and valves at the tip of the casing of an oil well that controls the flow of oil from the well.

Close-in: A well capable of producing oil or gas, but temporarily not producing.

Collar: A coupling device used to join two lengths of pipe. A combination collar has left-hand threads in one end and right-hand threads in the other. A drill collar.

Commercial production: Oil and gas output of sufficient quantity to justify keeping a well in production.

Completion fluid: A special drilling mud used when a well is being completed. It is selected not only for its ability to control formation pressure, but also for its properties that minimize formation damage.

Completion operations: Work performed in an oil or gas well after the well has been drilled to the point at which the production string of casing is to be set. This work includes setting the casing, perforating, artificial stimulation, production testing, and equipping the well for production. It is done prior to the commencement of the actual production of oil or gas in paying quantities, or in the case of an injection or service well, prior to when the well is plugged and abandoned.

Corrosion: A complex chemical or electrochemical process by which metal is destroyed through reaction with its environment. Rust is an example of corrosion.

Crude oil: Unrefined liquid petroleum. It ranges in gravity from 9° to 55° API and in color from yellow to black, and it may have a paraffin, asphalt, or mixed base. If a crude oil, or crude, contains a sizable amount of sulfur or sulfur compounds, it is called a sour crude; if it has little or no sulfur, it is called a sweet crude. In addition, crude oils may be referred to as heavy or light according to API gravity, the lighter oils having the higher gravities.

Cuttings: The fragments of rock dislodged by the bit and brought to the surface in the drilling mud. Washed and dried samples of the cuttings are analyzed by geologists to obtain information about the formations drilled.

Demulsify: To resolve an emulsion, especially of water and oil, into its components.

Desander: A centrifugal device used to remove fine particles of sand from drilling fluid to prevent abrasion of the pumps. A desander usually operates on the principle of a fast-moving stream of fluid being put into a whirling motion inside a cone-shaped vessel.

Desilter: A centrifugal device, similar to a desander, used to remove very fine particles, or silt, from drilling fluid to keep the amount of solids in the fluid to the lowest possible level. The lower the solids content of the mud, the faster the rate of penetration.

Disposal well: A well into which salt water is pumped; usually part of a saltwater-disposal system.

Drill: To bore a hole in the earth, usually to find and remove subsurface formation fluids such as oil and gas.

Drill collar: A heavy, thick-walled tube, usually steel, used between the drill pipe and the bit in the drill stem to weight the bit in order to improve its performance.

Drill cutting: The formation rock fragments that are created by the drill bit during the drilling process.

Drilling fluid: The circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. A water-based drilling fluid is the conventional drilling mud in which water is the continuous phase and the suspended medium for solids, whether or not oil is present. An oil-based drilling fluid has diesel, crude, or some other oil as its continuous

phase with water as the dispersed phase. Drilling fluids are circulated down the drill pipe and back up the hole between the drill pipe and the walls of the hole, usually to a surface pit. Drilling fluids are used to lubricate the drill bit, to lift cuttings, to seal off porous zones, and to prevent blowouts. There are two basic drilling media: muds (liquid) and gases. Each medium comprises a number of general types. The type of drilling fluid may be further broken down into numerous specific formulations.

Drill pipe: The heavy seamless tubing used to rotate the bit and circulate the drilling fluid. Joints of pipe 30 ft long are coupled together by means of tool joints.

Drill site: The location of a drilling rig.

Drill stem: The entire length of tubular pipes, composed of the kelly, the drill pipe, and drill collars, that make up the drilling assembly from the surface to the bottom of the hole.

Drill string: The column, or string, of drill pipe, not including the drill collars or kelly. Often, however, the term is loosely applied to include both the drill pipe and drill collars.

Emulsion: A mixture in which one liquid, termed the dispersed phase, is uniformly distributed (usually as minute globules) in another liquid, called the continuous phase or dispersion medium. In an oil-water emulsion, the oil is the dispersed phase and the water the dispersion medium; in a water-oil emulsion the reverse holds. A typical product of oil wells, water-oil emulsion also is used as a drilling fluid.

Embrittlement: Through chemical reactions with H_2S , steel and other materials become more brittle and more likely to break.

Emulsion breaker: A system, device, or process used for breaking down an emulsion and rendering it into two or more easily separated compounds (like water and oil). Emulsion breakers may be (1) devices to heat the emulsion, thus achieving separation by lowering the viscosity of the emulsion and allowing the water to settle out; (2) chemical compounds, which destroy or weaken the film around each globule of water, thus uniting all the drops; (3) mechanical devices such as settling tanks and wash tanks; or (4) electrostatic treaters, which use an electric field to cause coalescence of the water globules. This is also called electric dehydration.

Enhanced oil recovery (EOR): A method or methods applied to depleted reservoirs to make them productive once again. After an oil well has reached depletion, a certain amount of oil remains in the reservoir, which enhanced recovery is targeted to produce. EOR can encompass secondary and tertiary production.

EPA: United States Environmental Protection Agency.

Exploration: The search for reservoirs of oil and gas, including aerial and geophysical surveys, geological studies, core testing, and the drilling of wildcats.

Extraction: The physical removal of oil and gas from a well.

Field: A geographical area in which a number of oil or gas wells produce from a continuous reservoir. A field may refer to surface area only or to underground productive formations as well. In a single field, there may be several separate reservoirs at varying depths.

Flare: Combustion of wastegases, such as H_2S or natural gas, which are not able to be profitably brought to market.

Flowing well: A well that produces oil or gas without any means of artificial lift.

Formation: A bed or deposit composed throughout of substantially the same kinds of rock; a lithologic unit. Each different formation is given a name, frequently as a result of the study of the formation outcrop at the surface and sometimes based on fossils found in the formation.

Gas plant: A plant for the processing of natural gas, by other than solely mechanical means, for the extraction of natural gas liquids, and/or the fractionation of the liquids into natural gas liquid products such as ethane, butane, propane, and natural gasoline.

Heater-treater: A vessel that heats an emulsion and removes water and gas from the oil to raise it to a quality acceptable for pipeline transmission. A heater-treater is a combination of a heater, free-water knockout, and oil and gas separator.

Hydrocarbons: Organic compounds of hydrogen and carbon, whose densities, boiling points, and freezing points increase as their molecular weights increase. Although composed of only two elements, hydrocarbons exist in a variety of compounds because of the strong affinity of the carbon atom for other atoms and for itself. The smallest molecules of hydrocarbons are gaseous; the largest are solid.

Ignitability (RCRA): The hazardous characteristic of ignitability for purposes of RCRA is defined in 40 CFR 261.21 and is generally a liquid with a flash point less than 140 degrees F., a non-liquid that causes fire under a friction condition, an ignitable compressed gas, or is an oxidizer.

Inhibitor: An additive used to retard undesirable chemical action in a product. It is added in small quantities to gasolines to prevent oxidation and gum formation, to lubricating oils to stop color change, and to corrosive environments to decrease corrosive action.

Injection well: A well in which fluids have been injected into an underground stratum to increase reservoir pressure.

Kelly: A pipe attached to the top of a drill string and turned during drilling. It transmits twisting torque from the rotary machinery to the drill string and ultimately to the bit.

LC₅₀ (median lethal concentration): The concentration of a chemical required to cause death in 50% of the exposed population when exposed for a specified time period, and observed for a specified period of time after exposure. Refers to inhalation exposure concentration in the context of air toxics (may refer to water concentration for tests of aquatic organisms or systems).

Lease: A legal document executed between a landowner (or a lessor) and a company or individual, as lessee, that grants the right to exploit the premises for minerals or other products. The area where production wells, stock tanks, separators, and production equipment are located.

Lowest-observed-adverse-effect level (LOAEL): The lowest dose or exposure level of a chemical in a study at which there is a statistically or biologically significant increase in the frequency or severity of an adverse effect in the exposed population as compared with an appropriate, unexposed control group.

Mud: The liquid circulated through the wellbore during rotary drilling and workover operations. In addition to its function of bringing cuttings to the surface, drilling mud cools and lubricates the bit and drill stem, protects against blowouts by holding back subsurface pressures, and deposits a mud cake on the wall of the borehole to prevent loss of fluids to the formation. Although it originally was a suspension of earth solids (especially clays) in water, the mud used in modern drilling operations is a more complex, three-phase mixture of liquids, reactive solids, and inert solids. The liquid phase may be fresh water, diesel oil, or crude oil and may contain one or more conditioners.

Natural gas: Naturally occurring mixture of hydrocarbon and non-hydrocarbon gases found in geologic formations beneath the earth's surface. The principal hydrocarbon constituent is methane.

No-observed-adverse-effect level (NOAEL). The highest experimental dose at which there is no statistically or biologically significant increases in frequency or severity of adverse health effects, as seen in the exposed population compared with an appropriate, unexposed population. Effects may be produced at this level, but they are not considered to be adverse.

Odor perception threshold: The lowest concentration at which a substance is first able to be smelled.

Oil base muds: A drilling fluid that is a water-oil emulsion with oil as the continuous phase. The oil content ranges from 50-98% oil. Oil muds are used to reduce drilling torque and to stabilize reactive shales that impede the drilling process.

Oil and gas separator: An item of production equipment used to separate the liquid components of the well stream from the gaseous elements. Separators are vertical or horizontal and are cylindrical or spherical in shape. Separation is accomplished principally by gravity, the heavier liquids falling to the bottom and the gas rising to the top. A float valve or other liquid-level control regulates the level of oil in the bottom of the separator.

Oil field: The surface area overlying an oil reservoir or reservoirs. Commonly, the term includes not only the surface area but also the reservoir, wells, and production equipment.

Operator: The person or company, either proprietor or lessee, actually operating an oil well or lease.

Packer: A piece of downhole equipment, consisting of a sealing device, a holding or setting device, and an inside passage for fluids. It is used to block the flow of fluids through the annular space between the tubing and the wall of the wellbore by sealing off the space. The packer is usually made up in the tubing string some distance above the producing zone. A sealing element expands to

prevent fluid flow except through the inside bore of the packer and into the tubing. Packers are classified according to configuration, use, and method of setting and whether or not they are retrievable (i.e., whether they can be removed when necessary, or whether they must be milled or drilled out and thus destroyed).

Perforate: To pierce the casing wall and cement to provide holes through which formation fluids may enter, or to provide holes in the casing so that materials may be introduced into the annulus between the casing and the wall of the borehole. Perforating is accomplished by lowering into the well a perforating gun, or perforator, that fires electrically detonated bullets or shaped charges from the surface.

Permeability: A measure of the ease with which fluids can flow through a porous rock.

pH: A measure of the acidity or alkalinity of a solution, numerically equal to 7 for neutral solutions, increasing with increasing alkalinity and decreasing with increasing acidity.

Primary recovery: Oil production in which only existing natural energy sources in the reservoir provide for movement of the well fluids to the wellbore.

Produced water: The water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas. It can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

Producing zone: The zone or formation from which oil or gas is produced.

Production: The phase of the petroleum industry that deals with bringing the well fluids to the surface and separating them. Production also includes storing, gauging, and otherwise preparing the product for the pipeline.

Production casing: The last string of casing or liner that is set in a well, inside of which is usually suspended the tubing string.

RCRA (Resource Conservation and Recovery Act): The Federal statute enacted in 1976 (and subsequent amendments) which amended the Solid Waste Disposal Act. Among other things, RCRA and its amendments established and/or augmented three significant programs: the hazardous waste management program, the solid waste program, and the underground storage tank program.

Reference concentration (RfC): An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

Reservoir: A subsurface, porous, permeable rock body in which oil or gas or both are stored. Most reservoir rocks are limestones, dolomites, sandstones, or a combination of these. The three basic types of hydrocarbon reservoirs are oil, gas, and condensate. An oil reservoir generally contains three fluids—gas, oil, and water—with oil the dominant product. In the typical oil reservoir, these fluids occur in different phases because of the variance in their gravities. Gas, the lightest, occupies the upper part of the reservoir rocks; water occupies the lower part; and oil occupies the intermediate section. In addition to occurring as a cap or in solution, gas may accumulate

independently of the oil; if so, the reservoir is called a gas reservoir. Associated with the gas, in most instances, are salt water and some oil. In a condensate reservoir, the hydrocarbons may exist as a gas, but when brought to the surface, some of the heavier ones condense to a liquid or condensate. At the surface the hydrocarbons from a condensate reservoir consist of gas and a high gravity crude (i.e., the condensate). Condensate wells are sometimes called gas-condensate reservoirs).

Rig: The derrick, drawworks, and attendant surface equipment of a drilling or workover unit.

Routine emissions: The anticipated emissions of a regulated substance or other extremely hazardous substance into the air from a stationary source during its normal operation.

Secondary recovery: Any method by which an essentially depleted reservoir is restored to producing status by the injection of liquids or gases (from extraneous sources) into the wellbore. This injection effects a restoration of reservoir energy, which moves the formerly unrecoverable secondary reserves through the reservoir to the wellbore.

Shale shaker: A series of trays with sieves that vibrate to remove cuttings from the circulating fluid in rotary drilling operations. The size of the openings in the sieve is carefully selected to match the size of the solids in the drilling fluid and the anticipated size of cuttings. It is also called a shaker.

Short-term exposure limit (STEL): A time-weighted average that the American Conference of Government and Industrial Hygienists (ACGIH) indicates should not be exceeded any time during the work day. Exposures at the STEL should not be longer than 15 minutes and should not be repeated more than 4 times per day. There should be at least 60 minutes between successive exposure at the STEL.

Shut-in well: A non-producing well with its pump turned off, and the stuffing box closed, which has been inspected to ensure there is no leakage.

Sour: Containing hydrogen sulfide or caused by hydrogen sulfide or another sulfur compound.

Stripper well: A well nearing depletion that produces a very small amount of oil or gas.

Tail gas: gas that leaves a sulfur recovery process after most of the H_2S has been converted to SO_2 .

Tank battery: A group of production tanks located in the field, used for storage of crude oil.

Tertiary recovery: A recovery method used to remove additional hydrocarbons after secondary recovery methods have been applied to a reservoir. Sometimes more hydrocarbons can be removed by injecting liquids or gases (usually different from those used in secondary recovery and applied with different techniques) into the reservoir.

Threshold limit value (TLV): The concentration of a substance below which no adverse health effects are expected to occur for workers, assuming exposure for 8 hours per day, 40 hours per week. TLVs are published by the American Conference of Governmental Hygienists (ACGIH). This listing may be useful in identifying substances used in the workplace and having the potential to be emitted into the ambient air.

Time-weighted average (TWA): An approach to calculating the average exposure over a specified time period.

Tubing: Small-diameter pipe that is run into a well to serve as a conduit for the passage of oil and gas to the surface.

Uncertainty factor (UF): One of several, generally 10-fold factors, applied to a NOAEL or a LOAEL to derive a reference dose (RfD) from experimental data. UFs are intended to account for (a) the variation in the sensitivity among the members of the human population; (b) the uncertainty in extrapolating animal data to humans; (c) the uncertainty in extrapolating from data obtained in a less-than-lifetime exposure study to chronic exposure; and (d) the uncertainty in using a LOAEL rather than a NOAEL for estimating the threshold region.

Volatile: Readily vaporized.

Waterflood: A method of secondary recovery in which water is injected into a reservoir to remove additional quantities of oil that have been left behind after primary recovery. Usually, a waterflood involves the injection of water through wells specially set up for water injection and the removal of the water and oil from the wells drilled adjacent to the injection wells.

Wellbore: A borehole; the hole drilled by the bit. A wellbore may have casing in it or may be open (i.e., uncased); or a portion of it may be cased and a portion of it may be open.

Well completion: The activities and methods necessary to prepare a well for the production of oil and gas; the method by which a flow line for hydrocarbons is established between the reservoir and the surface. The method of well completion used by the operator depends on the individual characteristics of the producing formation or formations. These techniques include open-hole completions, conventional perforated completions, sand-exclusion completions, tubingless completions, multiple completions, and miniaturized completions.

Wellhead: The equipment used to maintain surface control of a well, including the casinghead, tubing head, and Christmas tree.

Workover: One of more of a variety of remedial operations performed on a producing oil well to try to increase production. Some examples of workover operations are deepening, plugging back, pulling and resetting the liner, and squeeze-cementing.

Workover fluids: A special drilling mud used to keep a well under control when it is being worked over. A workover fluid is compounded carefully so it will not cause formation damage.

APPENDIX A

BACKGROUND INFORMATION ON THE OIL AND GAS PRODUCTION INDUSTRY

APPENDIX A

BACKGROUND INFORMATION ON THE OIL AND GAS PRODUCTION INDUSTRY

EXPLORATION AND DEVELOPMENT

Although geological and geophysical studies provide information about potential accumulations of petroleum, only exploratory drilling can confirm the presence of petroleum.

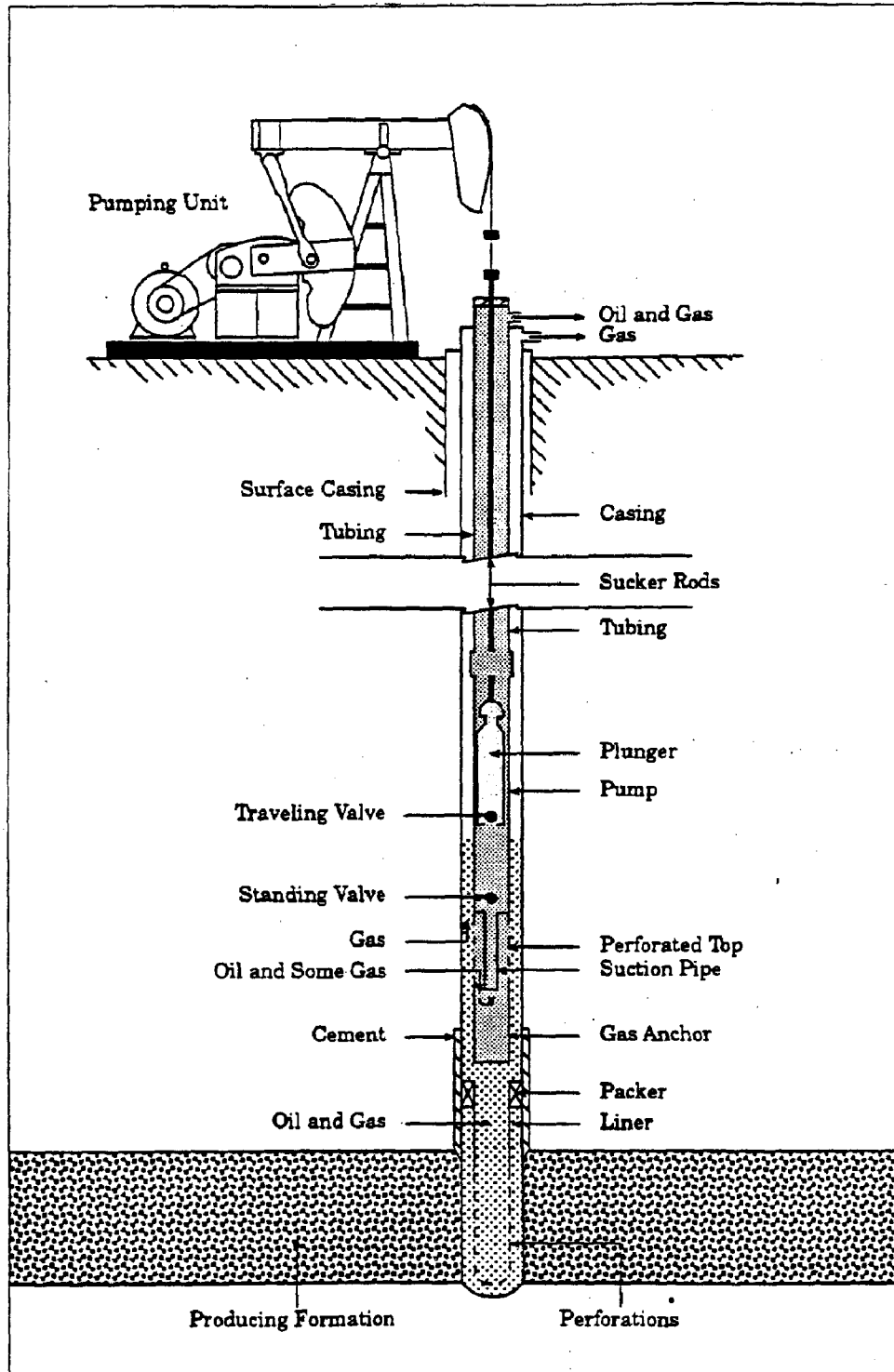
Rotary drilling, the primary drilling method in the United States, provides a safe way to control high-pressure oil/gas/water flows and allow for the simultaneous drilling of the well and removal of cuttings. This makes it possible to drill wells over 30,000 feet deep. Figure A-1 illustrates the process. Most rotary drilling operations employ a circulation system using a water- or oil-based fluid, called "mud" because of its appearance. The mud is pumped down the hollow drill pipe and across the face of the bit to provide lubrication and remove cuttings. Cuttings are removed at the surface by shale shakers, desanders, and desilters; they are then deposited in the reserve pit excavated or constructed next to the rig. Air drilling, which is considerably faster and less expensive than drilling with water- or oil-based fluids, is used in areas where high pressure or water-bearing formations are not anticipated.

Potential producing zones are normally measured and analyzed during exploratory drilling. If evidence of hydrocarbons is found, a drill stem test can show whether commercial quantities of oil and gas are present. If so, the well is prepared for production. This is called "completion." The most common method is the "cased hole" completion. Production casing is run into the hole and cemented permanently in place. Then one or more strings of production tubing are set in the hole, productive intervals are isolated with packers, and surface equipment is installed. The well is not actually completed until a gun or explosive charge perforates the production casing and begins the flow of petroleum into the well (U.S. EPA, 1987). Figure A-2 shows a cross section of a common well.

While a well is being drilled, heavy fittings have to be installed at the surface where the casing is attached, as each string of casing is inserted into the hole. Each part of the casing head is supported by a part of the casing head which was installed at the top of the next larger string of casing when it was run (U.S. EPA, 1987).

HOW OIL AND GAS ARE PRODUCED

Production operations generally include all activities associated with the recovery of oil and gas from geologic formations. They can be divided into activities associated with downhole operations and activities associated with surface operations. Downhole operations include primary secondary, and tertiary recovery methods, well workovers, and well stimulation activities. Activities associated with surface operations include oil/gas/water



Source: Royal Dutch/Shell, 1983.

Figure A-2. Cross section of a well pumping installation.

separation, fluid treatment, and disposal of produced water. The term "extraction" is commonly used to refer to activities associated with getting oil or gas to the surface; production includes both extraction and the surface operations involved in processing the materials extracted from the well. Production, as discussed in this report, is limited to the processing and storage that occurs at the well site. Transportation and further processing is not included in the scope of this report.

Downhole Operations

The initial production of oil or gas from the reservoir is called primary recovery. Natural pressure or artificial lift methods (surface or subsurface pumps and gas lifts) are used to bring the gas or oil out of the formation and to the surface (see Figure A-3). High-pressure gas can also be injected to lift the oil from the reservoir.

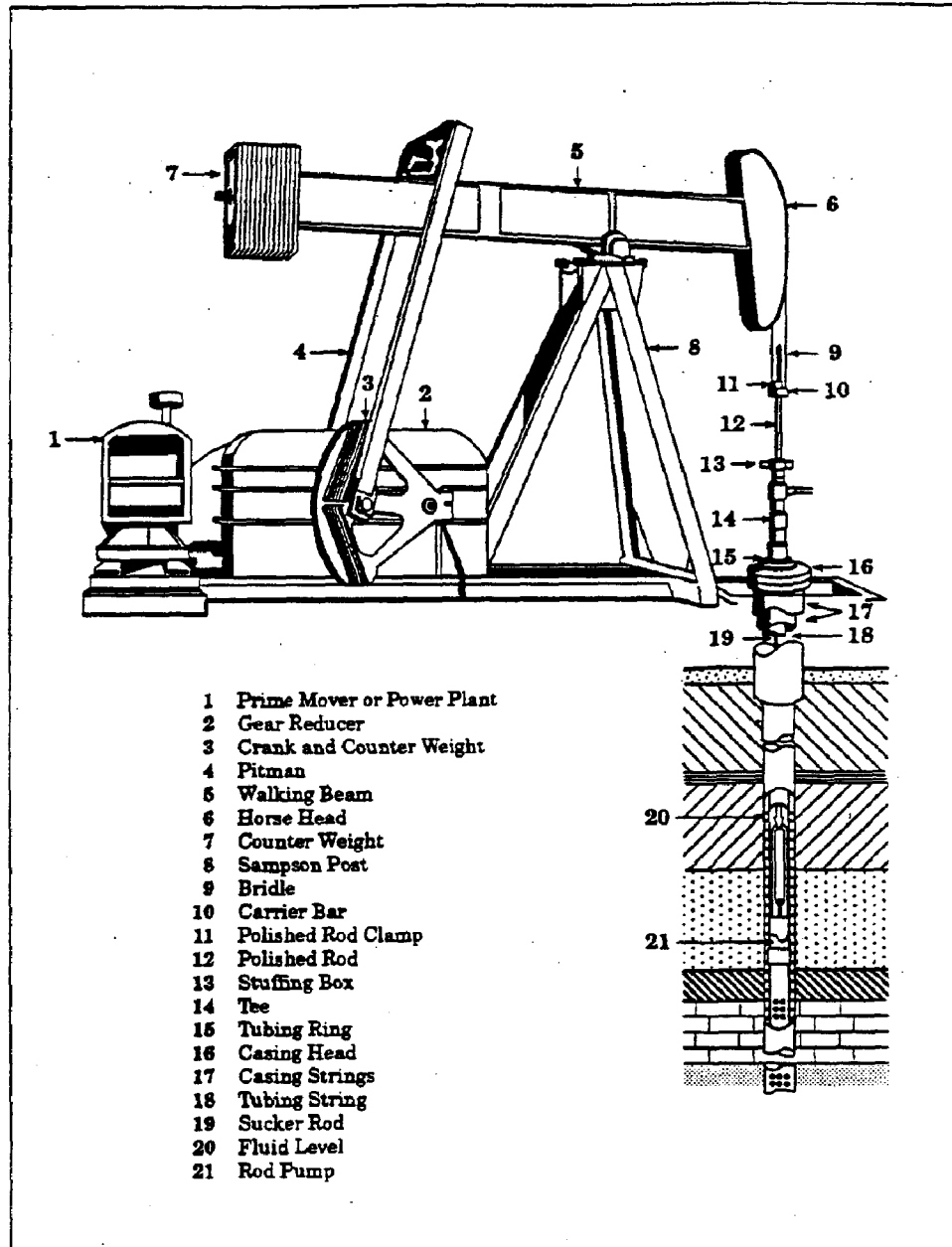
During the primary recovery stage, natural pressure in the reservoir may decline and artificial lift may be needed. One of three general types of pumps may be used: (1) pumps at the bottom of the hole run by a string of rods; (2) pumps at the bottom of the hole run by high-pressure liquids; and (3) bottom-hole centrifugal pumps (API, 1976).

The pumping unit includes a complete set of surface equipment that imparts an up-and-down motion to the sucker-rod string, which is connected the bottom-hole pump. Figure A-2 shows the parts of such as unit. Deep wells often require the long-stroke pumping provided by hydraulic units.

A stuffing box is used in a pumping well to pack or seal off the pressure inside the tubing so that liquid and gas cannot leak outside the polished rod. A stuffing box consists of flexible material or packing housed in a box which provides a method of compressing the packing. The packing material gradually wears out and must be replaced before it loses its effectiveness as a seal (API, 1976).

Primary recovery methods alone can produce oil and gas from most reservoirs, but over the life of the well production gradually decreases. Some form of secondary recovery will eventually be needed in nearly all wells. Secondary recovery methods inject gas or liquid into the reservoir to maintain pressure. The most frequent method is waterflooding, which involves injecting treated water (seawater, fresh water or produced water) into the formation through a separate well.

When secondary recovery methods are no longer adequate, the last portion of the oil that can be economically produced is recovered by tertiary methods. These include chemical, physical, and thermal methods or some combination. Chemical methods involve injection of fluids containing substances such as surfactants and polymers. Miscible oil recovery methods inject gases such as carbon dioxide and natural gas that combine with the oil. Thermal recovery methods include steam injection and *in situ* combustion (or "fire flooding"). The injected gases or fluids from secondary and tertiary recovery operations are



Source: API, 1976.

Figure A-3. Main parts of a pumping unit.

dissolved or mixed with the oil produced by the well and must be removed during surface production operations (U.S. EPA, 1987).

Workovers are another type of downhole production operation. Workovers are used to restore or increase production when downhole mechanical failures or blockages, such as sand or paraffin deposits have inhibited the flow of a well. Fluids circulated into the well for a workover must be compatible with the formation and must not adversely affect permeability. The workover fluid may be reclaimed or disposed of when the well is put back into production. Workover fluids are similar to completion fluids, which are special fluids used when the well is completed (ready for the production phase), to minimize formation damage and control potential problems such as H₂S corrosion.

Other chemicals are used periodically or continuously to inhibit corrosion, reduce friction, or simply keep the well flowing (U.S. EPA, 1987).

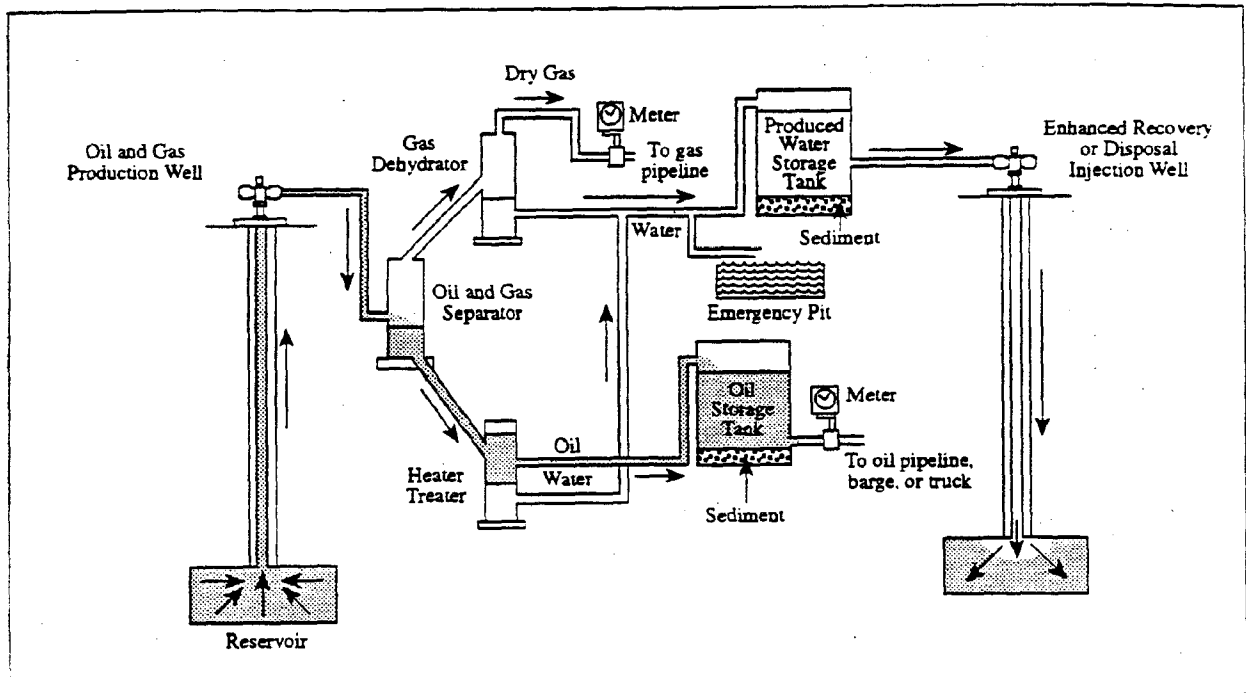
Surface Operations

As fluids are pumped to the surface, they are collected and treated to separate the various components (oil, gas, gas liquids, and water). Figure A-4 shows the separation process. These surface operations become more complex as secondary and tertiary recovery methods are employed. The ratio of water and other fluids to oil tends to increase as producing reservoirs are depleted. In new wells little or no water may be produced. The volume of water produced by stripper wells varies greatly. Stripper wells may produce more than 100 barrels of water for every barrel of oil, especially if waterflooding is used as a secondary recovery (U.S. EPA, 1987).

Separation involves the use of equipment to separate the gas, oil and water from each other. The actual separation may be accomplished in a single step or several steps depending on the relative amounts and the physical characteristics of the material which is delivered to the surface. Complete separation may require several stages involving different pressures, temperatures, and possibly additives if the material is delivered to the surface at a high pressure and the oil and gas are present in an emulsion.

After separation, the gas is transported by pipeline to a gas processing facility if the quantities from a specific well are adequate. If the quantities are inadequate, the gas is flared (burned). Gas processing facilities remove inerts (N₂, CO₂), hydrogen sulfide (H₂S), and liquids (oil and water) to produce pipeline quality gas which has a nominal heating value of 1000 BTU per cubic foot. Gas can also be re-injected into the well if necessary to help manage the reservoir or the production from the well.

Oil that is recovered from the separators at the well is placed in tanks and transported to a refinery for processing. This transportation is by pipeline if the quantities are adequate to justify installation of a pipeline or by truck if the production is small.



Source: U.S. EPA, 1987.

Figure A-4. Typical extraction operation showing separation of oil, gas, and water

Water recovered from the separators at the well is placed in tanks or pools. This water will ultimately be reinjected into the producing formation, injected into a disposal well, or discharged. Reinjection into the producing formation and injection into a disposal well are the most common methods for water disposal; discharge is rarely used. Permits are usually required for these water disposition options.

The equipment used at the surface to control the well is called the well head. If high production or significant gas pressure is expected, the well head is usually built of cast or forged steel, and machined to a close fit. These sealed fittings prevent well fluids from blowing or leaking at the surface. Parts of the well head may be designed to hold pressures up to 20,000 lb per sq in (psi). Some well heads are just simple assemblies to support the weight of the tubing in the well, and may not be built to hold pressure. For stripper wells, or other low-production, low-pressure wells, a simple well head can be used as long as only small amounts of gas are produced with the oil (API, 1976).

High pressures or corrosive gases such as H_2S require well heads with special valves and control equipment to control the flow of oil and gas from the well. These are constructed of heavy metal and installed above the casing head or tubing head before the well is completed. This collection of valves is called a Christmas tree because of its shape and the large number of fittings branching out above the well head. The tree diverts fluids through alternative chokes (API, 1976).

Safety measures should be adequate to prevent high pressure wells from going out of control. Equipment is available that automatically shuts off production if there is damage to the wellhead or to automatic surface safety valves at the wellhead.

Simpler types of Christmas trees can be used on low pressure or pumping wells. Pressure gauges on the well head and Christmas tree measure the pressure in the casing and tubing. If the pressures under various operating conditions are known, better control can be maintained (API, 1976).

OVERVIEW OF THE INDUSTRY

The U.S. petroleum industry drilled its first oil well in 1859. Since that first well, the oil and gas industry has grown to be extremely complex and diverse. In 1990, approximately 869,887 wells in over 33 States were producing oil and gas in the United States. The oil and gas obtained from these wells is found at depths ranging from 30 feet to 30,000 feet below the earth's surface. The major U.S. areas of onshore production include the southwest (including California), the midwest, and Alaska, with lesser contributions from the Appalachians. Table A-1 lists production estimates for the oil and gas producing States. In 1990-1991, Texas led all States in oil and natural gas production, turning out 705 million barrels of oil and 6.3 trillion cubic feet of natural gas (Petroleum Independent, 1992). Figure A-5 shows U.S. oil and gas production by State. The bar graph in Figure A-6 shows distribution of States containing more than 70 percent of gas wells in the U.S. Some of these

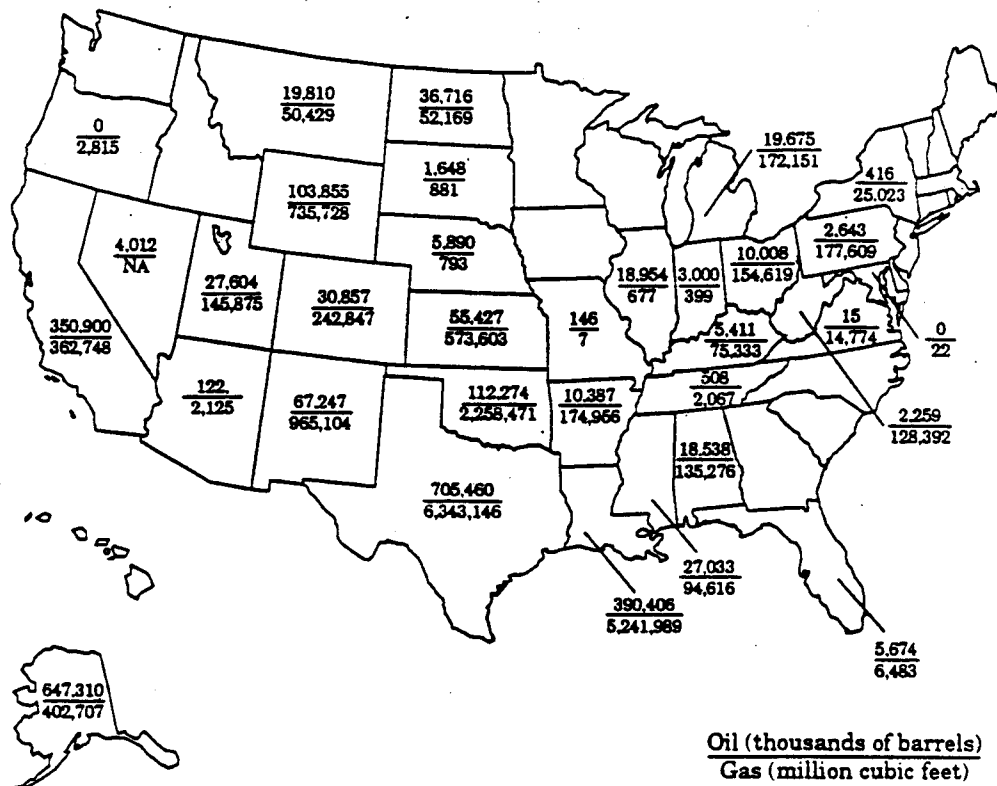
Table A-1. 1991 Oil and 1990 Gas Production Estimates

| State | Number of Producing Oil Wells ^a | Oil Production (thousands of barrels) ^b | Number of Producing Gas Wells ^a | Gas Production (million cubic feet) ^b |
|----------------|--------------------------------------------------|----------------------------------------------------------|--------------------------------------------------|--------------------------------------------------------|
| Alabama | 872 | 18,538 | 2,038 | 135,276 |
| Alaska | 1,466 | 647,310 | 109 | 402,907 |
| Arizona | 22 | 122 | NA | 2,125 |
| Arkansas | 7,265 | 10,387 | 3,460 | 174,956 |
| California | 43,375 | 350,900 | 1,169 | 362,748 |
| Colorado | 6,596 | 30,857 | 5,097 | 242,897 |
| Florida | 83 | 5,674 | NA | 6,483 |
| Illinois | 31,874 | 19,954 | 356 | 677 |
| Indiana | 7,506 | 3,000 | 1,311 | 399 |
| Kansas | 45,470 | 55,427 | 14,043 | 573,603 |
| Kentucky | 22,741 | 5,411 | 11,713 | 75,333 |
| Louisiana | 23,812 | 390,406 | 13,530 | 5,241,989 |
| Maryland | 0 | 0 | NA | 22 |
| Michigan | 4,570 | 19,675 | 1,438 | 172,151 |
| Mississippi | 2,168 | 27,033 | 629 | 94,616 |
| Missouri | 854 | 146 | NA | 7 |
| Montana | 3,854 | 19,810 | 2,428 | 50,429 |
| Nebraska | 1,440 | 5,890 | NA | 793 |
| Nevada | 46 | 4,012 | NA | NA |
| New Mexico | 18,546 | 67,247 | 19,537 | 965,104 |
| New York | 4,043 | 416 | 5,406 | 25,023 |
| North Dakota | 3,546 | 36,716 | 103 | 52,169 |
| Ohio | 30,089 | 10,008 | 34,697 | 154,619 |
| Oklahoma | 95,468 | 112,274 | 27,919 | 2,258,471 |
| Oregon | 0 | 0 | NA | 2,815 |
| Pennsylvania | 22,338 | 2,643 | 30,000 | 177,609 |
| South Dakota | 149 | 1,648 | 52 | 881 |
| Tennessee | 736 | 508 | 527 | 2,067 |
| Texas | 188,829 | 705,460 | 48,075 | 6,343,146 |
| Utah | 1,972 | 27,604 | 742 | 145,875 |
| Virginia | 25 | 15 | 819 | 14,774 |
| West Virginia | 15,950 | 2,143 | 37,000 | 178,000 |
| Wyoming | 11,397 | 103,855 | 2,431 | 735,728 |
| Federal Waters | 4,468 | NA | 3,591 | NA |
| Other | 25 | NA | 147 | NA |
| U.S. | 601,520 | 2,684,687 | 268,367 | 18,561,596 |

Combined Source: Petroleum Independent, September 1992, attributes the individual column sources to:

^aWorld Oil.^bEnergy Information Administration.

-NA Not available.

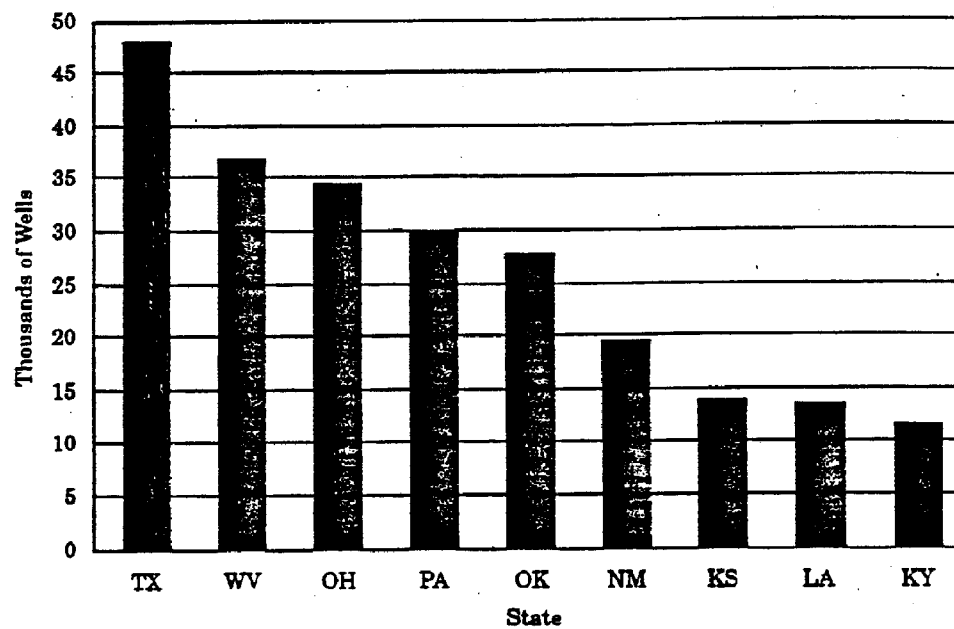


Oil (thousands of barrels)
Gas (million cubic feet)

U.S. Total 2,648,687
18,561,596

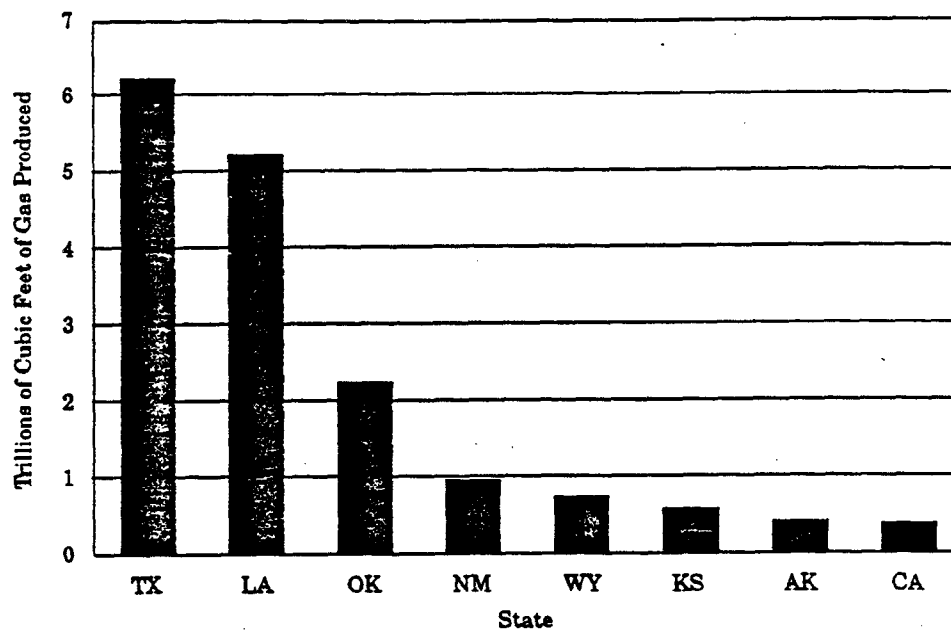
Combined Source: Petroleum Independent, September 1992, attributes the oil and gas sources to: World Oil Energy Information Administration.

Figure A-5. 1991 U.S. oil and gas production by State.



Source: World Oil (in Petroleum Independent, September 1992)

Figure A-6. States with the most producing gas wells in 1990.



Source: Energy Information Administration (in Petroleum Independent, September 1992).

Figure A-7. Gas production in 1990 from the top producing states.

States, however, are not the largest gas producers. Figure A-7 shows that Texas, Louisiana, Oklahoma, New Mexico, Wyoming, Kansas, Alaska, and California account for 92 percent of domestic gas production. Alaska, California, Louisiana, and Texas account for 78 percent of domestic oil production.

Principal Production Industry Groups

The industry can be divided into four groups. The first group consists of the major oil companies. These companies are highly vertically integrated, which means that they perform both "upstream" activities (oil exploration, development and production) and "downstream" activities (transportation, refining and marketing).

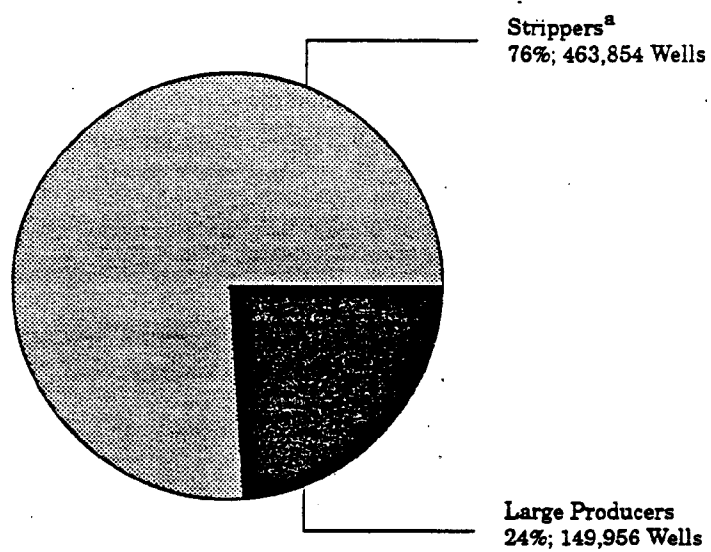
The second group is the large independents. These companies primarily explore, develop, and produce oil and gas, but do not perform downstream activities. Some large independents produce oil and gas only, while others provide such additional services as contract drilling and pipeline operations.

The third group is the small independents. Little information is available that would characterize this group quantitatively. However, small independents are known to have fewer wells and/or lower production wells. The lower operating expenses of small independents makes it more affordable to continue producing small quantities from low volume wells.

The fourth group consists of companies that provide a variety of specialized services to the oil and gas drilling rigs and platforms, such as designing, manufacturing, and installing specialized hardware. They also provide geophysical support, drilling mud, and logging services.

Diversity of Production

Production from individual wells varies greatly from a high of 11,500 barrels per day to less than 10 barrels per day. As shown in Figure A-8, over 70 percent of U.S. oil wells are "stripper" wells. The definition of a stripper well varies from State to State. However, these wells are generally defined as wells that produce 10 barrels of oil per day or less, or 100 thousand cubic feet (mcf) of gas per day or less. In 1990, 463,854 stripper wells existed and produced a total of 383,197,000 barrels of oil (NSWA, 1991). Stripper well production is shown in Table A-2. Figure A-9 shows that stripper wells produced 14 percent of the 2,684,687,000 barrels of oil produced in the United States in 1990 (U.S. EIA, 1991; U.S. EIA, 1987). Figure A-10 shows the proportion of stripper wells in the 10 States with the largest numbers of wells overall. In all 10 States, stripper wells comprised more 50 percent of producing wells. However, Figure A-11 demonstrates that in the 10 top oil producing States, oil from stripper wells is relatively low in volume. These wells typically are near depletion of recoverable natural resources and produce only a small quantity of oil or gas.



^a Strippers are defined as those producing 10 barrels a day or less.

Source: Interstate Oil and Gas Compact Commission and National Stripper Well Association.

Figure A-8. Number of producing oil wells in the U.S. in 1990.

Table A-2. 1990 Oil Production from Stripper Wells by State

| Location | Number of Producing Wells ^a | Number of Producing Stripper ^c Wells | Percentage of Producing Wells Which Are Stripper Wells ^a | Amount of Crude Oil Produced (thousands of barrels) ^b |
|---------------|----------------------------------------------|----------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Alabama | 872 | 514 | 58% | 18,538 |
| Alaska | 1,466 | 0 | 0% | 647,310 |
| Arizona | 22 | 12 | 55% | 122 |
| Arkansas | 7,265 | 7,290 | NA* | 10,387 |
| California | 43,375 | 26,128 | 60% | 350,900 |
| Colorado | 6,596 | 5,234 | 79% | 30,857 |
| Florida | 83 | 0 | 0% | 5,674 |
| Illinois | 31,874 | 33,700 | NA* | 19,954 |
| Indiana | 7,506 | 5,764 | 77% | 3,000 |
| Kansas | 45,470 | 45,227 | 99% | 55,427 |
| Kentucky | 22,741 | 19,330 | 85% | 5,411 |
| Louisiana | 23,812 | 17,695 | 74% | 390,406 |
| Michigan | 4,570 | 3,967 | 87% | 19,675 |
| Mississippi | 2,168 | 615 | 28% | 27,033 |
| Missouri | 854 | 375 | 44% | 146 |
| Montana | 3,854 | 3084 | 80% | 19,810 |
| Nebraska | 1,440 | 1,269 | 88% | 5,890 |
| Nevada | 46 | 0 | 0% | 4,012 |
| New Mexico | 18,546 | 15,261 | 82% | 67,247 |
| New York | 4,043 | 3,748 | 93% | 416 |
| North Dakota | 3,546 | 1,205 | 34% | 36,716 |
| Ohio | 30,089 | 29,576 | 98% | 10,008 |
| Oklahoma | 95,468 | 73,345 | 77% | 112,274 |
| Pennsylvania | 22,338 | 21,800 | 98% | 2,643 |
| South Dakota | 149 | 26 | 17% | 1,648 |
| Tennessee | 736 | 923 | NA* | 508 |
| Texas | 188,829 | 127,790 | 68% | 705,460 |
| Utah | 1,972 | 1,026 | 52% | 27,604 |
| Virginia | 25 | 22 | 88% | 15 |
| West Virginia | 15,950 | 15,975 | NA | 2,143 |
| Wyoming | 11,397 | 2,953 | 26% | 103,855 |
| U.S. | 601,520 | 463,854 | 77% | 2,684,687 |

Combined Source: Petroleum Independent, September 1992, attributes the individual column sources to:

^a World Oil.

^b Energy Information Administration.

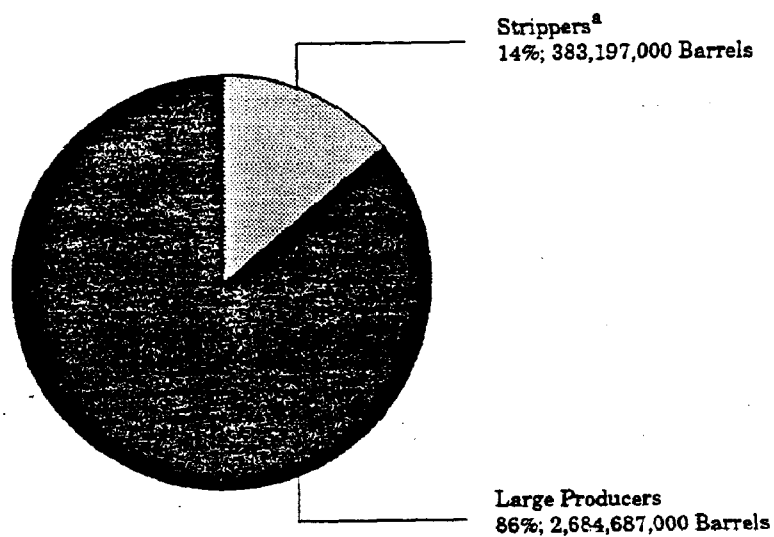
^c Interstate Oil and Gas Compact Commission and National Stripper Well Association.

*Petroleum Independent warns "[number of producing stripper wells]-data cannot be compared to "Producing Oil Wells" table due to different sources and technology."

NA Unable to calculate.

Table A-2. 1990 Oil Production from Stripper Wells by State (continued)

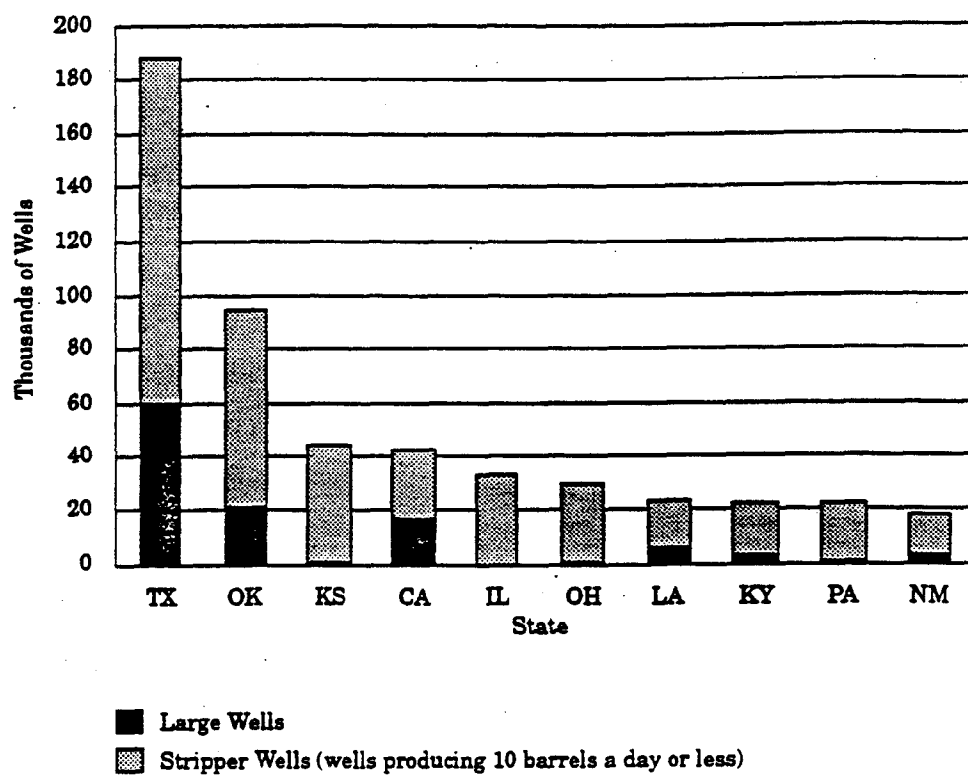
| Amount of Crude Oil Produced from Stripper Wells (thousands of barrels) ^c | Percentage of Crude Oil Produced from Stripper Wells |
|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| 1,486 | 8% |
| 0 | 0% |
| 26 | 21% |
| 5,693 | 55% |
| 36,405 | 10% |
| 5,698 | 19% |
| 0 | 0% |
| 18,520 | 93% |
| 3,002 | NA* |
| 40,873 | 74% |
| 4,338 | 80% |
| 7,154 | 2% |
| 4,599 | 23% |
| 802 | 3% |
| 120 | 82% |
| 2,449 | 12% |
| 2,011 | 34% |
| 0 | 0% |
| 14,296 | 21% |
| 383 | 92% |
| 2,053 | 6% |
| 7,271 | 73% |
| 78,599 | 70% |
| 2,622 | 99% |
| 64 | 4% |
| 419 | 83% |
| 135,850 | 19% |
| 1,035 | 4% |
| 12 | 80% |
| 2,122 | 99% |
| 5,297 | 5% |
| 389,197 | 14% |



^a Strippers are defined as those producing 10 barrels a day or less.

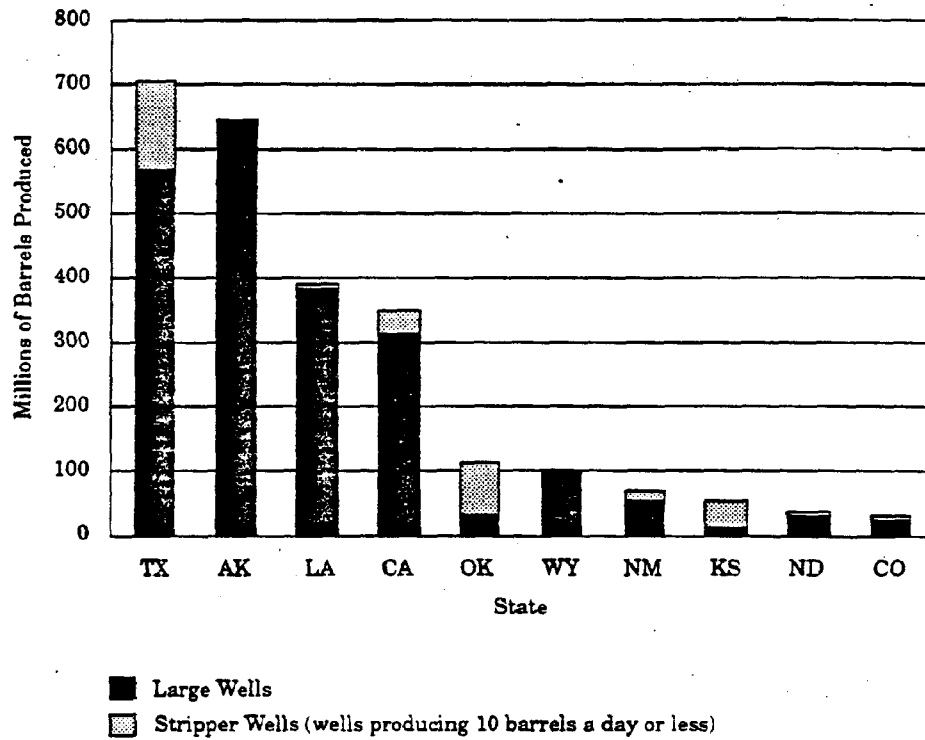
Source: Interstate Oil and Gas Compact Commission and National Stripper Well Association.

Figure A-9. 1990 U.S. oil production.



Source: World Oil (in Petroleum Independent, September 1992).

Figure A-10. States with the largest number of producing oil wells in 1990.



Source: World Oil (in Petroleum Independent, September 1992).

Figure A-11. Oil production in 1990 from the top producing states.

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APPENDIX B

SUBJECTS OF STATE H₂S REGULATIONS AND GUIDELINES

Table B-1. Subjects of State H₂S Regulations and Guidelines

| Regulations and Guidelines | Oklahoma | Texas | Michigan | California * |
|------------------------------------------------------------------------------------------------------------------------------------------------|----------|-------|----------|--------------|
| Characteristics and Effects of H ₂ S (including emergency rescue, resuscitators, effects on metal and artificial respiration) | NA | • | • | • |
| Initial Testing | • | NA | • | • |
| Periodic Gas Analyses | • | NA | NA | NA |
| Nuisance Odors | • | NA | NJ | NA |
| Guidelines for Safe Drilling Operations | | | | |
| A. Location Requirements | • | • | • | • |
| B. Drilling Equipment (Including blowout preventer, controls, piping and accessories, etc.) | • | • | • | • |
| C. Monitoring Equipment (including alarm systems and gas detection equipment) | • | • | • | • |
| D. Personal Protective Equipment (including all personnel, breathing apparatus, equipment specs., etc.) | • | • | • | • |
| E. Employee Physical Requirements | NA | • | NA | NA |
| F. Training Requirements | • | • | • | NA |
| G. Drills and Orientations | • | • | • | • |
| H. Maintenance of Equipment | • | • | • | • |
| I. Warning Systems | • | • | • | • |
| J. Evacuation | • | • | • | • |
| Guidelines for Safe Production Operations | | | | |
| A. Applicability | NA | • | • | NA |
| B. General Provisions | NA | • | • | NA |
| 1. Concentration Determination | • | • | • | NA |
| 2. Radius of Evacuation (ROE) | • | • | • | • |
| 3. Escape Rate Volume Determinators | • | • | • | NA |
| 4. Storage Tank Provisions | • | • | • | NA |
| 5. . . . ppm ROE in excess of . . . feet | • | • | • | • |
| 6. Implementation | • | • | • | NA |
| 7. Control and Safety Equipment | • | • | • | • |
| 8. Contingency Plan | • | • | • | • |
| 9. Training | • | • | • | NA |
| 10. Injection Provision | • | • | • | NA |
| 11. Certificate of Compliance Provision | • | • | • | NA |
| 12. Accident Notification | • | • | • | • |

NA Not available in reviewed literature.

- The subject was identified under the State's H₂S regulations or guidelines.

A Rule 36 references API RP19.

NJ Not under Congressional jurisdiction.

MMIOSH Required by Michigan OSHA.

*CA grants the supervisor of the Oil and Gas Division discretionary authority to control H₂S releases.

APPENDIX C

ATMOSPHERIC DISPERSION CALCULATIONS FOR H₂S RELEASES FROM OIL AND GAS EXTRACTION FACILITIES

APPENDIX C

ATMOSPHERIC DISPERSION CALCULATIONS FOR H₂S RELEASES FROM OIL AND GAS EXTRACTION FACILITIES

INTRODUCTION

The purpose of this appendix is to provide supporting details for the analyses of atmospheric dispersion of H₂S conducted for this report. In Chapter III, computer models were used, together with information on published studies of sour gas releases, to examine the range of predictions of the distances of concern for scenarios of H₂S releases from wellheads or pipelines. The inputs to the analyses are reviewed, and the outputs of three sample calculations for two of the scenarios are described. Outputs for a horizontal wellhead release are described for calculations using the SLAB and SAPLUME models. The output for a vertical wellhead release using the DEGADIS model is also described.

SUMMARY INPUT AND OUTPUT DATA

Summary data for the wellhead blowout and pipe rupture scenarios are presented in Tables C-1 and C-2, respectively. As described in Chapter III, analyses for wellhead blowouts were conducted using the SLAB, DEGADIS, and SAPLUME models. Analyses of the pipe rupture scenarios were conducted using the SACRUNCH and SAPLUME models.

The wellhead blowout scenarios in Chapter III result from various assumed flow rates as presented again in Table C-1. The following discussion presents some justification for the choice of these flow rates. Flow rates are functions of such factors as rock permeabilities, gas properties, depth, and tube and casing diameters. In practice, there are large variabilities in these parameters. One measure of the potential rate of flow from a well is the Calculated Absolute Open Flow Rate (CAOF), which is the rate of flow of gas into the well bore when the pressure is atmospheric. A sample of 15 wells in western Wyoming had CAOFs with a geometrical mean of 4.7×10^6 standard cubic feet per day (scf/d) or 1.3×10^5 cubic meters per day (m³/d) (Layton et al., 1983). The 95 percent confidence interval spanned the range from 2.1×10^5 scf/d (5.9×10^3 m³/d) to 10^8 scf/d (2.8×10^6 m³/d). Alp et al. (1990) considered CAOFs of between 5×10^4 and 5×10^6 m³/d as representative of wells in Alberta and chose 10^6 m³/d as representative for the purposes of risk analysis. The Quest report (1992) considered CAOFs in the range 2.2×10^5 to 7.3×10^6 m³/d for a system of wells in southwestern Wyoming. The actual flow rates out of a ruptured well will be less than the CAOF because of frictional effects in the pipework. By contrast, the Quest report and Layton et al. use the CAOF as a conservative estimate of flow rate. Based on the above discussions, a flow rate of 2×10^7 scf/d was chosen for representative calculations, with a flow rate of 10^8 scf/d being taken as an example of a very high flow rate.

TABLE C-1
SUMMARY OF INPUT AND OUTPUT DATA
WELLHEAD BLOWOUT SCENARIOS

| SCENARIO ^a | A | B | C | D | D(E)* |
|-------------------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| INPUTS | | | | | |
| Flow rate (m ³ /d) | 6x10 ⁵ | 6x10 ⁵ | 6x10 ⁵ | 6x10 ⁵ | 3x10 ⁶ |
| Vol. % H ₂ S | 7.5 | 27 | 15 | 30 | 30 |
| Density ^b @ 0°C (kg/m ³) | 0.862 | 1.293 | 1.038 | 1.128 | 1.128 |
| Release temperature (°C) | 0 | 0 | 0 | 0 | 0 |
| Total release rate (kg/s) | 5.99 | 8.98 | 7.21 | 7.83 | 39.2 |
| Release rate of H ₂ S (kg/s) | 0.79 | 2.85 | 1.58 | 3.17 | 15.8 |
| Ambient temperature (°C) | 5 | 5 | 5 | 5 | 5 |
| Relative humidity (%) | 75 | 75 | 75 | 75 | 75 |
| Atmospheric stability category | F | F | F | F | F |
| Windspeed (m/s) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Surface roughness length (m) | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Effective area of release (m ₂) | 0.02 | 0.02 | 0.02 | 0.02 | 0.1 |
| OUTPUTS: HORIZONTAL RELEASE | | | | | |
| SLAB: | | | | | |
| Distance to: | | | | | |
| LC ₀₁ (m) | 700 | 2,800 | 1,500 | 2,900 | 7,000 |
| ERPG-2(m) | 2,800 | 7,000 | 4,700 | 7,000 | > 10,000 |
| SAPLUME: | | | | | |
| Distance to: | | | | | |
| LC ₀₁ (m) | 1,000 | 2,700 | 1,500 | 3,000 | > 10,000 |
| ERPG-2(m) | 3,100 | 10,000 | 5,700 | 10,000 | > 10,000 |
| OUTPUTS: VERTICAL RELEASE | | | | | |
| SLAB: | | | | | |
| Distance to: | | | | | |
| LC ₀₁ (m) | 0 | 0 | 0 | 0 | 0 |
| ERPG-2(m) | 0 | 0 | 0 | 0 | 0 |
| DEGADIS: | | | | | |
| Distance to: | | | | | |
| LC ₀₁ (m) | 0 | 0 | 0 | 0 | 0 |
| ERPG-2(m) | 0 | 0 | 0 | 0 | 0 |
| SAPLUME: | | | | | |
| Distance to: | | | | | |
| LC ₀₁ (m) | 0 | 0 | 0 | 0 | 0 |
| ERPG-2(m) | 0 | 0 | 0 | 0 | 0 |

^a Scenarios from Table III-7.

^b For comparison, density of air @ 0°C = 1.293 kg/m³.

* E= Extreme Case.

TABLE C-2
PIPE RUPTURE SCENARIOS
INPUTS AND OUTPUTS (SADENZ MODEL)

| Parameters/Scenario | Composition A ^a , rupture of 4" diameter pipeline ^b | Composition D ^a , rupture of 16" diameter pipeline ^c |
|---------------------------------------|------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| <u>INPUTS</u> | | |
| Total mass released (kg) ^d | 640 | 31,000 |
| Total mass of H ₂ S (kg) | 84 | 12,500 |
| Duration of release (s) ^d | 16 | 310 |
| Density @ 0°C (kg/m ³) | 0.862 | 1.128 |
| Release temperature (°C) | 0 (32 °F) | 0 (32 °F) |
| Ambient temperature (°C) | 5 (41 °F) | 5 (41 °F) |
| Relative humidity (%) | 75 | 75 |
| Atmospheric stability category | F | F |
| Windspeed (m/s) | 1.5 | 1.5 |
| Surface roughness length(m) | 0.1 | 0.1 |
| <u>OUTPUTS</u> | | |
| Distance to: | | |
| LC ₅₀ (m) | 600 | 4,300 |
| ERPG-2 (m) | 750 | 5,600 |

^a Composition from Table III-5.

^b Spacing between emergency shutdown valves is 1,000 m.

^c Spacing between emergency shutdown valves is 3,000 m.

^d From Figure III-22.

Table C-1 also presents values for the effective area of release. These values are derived by dividing the volumetric release rate by the velocity of release and were not the bases for the release scenarios. As stated in Chapter III, the velocity of release was assumed to be "choked," or limited, to sonic velocity (approximately 330 m/s) as a result of the high initial gas pressure.

The temperature of the gas in a well prior to expansion to atmospheric pressure through a rupture depends on the depth of the gas reservoir. The amount of cooling that results from expansion to atmospheric pressure as a result of release depends on the initial pressure and the composition. Alp et al. (1990) assume a representative release temperature of 15°C (288 K) at atmospheric pressure. In the Quest report, the authors assume a reservoir temperature of 60°C and calculate expansion temperatures of between -9°C and 3°C. The calculated results of wellhead blowout and pipeline rupture scenarios in this study are based on a representative release temperature of 0°C. This temperature is below the assumed ambient temperature of 5°C.

Atmospheric conditions characterized by low turbulence and low wind speed provide for decreased dilution of a released chemical with the surrounding air. Thus, these conditions are directionally conservative in terms of potential exposure to accidental releases. Atmospheric thermal stability, impacted by the difference between surface and air temperatures, is often described by Pasquill atmospheric stability categories. These categories range from high turbulence (A) through low turbulence (F). The "F" category is typical of still, nighttime conditions (AIChE, 1989). This category was chosen for the calculations conducted to conservatively evaluate the wellhead blowout and pipeline rupture scenarios. Wind speeds of less than 2 m/s are considered low and create little turbulence. The calculations used in this study's analyses assume a wind speed of 1.5 m/s to conservatively simulate nonturbulent conditions. Actual conditions of A - D stability and higher wind speeds will cause more rapid dilution of an accidental release and will result in a decreased affected distance. The assumption that conditions of low wind speed and stable atmospheric conditions exist uniformly for extended distances also provides conservatism to the analyses.

Terrain is another factor that may influence atmospheric dispersion of a release. The surface roughness length is a measure of the "roughness" of the terrain. Roughness is a function of the type of terrain and the presence of such features as trees and buildings. The models in this study assume that the study of the behavior of dense gas flow around obstacles and through rough terrain is controversial and is an area where further research is needed. Rough terrain will cause more turbulence to atmospheric flows above it than smooth terrain. The value of surface roughness length, 0.1 m, used in the calculated dispersion predictions, is considered to be an intermediate roughness length and typical of highly vegetated rural terrain. It should be noted that lower, more conservative values would be more appropriate in flat, barren terrain.

SAMPLE SLAB CALCULATIONS

SLAB Input

The following illustrates how the input is prepared for SLAB, using composition D from Table III-5 as an example. The SLAB input is displayed on Table C-3. The SLAB users' manual provides further guidance (Ermak, 1989).

Line 1: IDSPL is the spill source type. For an evaporating pool, IDSPL = 1. For a horizontal jet release IDSPL = 2. For a vertical jet release IDSPL = 3. For a puff, IDSPL = 4. For the present example, the release is assumed to be horizontal, IDSPL = 2.

Line 2: NCALC is a numerical substep parameter. The code developer recommends using NCALC = 1. However, NCALC can be increased if numerical stability problems are encountered.

Line 3: WMS is the molecular weight of the wellhead gas in kg/gmole. From Table III-6, it is 0.0252 kg/gmol (from 25.2 g/gmol). Note, however, that the value given in Table C-3 is 0.0289 kg/gmol, for the following reason. Initially, the dilution of the plume is dominated by entrainment caused by its high momentum (its initial velocity equals that of sound). There is considerable dilution in this early phase and, by the time it is over, the density of the plume is only slightly less than that of the surrounding atmosphere. Work on marginally buoyant plumes shows that they are not likely to lift off the ground (Briggs, 1973). However, SLAB runs with WMS = 0.0252 kg/gmol show predicted plume rise that continues to a height of over 100 m. This is regarded as physically unrealistic and the computer model is "fooled" into ignoring plume rise by setting WMS equal to the effective molecular weight of air which is 28.9 g/gmol (0.0289 kg/gmol). As noted above, this is thought to be physically realistic. The results predicted in this way will be conservative if plume rise does in fact take place.

Line 4: CPS is the vapor heat capacity at constant pressure. Similar to the above molecular weight calculation, the gas mixture vapor heat capacity is calculated by summing the product of the constituents' mole percent and vapor heat capacity. For composition D it is approximately 1,500 J/kg/K.

Line 5: TBP is the boiling point of the released material. For a pure vapor release, SLAB does not in fact use this quantity, which has been arbitrarily set equal to the boiling point of methane, 111.5K.

Line 6: CMEDO is the liquid mass fraction in the initial release and is set to zero because the release is pure vapor.

Lines 7, 8: DHE = 509,880 (J/kg) and CPSL = 3,349 (J/kg/K) are the heat of vaporization and the liquid specific heat for methane. Their values are taken from Table 2 of the SLAB

Users' Guide. When the released material is pure vapor, as it is in the present case, and the temperature of the cloud does not drop below the boiling point, these values are adequate because the liquid properties will not be used in the SLAB calculation. However, a value for all SLAB input properties must be specified whether they are used or not.

Line 9: RHOSL is the liquid density of the released material. This is another quantity that is not used in the calculations. It has been set equal to the density of water (1,000 kg/m³).

Lines 10,11: SPB and SPC are parameters that go into the saturated vapor pressure formula:

$$P_s = P_a * \exp[(SPA - SPB / (T + SPC))],$$

where P_s is the saturated vapor pressure, P_a is the ambient pressure (1.01×10^5 N/m²), SPA is defined in the code and T is the local cloud temperature. Table 2 of the SLAB Users' Guide contains some values of SPB and SPC, but not for the mixture modeled here. When these values are unknown, the Users' Guide recommends default values of SPB = -1 and SPC = 0. The code then uses the Clapeyron equation to define the value of SPB. When the released material is pure vapor, as it is in the present case, and the temperature of the cloud does not drop below the boiling point, this default is adequate because the saturation pressure will not be used in the SLAB calculation. However, a value for all SLAB input properties must be specified whether they are used or not.

Lines 12-17: These lines specify the spill parameters. TS is the temperature of the released material, taken to be 273K. QS is the rate of release, estimated at 20 million scfd (7.69 kg/s). AS is the effective area of the release, 1.93×10^{-2} m², obtained by dividing the volumetric flow rate by the speed of sound (340 m/s). TSD is the duration of the release, 3,600 s, the assumed duration of release for a wellhead blowout. QTIS is zero except when modeling an instantaneous puff release. Finally, HS is the height of the release, arbitrarily taken to be 5 m (close to the ground).

Line 18: TAV is the concentration averaging time. This is set equal to 3,600 to be consistent with the exposure time of concern.

Line 19: XFFM is the maximum downwind extent of the calculation. A value of 10 km is used in order to obtain cloud concentration results at large distances away from the release. It is set to 2×10^4 m, which should be enough to ensure that any results of interest lie within this distance.

Lines 20-23: ZP(I) allows the user to specify up to four heights at which the concentration is calculated as a function of downwind distance. ZP(1) is set to 1.6 m (approximate head elevation above grade). The remaining ZP(I)s are zero, which means that SLAB only considers the first height.

Lines 24-29: These lines specify the meteorological conditions. ZO is the surface roughness length, which is set to 0.1 m, depicting a relatively smooth surface. ZA is the height at

which the windspeed is measured (10 m). UA is the windspeed at height ZA (1.5 m/s). TA is the ambient temperature (273K). RH is the relative humidity (75%, chosen as being typical of Category F weather conditions). Finally, STAB is the stability class (F=stable). The weather conditions (Category F with a low windspeed of 1.5 m/s) have been chosen to simulate unfavorable (close to worst case) conditions.

Line 30: TER is the end of file designator. TER < 0 terminates the run.

SLAB Output

A partial SLAB output corresponding to the inputs of Table C-3 is given in Table C-4. The interpretation is as follows. The first column gives the downwind distance, x. The second column gives the time at which the maximum concentration arrives at x and the third gives the duration of cloud passage. As can be seen, the duration of passage remains equal to the duration of release until the cloud has traveled several kilometers downwind. The fourth column gives the approximate half-width of the plume, bbc. The remaining six columns give the average concentration (volume fraction) at a height of 1.6 m (as chosen in the SLAB input) for six off-axis distances that are multiples of bbc, 0.5, 1.0, 1.5, etc. The predicted concentrations are zero close in because the plume was arbitrarily released at a height of 5 m. As the plume broadens, the concentrations at height 5 m rise above zero to a maximum at about 25 m to 30 m downwind and then begin to decline as the plume dilutes further.

The effective ERPG-2 is 100 ppm and the effective LC_{01} is about 4.7×10^5 ppb. These number values are derived as follows: the ERPG-2 for pure H_2S for an exposure time of 1 hour is 3×10^4 ppb. The volume concentration of H_2S in composition D is 30 percent (see Table III-5). Therefore, the overall concentration of the total released material when the H_2S in it is at 3×10^4 ppb is $30/0.3 = 1 \times 10^5$ ppb. Similarly, the LC_{01} for pure H_2S is 1.4×10^5 ppb for an exposure time of 1 hour (see Chapter III). Therefore, the effective LC_{01} for the plume is $140/0.3 = 4.7 \times 10^5$ ppb. As explained in Chapter III, the ERPG-2 is regarded as a threshold at which emergency response might be necessary and the LC_{01} is an approximate threshold for the occurrence of fatalities among the affected population. Reading down the column headed "y/bbc=0," the concentrations first fall below 4.7×10^5 ppb (= a volume fraction of 4.7×10^{-4}) at a distance of about 3 km and below 1×10^5 ppb (= a volume fraction of 1.0×10^{-4}) at a distance of about 7 km.

SAMPLE DEGADIS CALCULATIONS

DEGADIS Input

Table C-5 displays the DEGADIS input for the same case as was prepared for SLAB in Table C-3 except that DEGADIS can only simulate a vertical jet release. The chosen values for most of the parameters have already been explained in the section on SLAB.

Lines 1-4 allow the user to input up to four lines of title.

Line 5 requires the windspeed (1.5 m/s) and the height at which the windspeed is measured (10 m).

Line 6 gives the surface roughness length (0.1 m).

Line 7 requires the parameter INDVEL, the atmospheric stability category ($F=6$) and the Monin-Obukhov length RML. For INDVEL=1 (the present case) the model calculates RML from the stability category and the surface roughness length, so the user does not need to specify a value for RML.

Line 8 requires the ambient temperature (273K), the ambient pressure (1 atmosphere) and the relative humidity (75 %).

Line 9 gives the surface temperature, which is here set equal to the ambient temperature (273K).

Line 10 is a name for the released gas, in this case CPD for ComPosition D.

Line 11 is the molecular weight, 25.2.

Line 12 is the averaging time, taken to be equal to the duration of release, 3,600 s. It is used to calculate the increase in the effective width of the plume as a function of exposure time.

Line 13 is the temperature of the released gas, 273K.

Line 14 contains the upper level of concern (470 ppm, expressed as a volume fraction), the lower level of concern (100 ppm) and the height at which the concentrations are calculated (1.6 m).

Line 15 contains first a variable INDHT=0, meaning that heat transfer from the ground is not included, which does not matter here because the plume, air, and ground all have the same temperature. The second entry is the specific heat of the released gas at constant pressure (1,500 J/kg/K). The third entry, CPP=0, indicates that an approximation was made in which the specific heat does not vary with temperature.

Line 16 is a parameter "NDEN" that is used to specify the density profile of the released material. For NDEN=0, the release is assumed to be an ideal gas with specific heat at constant pressure 1500J/kg/K. Water condensation effects are taken into account.

Line 17 is the mass rate of release, 7.69 kg/s.

Table C-3. SLAB Input - Horizontal Wellhead Release

| Value | Parameter | Line No. |
|------------------------------|-----------|----------|
| 2 (horizontal), 3 (vertical) | IDSPL | 1 |
| 1 | NCALC | 2 |
| 0.0289 | WMS | 3 |
| 1500. | CPS | 4 |
| 111.50 | TBP | 5 |
| 0.0 | CMEDO | 6 |
| 509,880. | DHE | 7 |
| 3,349. | CPSL | 8 |
| 1,000. | RHOSL | 9 |
| -1.0 | SPB | 10 |
| 0.0 | SPC | 11 |
| 273. | TS | 12 |
| 7.69 | QS | 13 |
| 1.93×10^{-2} | AS | 14 |
| 3,600. | TSD | 15 |
| 0. | QTIS | 16 |
| 5. | HS | 17 |
| 3,600. | TAV | 18 |
| 20,000. | XFFM | 19 |
| 1.6 | ZP(1) | 20 |
| 0. | ZP(2) | 21 |
| 0. | ZP(3) | 22 |
| 0. | ZP(4) | 23 |
| 0.1 | ZO | 24 |
| 10. | ZA | 25 |
| 1.5 | UA | 26 |
| 273. | TA | 27 |
| 75. | RH | 28 |
| F | STAB | 29 |
| -1. | TER | 30 |

Table C-4. Partial SLAB Output

Time Averaged (TAV = 3,600 s) Volume Concentration: Concentration in the $z = 1.60$ Plane.

| Downwind Distance x (m) | Time of Max Conc (s) | Cloud Duration (s) | Effective Half Width bbc (m) | Average Concentration (Volume Fraction) at (x,y,z) , $y/bbc =$ | | | | | |
|------------------------------|-------------------------|-----------------------|---------------------------------|---------------------------------------------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| | | | | 0.0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| 1.00 | 1.80×10^3 | 3.60×10^3 | 6.95×10^{-2} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.02 | 1.80×10^3 | 3.60×10^3 | 7.73×10^{-2} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.05 | 1.80×10^3 | 3.60×10^3 | 8.71×10^{-2} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.08 | 1.80×10^3 | 3.60×10^3 | 9.92×10^{-2} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.13 | 1.80×10^3 | 3.60×10^3 | 1.14×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.18 | 1.80×10^3 | 3.60×10^3 | 1.32×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.24 | 1.80×10^3 | 3.60×10^3 | 1.54×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.32 | 1.80×10^3 | 3.60×10^3 | 1.81×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.41 | 1.80×10^3 | 3.60×10^3 | 2.14×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.52 | 1.80×10^3 | 3.60×10^3 | 2.54×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.66 | 1.80×10^3 | 3.60×10^3 | 3.03×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1.84 | 1.80×10^3 | 3.60×10^3 | 3.63×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2.05 | 1.80×10^3 | 3.60×10^3 | 4.36×10^{-1} | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2.31 | 1.80×10^3 | 3.60×10^3 | 5.24×10^{-1} | 8.35×10^{-41} | 5.76×10^{-41} | 1.88×10^{-41} | 2.84×10^{-42} | 1.93×10^{-43} | 5.61×10^{-45} |
| 2.63 | 1.80×10^3 | 3.60×10^3 | 6.31×10^{-1} | 1.18×10^{-28} | 8.13×10^{-29} | 2.65×10^{-29} | 4.02×10^{-30} | 2.79×10^{-31} | 8.76×10^{-33} |
| 3.01 | 1.80×10^3 | 3.60×10^3 | 7.61×10^{-1} | 3.14×10^{-20} | 2.16×10^{-20} | 7.03×10^{-21} | 1.07×10^{-21} | 7.54×10^{-23} | 2.42×10^{-24} |
| 3.49 | 1.80×10^3 | 3.60×10^3 | 9.17×10^{-1} | 1.99×10^{-14} | 1.37×10^{-14} | 4.45×10^{-15} | 6.79×10^{-16} | 4.82×10^{-17} | 1.58×10^{-18} |
| 4.08 | 1.80×10^3 | 3.60×10^3 | 1.10 | 1.86×10^{-10} | 1.28×10^{-10} | 4.16×10^{-11} | 6.36×10^{-12} | 4.55×10^{-13} | 1.51×10^{-14} |
| 4.79 | 1.80×10^3 | 3.60×10^3 | 1.33 | 9.38×10^{-8} | 6.45×10^{-8} | 2.10×10^{-8} | 3.21×10^{-9} | 2.30×10^{-10} | 7.71×10^{-12} |
| 5.67 | 1.80×10^3 | 3.60×10^3 | 1.60 | 6.31×10^{-6} | 4.34×10^{-6} | 1.41×10^{-6} | 2.16×10^{-7} | 1.55×10^{-8} | 5.23×10^{-10} |
| 6.75 | 1.80×10^3 | 3.60×10^3 | 1.91 | 1.07×10^{-4} | 7.33×10^{-5} | 2.38×10^{-5} | 3.65×10^{-6} | 2.63×10^{-7} | 8.89×10^{-9} |
| 8.07 | 1.80×10^3 | 3.60×10^3 | 2.28 | 6.99×10^{-4} | 4.81×10^{-4} | 1.56×10^{-4} | 2.39×10^{-5} | 1.73×10^{-6} | 5.87×10^{-8} |
| 9.68 | 1.80×10^3 | 3.60×10^3 | 2.72 | 2.41×10^{-3} | 1.66×10^{-3} | 5.37×10^{-4} | 8.24×10^{-5} | 5.95×10^{-6} | 2.03×10^{-7} |
| 1.17×10^1 | 1.80×10^3 | 3.60×10^3 | 3.22 | 5.35×10^{-3} | 3.68×10^{-3} | 1.19×10^{-3} | 1.83×10^{-4} | 1.32×10^{-5} | 4.51×10^{-7} |
| 1.41×10^1 | 1.81×10^3 | 3.60×10^3 | 3.79 | 8.87×10^{-3} | 6.09×10^{-3} | 1.98×10^{-3} | 3.03×10^{-4} | 2.19×10^{-5} | 7.48×10^{-7} |
| 1.71×10^1 | 1.81×10^3 | 3.60×10^3 | 4.43 | 1.22×10^{-2} | 8.38×10^{-3} | 2.72×10^{-3} | 4.17×10^{-4} | 3.02×10^{-5} | 1.03×10^{-6} |
| 2.07×10^1 | 1.81×10^3 | 3.60×10^3 | 5.11 | 1.49×10^{-2} | 1.03×10^{-2} | 3.33×10^{-3} | 5.11×10^{-4} | 3.70×10^{-5} | 1.27×10^{-6} |
| 2.52×10^1 | 1.81×10^3 | 3.60×10^3 | 5.79 | 1.69×10^{-2} | 1.16×10^{-2} | 3.78×10^{-3} | 5.80×10^{-4} | 4.20×10^{-5} | 1.43×10^{-6} |
| 3.07×10^1 | 1.81×10^3 | 3.60×10^3 | 6.55 | 1.82×10^{-2} | 1.25×10^{-2} | 4.05×10^{-3} | 6.22×10^{-4} | 4.50×10^{-5} | 1.54×10^{-6} |
| | | | | 1.84×10^{-2} | 1.27×10^{-2} | 4.11×10^{-3} | 6.31×10^{-4} | 4.57×10^{-5} | 1.57×10^{-6} |

(continued)

Table C-4 (cont)
Time Averaged (TAV = 3,600 s) Volume Concentration: Concentration in the z = 1.60 Plane.

| Downwind Distance x (m) | Time of Max Conc (s) | Cloud Duration (s) | Effective Half Width bbc (m) | Average Concentration (Volume Fraction) at (x,y,z), y/bbc = | | | | | |
|----------------------------|-------------------------|------------------------|---------------------------------|----------------------------------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| | | | | 0.0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| 3.74 x 10 ¹ | 1.82 x 10 ³ | 3.60 x 10 ³ | 7.42 | 1.80 x 10 ⁻² | 1.23 x 10 ⁻² | 4.01 x 10 ⁻³ | 6.15 x 10 ⁻⁴ | 4.45 x 10 ⁻⁵ | 1.52 x 10 ⁻⁶ |
| 4.56 x 10 ¹ | 1.82 x 10 ³ | 3.60 x 10 ³ | 8.39 | 1.70 x 10 ⁻² | 1.17 x 10 ⁻² | 3.78 x 10 ⁻³ | 5.80 x 10 ⁻⁴ | 4.20 x 10 ⁻⁵ | 1.43 x 10 ⁻⁶ |
| 5.57 x 10 ¹ | 1.83 x 10 ³ | 3.60 x 10 ³ | 9.47 | 1.56 x 10 ⁻² | 1.08 x 10 ⁻² | 3.49 x 10 ⁻³ | 5.35 x 10 ⁻⁴ | 3.88 x 10 ⁻⁵ | 1.33 x 10 ⁻⁶ |
| 6.81 x 10 ¹ | 1.83 x 10 ³ | 3.60 x 10 ³ | 1.07 x 10 ¹ | 1.42 x 10 ⁻² | 9.77 x 10 ⁻³ | 3.17 x 10 ⁻³ | 4.86 x 10 ⁻⁴ | 3.52 x 10 ⁻⁵ | 1.20 x 10 ⁻⁶ |
| 8.32 x 10 ¹ | 1.84 x 10 ³ | 3.60 x 10 ³ | 1.20 x 10 ¹ | 1.28 x 10 ⁻² | 8.77 x 10 ⁻³ | 2.85 x 10 ⁻³ | 4.37 x 10 ⁻⁴ | 3.16 x 10 ⁻⁵ | 1.08 x 10 ⁻⁶ |
| 1.02 x 10 ² | 1.85 x 10 ³ | 3.60 x 10 ³ | 1.34 x 10 ¹ | 1.14 x 10 ⁻² | 7.81 x 10 ⁻³ | 2.53 x 10 ⁻³ | 3.89 x 10 ⁻⁴ | 2.82 x 10 ⁻⁵ | 9.63 x 10 ⁻⁷ |
| 1.25 x 10 ² | 1.86 x 10 ³ | 3.60 x 10 ³ | 1.51 x 10 ¹ | 1.00 x 10 ⁻² | 6.90 x 10 ⁻³ | 2.24 x 10 ⁻³ | 3.43 x 10 ⁻⁴ | 2.49 x 10 ⁻⁵ | 8.50 x 10 ⁻⁷ |
| 1.52 x 10 ² | 1.87 x 10 ³ | 3.60 x 10 ³ | 1.70 x 10 ¹ | 8.80 x 10 ⁻³ | 6.05 x 10 ⁻³ | 1.96 x 10 ⁻³ | 3.01 x 10 ⁻⁴ | 2.18 x 10 ⁻⁵ | 7.44 x 10 ⁻⁷ |
| 1.87 x 10 ² | 1.89 x 10 ³ | 3.60 x 10 ³ | 1.92 x 10 ¹ | 7.68 x 10 ⁻³ | 5.28 x 10 ⁻³ | 1.71 x 10 ⁻³ | 2.63 x 10 ⁻⁴ | 1.90 x 10 ⁻⁵ | 6.51 x 10 ⁻⁷ |
| 2.29 x 10 ² | 1.90 x 10 ³ | 3.60 x 10 ³ | 2.18 x 10 ¹ | 6.65 x 10 ⁻³ | 4.57 x 10 ⁻³ | 1.48 x 10 ⁻³ | 2.27 x 10 ⁻⁴ | 1.65 x 10 ⁻⁵ | 5.61 x 10 ⁻⁷ |
| 2.80 x 10 ² | 1.93 x 10 ³ | 3.60 x 10 ³ | 2.49 x 10 ¹ | 5.71 x 10 ⁻³ | 3.92 x 10 ⁻³ | 1.27 x 10 ⁻³ | 1.95 x 10 ⁻⁴ | 1.41 x 10 ⁻⁵ | 4.84 x 10 ⁻⁷ |
| 3.43 x 10 ² | 1.96 x 10 ³ | 3.60 x 10 ³ | 2.87 x 10 ¹ | 4.85 x 10 ⁻³ | 3.33 x 10 ⁻³ | 1.08 x 10 ⁻³ | 1.66 x 10 ⁻⁴ | 1.20 x 10 ⁻⁵ | 4.10 x 10 ⁻⁷ |
| 4.20 x 10 ² | 1.99 x 10 ³ | 3.60 x 10 ³ | 3.33 x 10 ¹ | 4.07 x 10 ⁻³ | 2.80 x 10 ⁻³ | 9.09 x 10 ⁻⁴ | 1.39 x 10 ⁻⁴ | 1.01 x 10 ⁻⁵ | 3.44 x 10 ⁻⁷ |
| 5.15 x 10 ² | 2.04 x 10 ³ | 3.60 x 10 ³ | 3.91 x 10 ¹ | 3.38 x 10 ⁻³ | 2.32 x 10 ⁻³ | 7.55 x 10 ⁻⁴ | 1.16 x 10 ⁻⁴ | 8.38 x 10 ⁻⁶ | 2.89 x 10 ⁻⁷ |
| 6.30 x 10 ² | 2.09 x 10 ³ | 3.60 x 10 ³ | 4.65 x 10 ¹ | 2.77 x 10 ⁻³ | 1.91 x 10 ⁻³ | 6.19 x 10 ⁻⁴ | 9.49 x 10 ⁻⁵ | 6.87 x 10 ⁻⁶ | 2.36 x 10 ⁻⁷ |
| 7.73 x 10 ² | 2.15 x 10 ³ | 3.60 x 10 ³ | 5.58 x 10 ¹ | 2.25 x 10 ⁻³ | 1.54 x 10 ⁻³ | 5.01 x 10 ⁻⁴ | 7.68 x 10 ⁻⁵ | 5.57 x 10 ⁻⁶ | 1.90 x 10 ⁻⁷ |
| 9.47 x 10 ² | 2.23 x 10 ³ | 3.60 x 10 ³ | 6.75 x 10 ¹ | 1.80 x 10 ⁻³ | 1.24 x 10 ⁻³ | 4.02 x 10 ⁻⁴ | 6.16 x 10 ⁻⁵ | 4.46 x 10 ⁻⁶ | 1.49 x 10 ⁻⁷ |
| 1.16 x 10 ³ | 2.33 x 10 ³ | 3.60 x 10 ³ | 8.23 x 10 ¹ | 1.43 x 10 ⁻³ | 9.82 x 10 ⁻⁴ | 3.19 x 10 ⁻⁴ | 4.89 x 10 ⁻⁵ | 3.54 x 10 ⁻⁶ | 1.22 x 10 ⁻⁷ |
| 1.42 x 10 ³ | 2.45 x 10 ³ | 3.60 x 10 ³ | 1.01 x 10 ² | 1.12 x 10 ⁻³ | 7.73 x 10 ⁻⁴ | 2.51 x 10 ⁻⁴ | 3.85 x 10 ⁻⁵ | 2.79 x 10 ⁻⁶ | 9.64 x 10 ⁻⁸ |
| 1.74 x 10 ³ | 2.60 x 10 ³ | 3.60 x 10 ³ | 1.24 x 10 ² | 8.81 x 10 ⁻⁴ | 6.05 x 10 ⁻⁴ | 1.96 x 10 ⁻⁴ | 3.01 x 10 ⁻⁵ | 2.18 x 10 ⁻⁶ | 7.55 x 10 ⁻⁸ |
| 2.13 x 10 ³ | 2.78 x 10 ³ | 3.60 x 10 ³ | 1.52 x 10 ² | 6.86 x 10 ⁻⁴ | 4.71 x 10 ⁻⁴ | 1.53 x 10 ⁻⁴ | 2.35 x 10 ⁻⁵ | 1.70 x 10 ⁻⁶ | 5.91 x 10 ⁻⁸ |
| 2.62 x 10 ³ | 3.00 x 10 ³ | 3.60 x 10 ³ | 1.86 x 10 ² | 5.31 x 10 ⁻⁴ | 3.65 x 10 ⁻⁴ | 1.19 x 10 ⁻⁴ | 1.82 x 10 ⁻⁵ | 1.32 x 10 ⁻⁶ | 4.37 x 10 ⁻⁸ |
| 3.21 x 10 ³ | 3.27 x 10 ³ | 3.60 x 10 ³ | 2.28 x 10 ² | 4.08 x 10 ⁻⁴ | 2.81 x 10 ⁻⁴ | 9.11 x 10 ⁻⁵ | 1.40 x 10 ⁻⁵ | 1.01 x 10 ⁻⁶ | 3.52 x 10 ⁻⁸ |
| 3.93 x 10 ³ | 3.60 x 10 ³ | 3.60 x 10 ³ | 2.77 x 10 ² | 3.09 x 10 ⁻⁴ | 2.13 x 10 ⁻⁴ | 6.90 x 10 ⁻⁵ | 1.06 x 10 ⁻⁵ | 7.65 x 10 ⁻⁷ | 2.70 x 10 ⁻⁸ |
| 4.82 x 10 ³ | 4.10 x 10 ³ | 3.87 x 10 ³ | 3.40 x 10 ² | 2.05 x 10 ⁻⁴ | 1.41 x 10 ⁻⁴ | 4.58 x 10 ⁻⁵ | 7.02 x 10 ⁻⁶ | 5.10 x 10 ⁻⁷ | 1.76 x 10 ⁻⁸ |
| 5.94 x 10 ³ | 4.70 x 10 ³ | 4.19 x 10 ³ | 4.14 x 10 ² | 1.39 x 10 ⁻⁴ | 9.57 x 10 ⁻⁵ | 3.11 x 10 ⁻⁵ | 4.77 x 10 ⁻⁶ | 3.46 x 10 ⁻⁷ | 1.09 x 10 ⁻⁸ |
| 7.33 x 10 ³ | 5.45 x 10 ³ | 4.58 x 10 ³ | 5.02 x 10 ² | 9.06 x 10 ⁻⁵ | 6.22 x 10 ⁻⁵ | 2.02 x 10 ⁻⁵ | 3.70 x 10 ⁻⁶ | 2.24 x 10 ⁻⁷ | 8.61 x 10 ⁻⁹ |
| 9.07 x 10 ³ | 6.36 x 10 ³ | 5.03 x 10 ³ | 6.05 x 10 ² | 5.27 x 10 ⁻⁵ | 3.62 x 10 ⁻⁵ | 1.17 x 10 ⁻⁵ | 1.80 x 10 ⁻⁶ | 1.31 x 10 ⁻⁷ | 4.02 x 10 ⁻⁹ |
| 1.13 x 10 ⁴ | 7.47 x 10 ³ | 5.57 x 10 ³ | 7.23 x 10 ² | 2.55 x 10 ⁻⁵ | 1.75 x 10 ⁻⁵ | 5.70 x 10 ⁻⁶ | 8.73 x 10 ⁻⁷ | 6.35 x 10 ⁻⁸ | 2.33 x 10 ⁻⁹ |
| 1.40 x 10 ⁴ | 8.84 x 10 ³ | 6.11 x 10 ³ | 8.62 x 10 ² | 1.46 x 10 ⁻⁵ | 1.00 x 10 ⁻⁵ | 3.26 x 10 ⁻⁶ | 5.00 x 10 ⁻⁷ | 3.61 x 10 ⁻⁸ | 1.59 x 10 ⁻⁹ |
| 1.75 x 10 ⁴ | 1.05 x 10 ⁴ | 6.67 x 10 ³ | 1.02 x 10 ³ | 1.04 x 10 ⁻⁵ | 7.13 x 10 ⁻⁶ | 2.31 x 10 ⁻⁶ | 3.55 x 10 ⁻⁷ | 2.58 x 10 ⁻⁸ | 6.70 x 10 ⁻¹⁰ |
| 2.20 x 10 ⁴ | 1.26 x 10 ⁴ | 7.49 x 10 ³ | 1.21 x 10 ³ | 5.98 x 10 ⁻⁶ | 4.11 x 10 ⁻⁶ | 1.33 x 10 ⁻⁶ | 2.05 x 10 ⁻⁷ | 1.48 x 10 ⁻⁸ | 4.55 x 10 ⁻¹⁰ |

Table C-5. Input for DEGADIS Simulation of a Vertical Wellhead Release

| <u>Value</u> | | | <u>Line Number</u> |
|---------------------------------------------------------|----------------------|-----|--------------------|
| Release from a Well Head: Verticle Jet Simulation | } | | 1 |
| | | | 2 |
| | | | 3 |
| | | | 4 |
| 1.5 | 10. | | 5 |
| 0.1 | | | 6 |
| 1 | 6 | 0. | 7 |
| 273. | 1. | 75. | 8 |
| 273. | | | 9 |
| CPD | | | 10 |
| 25.2 | | | 11 |
| 3,600. | | | 12 |
| 273. | | | 13 |
| 4.7×10^{-4} | 1.0×10^{-4} | 1.6 | 14 |
| 0 | 1,500. | 0.0 | 15 |
| 0 | | | 16 |
| 7.69 | | | 17 |
| 5.0 | 0.0192 | | 18 |
| 3,600. | | | 19 |
| 50. | | | 20 |

Line 18 contains the height of release (5 m) and the effective diameter (0.0192 m)

Line 19 is the duration of release, 3,600 s.

Line 20 is the distance between points at which DEGADIS calculates the output.

DEGADIS Output

A partial DEGADIS output is given in Table C-6. The first column gives the distance downwind and the second gives the elevation. As can be seen, the plume rises substantially because of its initial momentum. The third column gives the concentration of the released gas as a mole fraction, the fourth column gives the concentration in kg/m^3 and the fifth column gives the density in kg/m^3 . As can be seen, the density rapidly approaches that of the surrounding air, $1.29 \text{ kg}/\text{m}^3$. The fifth column gives the temperature of the plume, which remains constant at 273K because the released plume and the air both have that temperature. The sixth column gives the plume horizontal standard deviation, σ_y , and the seventh column gives the vertical standard deviation, σ_z (the concentration across the plume is approximated by a Gaussian distribution in DEGADIS). As can be seen, at a height of 1.60 m, the predicted width of the plume (the distance across the wind to the upper or lower Levels of Concern, LC_{01} and ERPG-2) is zero so that LOCs are not predicted to be seen at ground level. This is a typical result for vertical jets of sour gas in stable weather conditions, whether DEGADIS, SLAB, or SAPLUME is used.

SAMPLE SAPLUME CALCULATIONS

SAPLUME Input

Table C-7 contains the input for the model SAPLUME corresponding to Table C-3, which contains the SLAB input for a horizontal release with composition D. The first few lines of input begin with four asterisks and are title cards, followed by a blank which tells the code that the titles have ended. Each subsequent line or group of lines begins with a keyword, followed by numbers in exponential notation to three significant figures.

"SITE" tells SAPLUME that there is a site with one radius and one sector (this is the default when the model is not considering a real site). The following line gives the one radius, arbitrarily set at 10,000 m, with one person arbitrarily set at that point (in the mode of operation chosen for the current problem, the model ignores these numbers).

"WEATHER" specifies that one weather condition only, category F, is being considered (because the 1.000 that follows WEATHER begins at space 61. For E the space would be 51, for D, 41 and so forth. The model can consider all six weather categories at once with up to four velocity subdivisions in each.) In this case, there is one velocity subdivision, specified as 1.5 m/s (first line after weather), and the probability that the wind blows into the one sector is unity (second line after weather):

Table C-6. Partial DEGADIS Output - Vertical Jet
Release from a Wellhead Pipeline Vertical Jet Simulation

| Downwind Distance (m) | Elevation (m) | Mole Fraction | Concentration (kg/m ³) | Density (kg/m ³) | Temperature (K) | σ_y (m) | σ_z (m) | Mole Fraction | Width to mol%; 1.00×10^{-3} 4.70 $\times 10^{-3}$ | | Maximum Mole Fraction | Elevation for Maximum Mole Fraction (m) |
|--------------------------|------------------|------------------------|---------------------------------------|---------------------------------|--------------------|------------------------|------------------------|---------------|---------------------------------------------------------------|-----|------------------------|--------------------------------------------|
| | | | | | | | | | (m) | (m) | | |
| | | | | | | | | | At z = 1.60 m | | | |
| 1.000×10^3 | 515 | 1.00 | 1.13 | 1.13 | 273 | 1.060×10^{-3} | 1.059×10^{-3} | .000 | 0 | 0 | 1.00 | 515 |
| 29.5 | 120. | 8.279×10^{-4} | 9.314×10^{-4} | 1.29 | 273 | 12.1 | 12.0 | .000 | 0 | 0 | 8.279×10^{-4} | 120. |
| 61.4 | 142. | 5.644×10^{-4} | 6.349×10^{-4} | 1.29 | 273 | 16.0 | 15.6 | .000 | 0 | 0 | 5.644×10^{-4} | 142. |
| 99.6 | 157. | 4.254×10^{-4} | 4.786×10^{-4} | 1.29 | 273 | 19.2 | 18.4 | .000 | 0 | 0 | 4.254×10^{-4} | 157. |
| 142. | 169. | 3.425×10^{-4} | 3.853×10^{-4} | 1.29 | 273 | 22.0 | 20.6 | .000 | 0 | 0 | 3.425×10^{-4} | 169. |
| 191. | 180. | 2.832×10^{-4} | 3.186×10^{-4} | 1.29 | 273 | 24.6 | 22.4 | .000 | 0 | 0 | 2.832×10^{-4} | 180. |
| 240. | 188. | 2.432×10^{-4} | 2.736×10^{-4} | 1.29 | 273 | 27.0 | 23.9 | .000 | 0 | 0 | 2.432×10^{-4} | 188. |
| 289. | 196. | 2.140×10^{-4} | 2.408×10^{-4} | 1.29 | 273 | 29.2 | 25.2 | .000 | 0 | 0 | 2.140×10^{-4} | 196. |
| 339. | 202. | 1.915×10^{-4} | 2.155×10^{-4} | 1.29 | 273 | 31.4 | 26.3 | .000 | 0 | 0 | 1.915×10^{-4} | 202. |
| 389. | 207. | 1.736×10^{-4} | 1.953×10^{-4} | 1.29 | 273 | 33.4 | 27.2 | .000 | 0 | 0 | 1.736×10^{-4} | 207. |
| 438. | 212. | 1.588×10^{-4} | 1.786×10^{-4} | 1.29 | 273 | 35.5 | 28.1 | .000 | 0 | 0 | 1.588×10^{-4} | 212. |
| 488. | 217. | 1.464×10^{-4} | 1.647×10^{-4} | 1.29 | 273 | 37.5 | 28.8 | .000 | 0 | 0 | 1.464×10^{-4} | 217. |
| 538. | 221. | 1.358×10^{-4} | 1.528×10^{-4} | 1.29 | 273 | 39.4 | 29.5 | .000 | 0 | 0 | 1.358×10^{-4} | 221. |
| 588. | 225. | 1.267×10^{-4} | 1.425×10^{-4} | 1.29 | 273 | 41.4 | 30.1 | .000 | 0 | 0 | 1.267×10^{-4} | 225. |
| 638. | 228. | 1.187×10^{-4} | 1.335×10^{-4} | 1.29 | 273 | 43.4 | 30.7 | .000 | 0 | 0 | 1.187×10^{-4} | 228. |
| 688. | 231. | 1.116×10^{-4} | 1.255×10^{-4} | 1.29 | 273 | 45.3 | 31.2 | .000 | 0 | 0 | 1.116×10^{-4} | 231. |
| 738. | 234. | 1.053×10^{-4} | 1.185×10^{-4} | 1.29 | 273 | 47.2 | 31.7 | .000 | 0 | 0 | 1.053×10^{-4} | 234. |
| 787. | 237. | 9.965×10^{-5} | 1.121×10^{-4} | 1.29 | 273 | 49.2 | 32.2 | .000 | 0 | 0 | 9.965×10^{-5} | 237. |
| 837. | 240. | 9.457×10^{-5} | 1.064×10^{-4} | 1.29 | 273 | 51.1 | 32.6 | .000 | 0 | 0 | 9.457×10^{-5} | 240. |
| 887. | 242. | 8.995×10^{-5} | 1.012×10^{-4} | 1.29 | 273 | 53.1 | 33.0 | .000 | 0 | 0 | 8.995×10^{-5} | 242. |
| 937. | 245. | 8.575×10^{-5} | 9.647×10^{-5} | 1.29 | 273 | 55.0 | 33.4 | .000 | 0 | 0 | 8.575×10^{-5} | 245. |
| 987. | 247. | 8.190×10^{-5} | 9.213×10^{-5} | 1.29 | 273 | 56.9 | 33.8 | .000 | 0 | 0 | 8.190×10^{-5} | 247. |
| 1.037×10^3 | 249. | 7.836×10^{-5} | 8.816×10^{-5} | 1.29 | 273 | 58.9 | 34.2 | .000 | 0 | 0 | 7.836×10^{-5} | 249. |
| 1.087×10^3 | 251. | 7.510×10^{-5} | 8.449×10^{-5} | 1.29 | 273 | 60.8 | 34.5 | .000 | 0 | 0 | 7.510×10^{-5} | 251. |
| 1.137×10^3 | 253. | 7.208×10^{-5} | 8.109×10^{-5} | 1.29 | 273 | 62.7 | 34.9 | .000 | 0 | 0 | 7.208×10^{-5} | 253. |
| 1.187×10^3 | 255. | 6.928×10^{-5} | 7.794×10^{-5} | 1.29 | 273 | 64.7 | 35.2 | .000 | 0 | 0 | 6.928×10^{-5} | 255. |
| 1.237×10^3 | 257. | 6.667×10^{-5} | 7.501×10^{-5} | 1.29 | 273 | 66.6 | 35.5 | .000 | 0 | 0 | 6.667×10^{-5} | 257. |
| 1.287×10^3 | 258. | 6.424×10^{-5} | 7.228×10^{-5} | 1.29 | 273 | 68.5 | 35.8 | .000 | 0 | 0 | 6.424×10^{-5} | 258. |
| 1.337×10^3 | 260. | 6.197×10^{-5} | 6.972×10^{-5} | 1.29 | 273 | 70.5 | 36.1 | .000 | 0 | 0 | 6.197×10^{-5} | 260. |
| 1.387×10^3 | 262. | 5.984×10^{-5} | 6.733×10^{-5} | 1.29 | 273 | 72.4 | 36.3 | .000 | 0 | 0 | 5.984×10^{-5} | 262. |

Table C-6 (cont)

| Downwind Distance (m) | Elevation (m) | Mole Fraction | Concentration (kg/m ³) | Density (kg/m ³) | Temperature (K) | σ_T (m) | σ_z (m) | At $z = 1.60$ m | | | Maximum Mole Fraction | Elevation for Maximum Mole Fraction (m) |
|-------------------------|---------------|--------------------------|------------------------------------|------------------------------|-----------------|----------------|----------------|-----------------|--------------------------------------------|--------------------------------------------|--------------------------|-----------------------------------------|
| | | | | | | | | Mole Fraction | Width to mol%, 1.00 x 10 ⁻³ (m) | Width to mol%, 4.76 x 10 ⁻³ (m) | | |
| 1.437 x 10 ³ | 263. | 5.785 x 10 ⁻³ | 6.508 x 10 ⁻³ | 1.29 | 273 | 74.3 | 36.6 | .000 | 0 | 0 | 5.785 x 10 ⁻³ | 263. |
| 1.487 x 10 ³ | 265. | 5.597 x 10 ⁻³ | 6.296 x 10 ⁻³ | 1.29 | 273 | 76.3 | 36.9 | .000 | 0 | 0 | 5.597 x 10 ⁻³ | 265. |
| 1.537 x 10 ³ | 266. | 5.420 x 10 ⁻³ | 6.097 x 10 ⁻³ | 1.29 | 273 | 78.2 | 37.1 | .000 | 0 | 0 | 5.420 x 10 ⁻³ | 266. |
| 1.587 x 10 ³ | 267. | 5.253 x 10 ⁻³ | 5.909 x 10 ⁻³ | 1.29 | 273 | 80.2 | 37.4 | .000 | 0 | 0 | 5.253 x 10 ⁻³ | 267. |
| 1.637 x 10 ³ | 269. | 5.095 x 10 ⁻³ | 5.732 x 10 ⁻³ | 1.29 | 273 | 82.1 | 37.6 | .000 | 0 | 0 | 5.095 x 10 ⁻³ | 269. |
| 1.687 x 10 ³ | 270. | 4.945 x 10 ⁻³ | 5.564 x 10 ⁻³ | 1.29 | 273 | 84.0 | 37.9 | .000 | 0 | 0 | 4.945 x 10 ⁻³ | 270. |
| 1.737 x 10 ³ | 271. | 4.804 x 10 ⁻³ | 5.404 x 10 ⁻³ | 1.29 | 273 | 85.9 | 38.1 | .000 | 0 | 0 | 4.804 x 10 ⁻³ | 271. |
| 1.787 x 10 ³ | 273. | 4.669 x 10 ⁻³ | 5.253 x 10 ⁻³ | 1.29 | 273 | 87.9 | 38.3 | .000 | 0 | 0 | 4.669 x 10 ⁻³ | 273. |
| 1.837 x 10 ³ | 274. | 4.542 x 10 ⁻³ | 5.109 x 10 ⁻³ | 1.29 | 273 | 89.8 | 38.6 | .000 | 0 | 0 | 4.542 x 10 ⁻³ | 274. |
| 1.887 x 10 ³ | 275. | 4.420 x 10 ⁻³ | 4.973 x 10 ⁻³ | 1.29 | 273 | 91.7 | 38.8 | .000 | 0 | 0 | 4.420 x 10 ⁻³ | 275. |
| 1.937 x 10 ³ | 276. | 4.304 x 10 ⁻³ | 4.842 x 10 ⁻³ | 1.29 | 273 | 93.7 | 39.0 | .000 | 0 | 0 | 4.304 x 10 ⁻³ | 276. |
| 1.987 x 10 ³ | 277. | 4.194 x 10 ⁻³ | 4.718 x 10 ⁻³ | 1.29 | 273 | 95.6 | 39.2 | .000 | 0 | 0 | 4.194 x 10 ⁻³ | 277. |
| 2.037 x 10 ³ | 278. | 4.089 x 10 ⁻³ | 4.600 x 10 ⁻³ | 1.29 | 273 | 97.5 | 39.5 | .000 | 0 | 0 | 4.089 x 10 ⁻³ | 278. |
| 2.087 x 10 ³ | 279. | 3.988 x 10 ⁻³ | 4.487 x 10 ⁻³ | 1.29 | 273 | 99.4 | 39.7 | .000 | 0 | 0 | 3.988 x 10 ⁻³ | 279. |
| 2.137 x 10 ³ | 280. | 3.892 x 10 ⁻³ | 4.378 x 10 ⁻³ | 1.29 | 273 | 101. | 39.9 | .000 | 0 | 0 | 3.892 x 10 ⁻³ | 280. |
| 2.187 x 10 ³ | 281. | 3.800 x 10 ⁻³ | 4.275 x 10 ⁻³ | 1.29 | 273 | 103. | 40.1 | .000 | 0 | 0 | 3.800 x 10 ⁻³ | 281. |
| 2.237 x 10 ³ | 282. | 3.711 x 10 ⁻³ | 4.175 x 10 ⁻³ | 1.29 | 273 | 105. | 40.3 | .000 | 0 | 0 | 3.711 x 10 ⁻³ | 282. |
| 2.287 x 10 ³ | 283. | 3.627 x 10 ⁻³ | 4.080 x 10 ⁻³ | 1.29 | 273 | 107. | 40.5 | .000 | 0 | 0 | 3.627 x 10 ⁻³ | 283. |
| 2.337 x 10 ³ | 284. | 3.546 x 10 ⁻³ | 3.989 x 10 ⁻³ | 1.29 | 273 | 109. | 40.7 | .000 | 0 | 0 | 3.546 x 10 ⁻³ | 284. |
| 2.387 x 10 ³ | 285. | 3.468 x 10 ⁻³ | 3.901 x 10 ⁻³ | 1.29 | 273 | 111. | 40.9 | .000 | 0 | 0 | 3.468 x 10 ⁻³ | 285. |
| 2.437 x 10 ³ | 286. | 3.393 x 10 ⁻³ | 3.817 x 10 ⁻³ | 1.29 | 273 | 113. | 41.1 | .000 | 0 | 0 | 3.393 x 10 ⁻³ | 286. |
| 2.487 x 10 ³ | 286. | 3.321 x 10 ⁻³ | 3.736 x 10 ⁻³ | 1.29 | 273 | 115. | 41.2 | .000 | 0 | 0 | 3.321 x 10 ⁻³ | 286. |
| 2.537 x 10 ³ | 287. | 3.252 x 10 ⁻³ | 3.658 x 10 ⁻³ | 1.29 | 273 | 117. | 41.4 | .000 | 0 | 0 | 3.252 x 10 ⁻³ | 287. |
| 2.587 x 10 ³ | 288. | 3.185 x 10 ⁻³ | 3.583 x 10 ⁻³ | 1.29 | 273 | 119. | 41.6 | .000 | 0 | 0 | 3.185 x 10 ⁻³ | 288. |
| 2.637 x 10 ³ | 289. | 3.121 x 10 ⁻³ | 3.511 x 10 ⁻³ | 1.29 | 273 | 120. | 41.8 | .000 | 0 | 0 | 3.121 x 10 ⁻³ | 289. |
| 2.687 x 10 ³ | 290. | 3.059 x 10 ⁻³ | 3.441 x 10 ⁻³ | 1.29 | 273 | 122. | 42.0 | .000 | 0 | 0 | 3.059 x 10 ⁻³ | 290. |
| 2.737 x 10 ³ | 290. | 2.999 x 10 ⁻³ | 3.374 x 10 ⁻³ | 1.29 | 273 | 124. | 42.2 | .000 | 0 | 0 | 2.999 x 10 ⁻³ | 290. |
| 2.787 x 10 ³ | 291. | 2.941 x 10 ⁻³ | 3.309 x 10 ⁻³ | 1.29 | 273 | 126. | 42.3 | .000 | 0 | 0 | 2.941 x 10 ⁻³ | 291. |
| 2.837 x 10 ³ | 292. | 2.885 x 10 ⁻³ | 3.246 x 10 ⁻³ | 1.29 | 273 | 128. | 42.5 | .000 | 0 | 0 | 2.885 x 10 ⁻³ | 292. |
| 2.887 x 10 ³ | 293. | 2.831 x 10 ⁻³ | 3.185 x 10 ⁻³ | 1.29 | 273 | 130. | 42.7 | .000 | 0 | 0 | 2.831 x 10 ⁻³ | 293. |
| 2.937 x 10 ³ | 293. | 2.779 x 10 ⁻³ | 3.127 x 10 ⁻³ | 1.29 | 273 | 132. | 42.9 | .000 | 0 | 0 | 2.779 x 10 ⁻³ | 293. |
| 2.987 x 10 ³ | 294. | 2.729 x 10 ⁻³ | 3.070 x 10 ⁻³ | 1.29 | 273 | 134. | 43.0 | .000 | 0 | 0 | 2.729 x 10 ⁻³ | 294. |
| 3.037 x 10 ³ | 295. | 2.680 x 10 ⁻³ | 3.015 x 10 ⁻³ | 1.29 | 273 | 136. | 43.2 | .000 | 0 | 0 | 2.680 x 10 ⁻³ | 295. |

Table C-6 (cont)

| Downwind Distance (m) | Elevation (m) | Mole Fraction | Concentration (kg/m ³) | Temperature (K) | σ_y (m) | σ_z (m) | At $x = 1.60$ m | | | Elevation for Maximum Mole Fraction (m) |
|-----------------------------|------------------|------------------------|---------------------------------------|--------------------|-------------------|-------------------|------------------|-----------------------------------------------|-----------------------------|--------------------------------------------------|
| | | | | | | | Mole Fraction | Width to mol% 1.00×10^{-3} (m) | Maximum Mole Fraction | |
| 3.087×10^3 | 295. | 2.633×10^{-3} | 2.962×10^{-3} | 273 | 138. | 43.4 | .000 | 0 | 2.633×10^{-3} | 295. |
| 3.137×10^3 | 296. | 2.583×10^{-3} | 2.911×10^{-3} | 273 | 139. | 43.5 | .000 | 0 | 2.583×10^{-3} | 296. |
| 3.187×10^3 | 297. | 2.543×10^{-3} | 2.861×10^{-3} | 273 | 141. | 43.7 | .000 | 0 | 2.543×10^{-3} | 297. |
| 3.237×10^3 | 297. | 2.500×10^{-3} | 2.813×10^{-3} | 273 | 143. | 43.9 | .000 | 0 | 2.500×10^{-3} | 297. |
| 3.263×10^3 | 297. | 2.479×10^{-3} | 2.789×10^{-3} | 273 | 144. | 43.9 | .000 | 0 | 2.479×10^{-3} | 297. |

The entries on the "PROPERTIES" line are as follows: the ambient temperature is 273K at which temperature the density of air is 1.29 kg/m^3 and its specific heat at constant pressure is 990 J/kg/K . At a temperature of 273K, the density of the released gas is 1.141 kg/m^3 and the specific heat at constant pressure is $1,500 \text{ J/kg/K}$.

The entries on the "SOURCE" line are as follows: the rate of release is 7.69 kg/m^3 at a temperature of 273K. The amount of air initially entrained with the source is zero. The angle of release is zero radians (horizontal). The height of release is 5 m. The initial momentum flux is $2,540 \text{ kg m s}^{-2}$ and is the product of the rate of release and the exit velocity (the speed of sound is approximately 330 m/s).

The "INTERVAL" line specifies that SAPLUME calculations start at a downwind distance x of 0.1 m and that calculations are performed at a uniform spacing of 0.15 in $\log_{10}(x)$.

On the "ROUG" line, the surface roughness length is 0.1 m and the windspeed is measured at a height of 10 m.

The "HAZARD" line specifies two levels of concern. As explained above in the discussion of the SLAB results, these are the LC_{01} of 470 ppm (approximately $5.32 \times 10^{-4} \text{ kg/m}^3$) and the ERPG-2 of 100 ppm ($1.141 \times 10^{-4} \text{ kg/m}^3$).

"VGRAD" informs SAPLUME that it should consider the velocity gradient and the temperature gradient in the atmosphere. SAPLUME uses standard textbook formulae for these gradients. If the first entry after VGRAD were zero, velocity would be constant as a function of height. Similarly, if the second entry after VGRAD were zero, the temperature of the atmosphere would remain constant as height increases.

A value of 3 after "NEUT" specifies one of three parametrizations for the standard deviations in the Gaussian model once the released material has evolved out of the jet phase. NEUT = 3 corresponds to a parameterization that is appropriate for a rural site. "DUR" specifies that the duration of release is one hour.

Finally, the repetition of "END" terminates the run of SAPLUME.

SAPLUME Output

A partial SAPLUME output corresponding to the input in Table C-7 is given in Table C-8. This table indicates that, for hazard level 1 (i.e., the LC_{01} of 470 ppm discussed above) the plume touches down at a downwind distance of approximately 63 m and extends to about 3 km, covering an area of about 10^5 m^2 (one tenth of a square kilometer). The table of pairs of values of downwind distance, x , and width can be coupled to a plotting routine to give contours of constant concentration. Similarly, hazard level 2 (the ERPG-2 of 100 ppm)

Table C-7. Input for SAPLUME Runs

| | | | | | | |
|------------------------|-----------------------------------------------------------------|-------------------------|-----------------------|-----------------------|-------|-----------------------|
| **** | EPA Hydrogen Sulfide Runs | | | | | |
| **** | January 1993 | | | | | |
| **** | No Protective Measures | | | | | |
| **** | Composition D - 30% H ₂ S at Wellhead | | | | | |
| **** | 2x10 ⁷ SCFD: | | | | | |
| **** | Horizontal Release | | | | | |
| **** | H ₂ S Release Rate - 3.073 kg/s | | | | | |
| **** | Total Mixture Release Rate - 7.69 kg/s | | | | | |
| **** | Hazard Level - ERPG-2 (100 ppm) and | | | | | |
| **** | LC ₀₁ (470 ppm) Both Adjusted for Stream Composition | | | | | |
| **** | Category F Weather, Windspeed 1.5 m/s | | | | | |
| SITE | 1.000 | 1.000 | | | | |
| 1.000x10 ⁴ | | | | | | |
| 1.000 | | | | | | |
| WEATHER | 1.000 | | | | | |
| 1.500 | | | | | | |
| 2.500x10 ⁻¹ | | | | | | |
| PROP | 2.730x10 ² | 1.290 | 9.900x10 ² | 2.730x10 ² | 1.141 | 1.500x10 ³ |
| SOURCE | 7.690 | 2.730x10 ² | 0.000 | 0.000 | 5.000 | 2.540x10 ³ |
| INTERVAL | 1.000x10 ⁻¹ | 1.5000x10 ⁻¹ | | | | |
| ROUG | 1.0000x10 ⁻¹ | 1.000x10 ¹ | | | | |
| HAZARD | 2.000 | | | | | |
| 5.320x10 ⁻⁴ | 1.141x10 ⁻⁴ | | | | | |
| VGRAD | 1.000 | 1.000 | | | | |
| NEUT | 3.000 | | | | | |
| DUR | 1.000 | | | | | |
| END | | | | | | |
| END | | | | | | |

Table C-8. Partial SAPLUME Output for Horizontal Plume

| FOR HAZARD LEVEL 1, WINDSPEED 1500 m/s AND CATEGORY 6 | | | | | | | | | | | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|
| THE HAZARDOUS CLOUD EXTENDS FROM 6.327x10 ⁴ TO 3.125x10 ⁵ METERS DOWNWIND AND HAS AN AREA OF 1.129x10 ⁵ m ² | | | | | | | | | | | |
| CLOUD BOUNDARIES | | | | | | | | | | | |
| X* (m) | WIDTH (m) | X (m) | WIDTH (m) | X (m) | WIDTH (m) | X (m) | WIDTH (m) | X (m) | WIDTH (m) | X (m) | WIDTH (m) |
| 0.000 | 0.000 | 1.000x10 ⁻¹ | 0.000 | 1.162x10 ⁻¹ | 0.000 | 1.350x10 ⁻¹ | 0.000 | 1.568x10 ⁻¹ | 0.000 | 1.568x10 ⁻¹ | 0.000 |
| 1.822x10 ⁻¹ | 0.000 | 2.117x10 ⁻¹ | 0.000 | 2.460x10 ⁻¹ | 0.000 | 2.858x10 ⁻¹ | 0.000 | 3.320x10 ⁻¹ | 0.000 | 3.320x10 ⁻¹ | 0.000 |
| 3.837x10 ⁻¹ | 0.000 | 4.482x10 ⁻¹ | 0.000 | 5.207x10 ⁻¹ | 0.000 | 6.050x10 ⁻¹ | 0.000 | 7.029x10 ⁻¹ | 0.000 | 7.029x10 ⁻¹ | 0.000 |
| 8.166x10 ⁻¹ | 0.000 | 9.488x10 ⁻¹ | 0.000 | 1.102 | 0.000 | 1.281 | 0.000 | 1.488 | 0.000 | 1.488 | 0.000 |
| 1.729 | 0.000 | 2.009 | 0.000 | 2.334 | 0.000 | 2.711 | 0.000 | 3.150 | 0.000 | 3.150 | 0.000 |
| 3.660 | 0.000 | 4.252 | 0.000 | 4.940 | 0.000 | 5.740 | 0.000 | 6.669 | 0.000 | 6.669 | 0.000 |
| 7.748 | 0.000 | 9.002 | 0.000 | 1.046x10 ¹ | 0.000 | 1.215x10 ¹ | 0.000 | 1.412x10 ¹ | 0.000 | 1.412x10 ¹ | 0.000 |
| 1.640x10 ¹ | 0.000 | 1.906x10 ¹ | 0.000 | 2.214x10 ¹ | 0.000 | 2.572x10 ¹ | 0.000 | 2.989x10 ¹ | 0.000 | 2.989x10 ¹ | 0.000 |
| 3.472x10 ¹ | 0.000 | 4.034x10 ¹ | 0.000 | 4.687x10 ¹ | 0.000 | 5.446x10 ¹ | 0.000 | 6.327x10 ¹ | 5.555 | 6.327x10 ¹ | 5.555 |
| 7.351x10 ¹ | 2.627 | 8.540x10 ¹ | 2.739 | 9.922x10 ¹ | 2.955 | 1.153x10 ² | 3.294 | 1.339x10 ² | 3.768 | 1.339x10 ² | 3.768 |
| 1.556x10 ² | 4.385 | 1.808x10 ² | 5.149 | 2.101x10 ² | 6.066 | 2.441x10 ² | 7.143 | 2.835x10 ² | 8.388 | 2.835x10 ² | 8.388 |
| 3.294x10 ² | 9.811 | 3.827x10 ² | 1.142x10 ¹ | 4.447x10 ² | 1.324x10 ¹ | 5.167x10 ² | 1.527x10 ¹ | 6.003x10 ² | 1.701x10 ¹ | 6.003x10 ² | 1.701x10 ¹ |
| 6.974x10 ² | 1.856x10 ¹ | 8.103x10 ² | 2.005x10 ¹ | 9.414x10 ² | 2.140x10 ¹ | 1.094x10 ³ | 2.257x10 ¹ | 1.271x10 ³ | 2.345x10 ¹ | 1.271x10 ³ | 2.345x10 ¹ |
| 1.476x10 ³ | 2.393x10 ¹ | 1.715x10 ³ | 2.384x10 ¹ | 1.993x10 ³ | 2.295x10 ¹ | 2.315x10 ³ | 2.082x10 ¹ | 2.690x10 ³ | 1.653x10 ¹ | 2.690x10 ³ | 1.653x10 ¹ |
| 3.126x10 ³ | 5.139 | | | | | | | | | | |

*x = Downwind distance.

extends from about 60 m to about 12 km downwind, covering an area of approximately 10^6 m^2 .

The above results are close to those predicted by SLAB. The higher result is about 50% larger than that predicted by SLAB. However, the difference is within the range of uncertainties expected for these dispersion models. As noted above, the neglect of dry deposition means that the predictions are likely to be conservative.

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