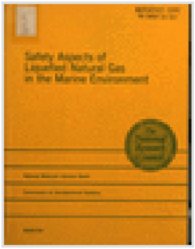

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SAFETY ASPECTS OF LIQUEFIED NATURAL GAS IN THE MARINE ENVIRONMENT

Report of the

PANEL ON

LIQUEFIED NATURAL GAS SAFETY EVALUATION

Committee on Maritime Hazardous Materials

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

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NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard to appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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PREFACE

Water transportation of hazardous cargoes has been increasing dramatically--at sea, in congested port areas, and on inland waterways. The marine industry and the federal government have expended considerable effort on research and development in cargo properties, ship and facility design, and operating practices to assure that transportation, delivery, and storage are accomplished safely and without unreasonable risks to the environment and the public.

The U.S. Coast Guard recognized at an early date (1961) the hazards to the public that could result from accidents involving maritime transportation of hazardous materials, including liquefied natural gas (LNG), liquefied petroleum gas (LPG), and other flammable gases. To fulfill its responsibility for the safety and security of U.S. ports and waterways, the Coast Guard initiated and carried out a research program on the properties, behavior, and hazards of the materials to determine the requirements for effective containment systems, ships, and facilities and developed regulations for the design, construction, and operation of ships carrying these hazardous materials. Recognizing the international character of this developing trade, the Coast Guard initiated (in 1967) international consideration of such regulations for foreign-flag as well as U.S. ships. As a result, the Inter-Governmental Maritime Consultative Organization (IMCO) developed two codes: Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, 1971; and Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk, adopted in November 1975.

Relevant legislative action in the United States during this period includes the Ports and Waterways Safety Act of 1972, the Federal Water Pollution Control Act of 1972, the Hazardous Materials Transportation Act of 1974, and the Port and Tanker Safety Act of 1978.

In 1977 the National Materials Advisory Board (NMAB) was asked to establish a committee that would advise the Coast Guard on technical problems in the area of maritime hazardous materials. In response the NMAB formed its Committee on Maritime Hazardous Materials. This committee proposed, as the first of three tasks, to review the delivery of liquefied natural gas. To that end, the committee established a Panel on Liquefied Natural Gas Safety Evaluation.

The assignment to the panel was to provide an objective overview of the status of the maritime transportation of LNG with particular reference to the Coast Guard's safety responsibilities and the need for continued research into the nature of serious LNG accidents and their mitigation.

Panel members included persons with experience in design and safety of LNG ships and the physical-chemical principles involved in LNG spills, such as vaporization, dispersion, fuel-air cloud formation, ignition, burning, thermal radiation, explosion and blast, flameless vapor explosions, and risk assessments. The panel began its active deliberations in January 1978.

The panel assembled information by a variety of means. The members discussed the various safety issues relating to LNG and reviewed the research and development that had been accomplished. They reviewed more than 80 documents--codes, technical papers, research reports, technology assessments, hazard assessments, etc. The most pertinent of these documents are listed in this report, either as references or in the Bibliography. The panel visited a number of facilities, and tutorial presentations were made on these occasions as well as at meetings. These presentations were by invitation and were designed to obtain the thinking of the technical community, rather than the views of group advocates on the subject. Finally, the various chapters of the report were assigned to individual members of the panel.

The panel's report consists of an Executive Summary with general conclusions and recommendations, as well as specific conclusions and recommendations relating to three broad topics: causes, prevention, and mitigation of containment failures; consequences of containment failures; and risk assessment. The Executive Summary highlights the more important conclusions and recommendations in the report. The supporting text provides greater detail, and the appendices provide background information and references on LNG research.

On behalf of the panel we wish to express our appreciation to the following for information provided: Mr. Ivan La Fave, Chicago Bridge and Iron Co.; Dr. Elizabeth M. Drake, A.D. Little, Inc.; Dr. Frank Feakes and Dr. William Shipman, Cabot Corp.; Messrs. Peter Gwyn, James Gilliland, Alan Schuler, and William Clary and Dr. Rolf Glasfeld, Quincy Shipyards, General Dynamics Corp.; Mr. Max Levy, Columbia Natural Gas Company; Capt. Lynn Hein and Lt. Jerry Kichner, U.S. Coast Guard; Dr. James A. Fay, Massachusetts Institute of Technology; Dr. Jerry Havens, University of Arkansas; Dr. Reed Welker, Applied Technology Corp.; and Dr. C. Douglas Lind, U.S. Naval Weapons Center.

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CHAPTER I

INTRODUCTION

Natural gas is a key source of energy and provides about one third of the energy used in the United States. The known and probable deposits of natural gas are unevenly distributed in the world. Many are in such remote regions that their use is not possible for many years. Long-distance transportation, either by pipeline or as liquid in ships, is required to move the gas to market. Without such methods of delivery, large amounts of natural gas will be wasted as the accompanying petroleum is extracted. Worldwide, an estimated 7×10^{12} cu ft/yr of natural gas is flared into the atmosphere. In comparison, the total consumption of natural gas in the U.S. is about 20×10^{12} cu ft/yr.

The actual and perceived needs for the movement of natural gas over long distances depend on a complex mix of supply requirements, delivery costs, alternative fuel options, pricing policies, regional energy demands and projections, environmental pollution and public safety considerations, and politically determined restrictions on sources of supply. Industrialized nations like Japan and many of the countries of Western Europe must depend almost totally on imported natural gas (much of it as liquid). In contrast, the United States has enjoyed a variety of supply options, made up of substantial domestic reserves, long-distance pipeline supply from nearby countries, and imports of liquefied natural gas (LNG).* This array of choices has caused some difficulty in arriving at definitive policy decisions on importation. This uncertainty, in turn, has inhibited long-term commitments to provide infrastructures, such as pipelines or LNG liquefaction and shipping facilities, without which no sizable long-distance deliveries can take place.

In the United States, the interplay of these factors has recently produced major shifts in policies on the supply and use of natural gas. In 1979, the option of LNG imports

*The importation of LNG is likely to remain at a level of 1-2 percent of the total U.S. annual consumption (20×10^{12} cu ft/yr). In view of the prospects of large-scale natural gas importation from Mexico, Canada, and Alaska it is unlikely that this quantity will change very substantially in the 1980s.

into this country has been downgraded at the federal level, largely on the basis of economics and questions on reliability of supply. As a consequence, permits have been denied for the expansion of existing LNG-importation facilities and the construction of new ones. Importation currently is limited to the El Paso I Project (Cove Point, Md., and Elba Island, Ga.) and the Distrigas facility at Everett, Mass.

Much analytical, experimental, and design work has been done since the late 1950s, when marine transportation of LNG began. Many hypothetical situations have been analyzed for safety implications; actual installations and procedures have been scrutinized. In the U.S. and abroad, agencies charged with enforcing public safety have issued guidelines and operational procedures. Ships have been built, crews have been trained, port facilities have been constructed.

Why, then, is there a need for another review and another set of recommendations? In the panel's view, the consolidation of options into a relatively few designs, and the translation of these designs into workable transportation schemes, have resulted in systems that have been remarkably free of major accidents since the beginning of marine transportation of LNG in February 1959. However, despite the great care in design and execution and the impressive safety record, the panel realizes that serious accidents in the shipping, transfer, and storage of LNG occurring in or near populated areas may lead to large, uncontrolled releases. The consequences are potentially so damaging that the prevention of such accidents is the overriding priority in maintaining the safety of LNG importation and use. Therefore, continued reviews and assessments of the state of the art, refinements in the understanding of underlying design principles, and clarification of design assumptions are needed to assure that acceptable standards of public safety are maintained.

In principle, the LNG transport problem, as a hazards issue, is relatively simple. Excessive external or internal forces could rupture containment structures. The contents of tanks will then escape and mix and move with the surrounding atmosphere. If the mixture is within the combustible range and is ignited, the resulting burning cloud may cause damaging blast and thermal-radiation effects. Blast effects would result from deflagration reactions; it is uncertain whether free-air explosions of LNG/air mixtures can occur.

Small spills from leaking connections or larger spills from piping breaks are potentially damaging to the facility if ignited. However, they are not likely to have serious consequences for the public. Only massive breaches in containment, followed by ignition and fire, can be considered serious contenders for a major accident with LNG. The purpose of safety studies is to determine how such ruptures can be avoided and how to minimize the consequences if they should occur, and to estimate the damage in specific worst-case accidents.

To comply with the Coast Guard's request that we review and recommend research programs in the safe water transport, handling, and storage of hazardous cargo, the panel has undertaken three tasks. It has reviewed the likelihood of massive failure of shipboard tanks, principally from operational errors, and has suggested improvements that would mitigate such failure.* It has reviewed current knowledge of the blast and radiation effects of massive spills and has suggested what additional insights are needed. And finally, the panel has considered the difficult task of assessing the risks of transporting LNG in the manner currently practiced and putting these risks into perspective.

The panel elected to concentrate on LNG and not to extend its efforts to other substances, such as liquefied propane or other liquefied gases, that present similar though not identical problems. The panel also elected to concentrate on matters peculiar to Coast Guard responsibilities for ship and port safety rather than to analyze the entire LNG transportation and storage system. The panel had too little time to extend its coverage much beyond the self-imposed limits, although it was not always successful in staying within them. It is hoped that future studies will be extended to other areas that may present problems of concern.

Aspects of several LNG subsystems were not investigated. Prominent among them was the design of land-based storage tanks. Some consideration was given to evaporation of LNG in the region between tank and secondary containment, but the hazards to land-based tanks from natural forces or from sabotage were not considered in detail.

The panel's attention was drawn repeatedly to the suggestion that underground tanks would offer many attractive safety features. It has been suggested, in fact, that underground tanks would eliminate many concerns over the siting of base-load facilities (i.e., large plants along maritime shipping lanes) and peak-shaving plants (liquefication facilities near inland pipelines) in or near populated areas. Recent experiences in Japan have led the panel to believe that much of the disfavor toward older underground designs should not apply to structures built more recently. Therefore, it would appear that where LNG

*Tank failures brought about by sabotage or natural disasters were considered to be beyond the competence of the panel.

storage is contemplated in areas of moderate or high population density, the technical and economic feasibility of underground containment should be an important consideration.

In the panel's judgment, maritime transport of LNG has been introduced with considerable skill on the part of the designers responsible for the system, the regulatory agencies responsible for its integration into an existing transportation network, and the research community responsible for delineating the scientific and engineering principles involved. We note that this international development has benefited from the exchange of a great deal of technical information across national boundaries.

Improvements are possible with the advent of new design options and advances in areas such as navigation, maritime traffic control, and crew training. Better understanding of the behavior of the system and of the consequences of failures will expose potential weak points, which then can be strengthened to upgrade overall safety. Dangers from human misjudgments will never be absent, and they must be guarded against by constant attention to training, by developing good procedures, and by careful inspection.

The recommendations of this report should be read in the light of the panel's overall assessment: Transportation of LNG on a large scale can, indeed, meet the criterion that the public shall not be exposed to any undue risk, so long as the interaction among designers, regulators, and the public continues to be one of active multi-disciplinary probing and so long as vigorous programs of system improvement and quality assurance are maintained.

CHAPTER II

EXECUTIVE SUMMARY

A. INTRODUCTION

The panel was requested to provide an objective overview of the status of the maritime transportation of LNG. The overview was to be developed with particular reference to the Coast Guard's safety responsibilities and the need for continued research into the nature of serious LNG accidents and their mitigation.

It was the consensus of the panel that the potential consequences of serious accidents in the shipping, transfer, and storage of LNG that may lead to large, uncontrolled releases in or near populated areas are as unacceptable as other comparable mishaps affecting the general populace (such as collapse of a large dam or crash of a large airplane) brought about by design inadequacies or errors in operations. Therefore, the foremost concern of the panel is with the *prevention* of such accidents assuring the continued safety record of LNG importation and use. The panel addressed this concern by reviewing the design principles of LNG transportation systems, the operational principles involved in the shipment of LNG, and other factors that might reasonably be expected to improve further the safety of the system.

The panel's second concern is the development of measures to mitigate the consequences of potentially hazardous LNG releases in the event that, contrary to all expectations, preventive measures to maintain tank integrity should fail.

A third concern is that of improving the accuracy of understanding potential accidents and their consequences, through deeper knowledge of the underlying physical and chemical principles governing large LNG releases, including spill dynamics, dispersion (under and on water as well as land), ignition, and resulting fire and blast effects.

A fourth concern is the development of insights into how to proceeed to improve:

- The safety assessment of critical systems performance reliability data and prediction
- Human factor considerations in preventing accidents
- Understanding of risk level acceptability in the socio-political context

- Citizen participation in site selection or evaluation

B. GENERAL CONCLUSIONS AND RECOMMENDATIONS

The following general conclusions and recommendations are the product of deliberations and discussions at the meetings of the panel.

1. Understanding the Total System

One of the more important contributions that an outside review panel can make is to point out and emphasize that providing adequate safety in a complex system depends on thorough understanding of the total system and its interactions. Regulations that do not take the total system into account threaten rather than promote safety. Safety is threatened also whenever management does not understand the safety issues of the total system or where there exist overlapping responsibilities or gaps among the regulating agencies for specific subsystems. Only assessments of the total system will produce adequate safety.

This panel is concerned particularly with the interfacing of marine-transportation and land-storage subsystems of the total LNG importation system. It is the panel's understanding that the Coast Guard has primary responsibility for the safety of water transport and for mitigating the consequences of transportation failures. Other regulatory agencies deal with the storage and distribution of LNG. No one agency is responsible for the overall system.

The panel recommends that, in view of the tight linkage between the marine-transportation and land-storage subsystems, and of potential problem areas at the interface, the Coast Guard should have equal responsibility for the selection or at least the inspection of storage facilities that can be construed as harbor installations and, through a vigorous R&D effort, should establish the safety issues connected with such facilities.

2. Gathering and Analyzing Data on Mishaps

No system is immune to improvement by better design procedures, materials, components, etc. Much can be learned by detailed evaluation of component failures and human errors that occur while the system is operating. Because of the dispersed nature of ocean transport of LNG, no centralized mechanism exists that collects and analyzes data on failures and near misses and draws from them conclusions that would lead to improved designs and procedures.

The panel recommends that a procedure be developed in the LNG shipping industry for reporting to the responsible public agencies all mechanical malfunctions such as failure of critical navigation and maneuvering equipment and their correction, accidents and near misses, and any items pertaining to safety that were recorded in the ship's log. Under its authority for monitoring the entry of ships into territorial waters, the Coast Guard should require and obtain such a record during the pre-entry inspection.

3. Fostering Information-Sharing Among Importing Countries

The unequal global distribution of natural gas resources and the similarly unequal demand for gas place energy-consuming countries in different positions with regard to the immediacy of the need to develop safe transportation and storage systems.

The panel recommends that importing countries establish a network for sharing information on engineering matters closely related to the safety aspects of LNG transportation and storage. Ready access to engineering data that may indicate design deficiencies is particularly desirable.

4. Periodic Reviews of Operating Procedures and Crew Training

The panel recommends that periodic reviews of operating procedures and crew training be encouraged. Some of these functions would be shared with other federal and state agencies (including the Department of Energy (DoE), state and local agencies, etc.) and with operators of LNG ships and facilities. It is important that the Coast Guard take the lead in such information exchanges and so establish for itself a position from which it can influence decisions that concern vital aspects of the safety of the overall system.

5. Funding USCG R and D on LNG

The panel is concerned about the amount and allocation of funds for U.S. research and development programs on LNG hazards and of related safety issues with other cryogenic substances. Prior to the establishment of the Energy Research and Development Administration (ERDA) and more recently of its successor, the Department of Energy, a substantial portion of the federal research effort was supported by the United States Coast Guard, in cooperation with the American Gas Association, industrial companies, and other government agencies. Subsequently, DoE has assumed a large role in funding the R and D effort. The panel welcomes this development, but regrets that all concerned parties devote inadequate attention and sponsored research to the subject.

The panel recommends that a research plan be developed in which the various federal agencies that are responsible for specific aspects of the overall safety system contribute to the planning, funding, and execution of the technical program. The research program should extend over a minimum of three years, since one cannot expect viable results based on reliable data to be obtained in a shorter time. Particular attention should be given to research on the underlying principles of formation of large, reactive air/fuel clouds and the consequences of combustion on a large scale.

6. Improvement of Communication Among Government Agencies and the Public

The panel recommends that, in view of public concerns at the community level about the safety aspects of the LNG system, the federal agencies involved in regulation and research establish close liaison with state and local planning agencies in addition to the public. It should be possible to establish public understanding of the factors on which the safety of the system depends by candidly presenting the successes and difficulties of the developing LNG technology. A well informed public is essential in producing a climate of sound safety.

7. LNG Safety in Relation to Other Liquefied Gases

This report confines itself to the maritime transportation and transfer of LNG, but its scope and conclusions are not restricted to this specific cargo. Other liquefied gases, such as LPG, ammonia, chlorine, and hydrogen, present similar problems, although the specific hazards may differ. The conclusions and recommendations for LNG should apply to these other hazardous materials to the degree warranted by their properties and trading volume. The design of new research programs and research facilities for LNG should take this expanded view into account.

C. SPECIFIC CONCLUSIONS AND RECOMMENDATIONS

1. Causes, Prevention, and Mitigation of Containment Failures

The system now used for marine transportation and transfer (loading and discharge) of LNG has resulted from vigorous research and development. The integrated LNG system is extremely capital-intensive in all its parts (liquefaction, shipping, storage, and regasification) and to be competitive and profitable, it must be safe and reliable. The safety record is good, but the potential hazards are great; therefore continuing, strong effort is required to maintain vigilance, especially in the area of accident prevention. Additional research and improvements in regulations and operational procedures will assist in reducing accidents, minimizing risks, by identifying unforeseen problems, and thereby preventing large spills that could be hazardous to the public.

a) Improved Regulations for Ships

Recent studies are in general agreement that LNG ships are designed and constructed to high standards of reliability and safety. Indeed, no serious accidents have occurred during the more than 4600 voyages completed as of Jan. 1, 1980.

Based on a review of these studies that focus on the design and construction standards, and the operating experience of the ships, it is concluded that a large release of the LNG cargo (one that would be hazardous to the public) is significantly more likely to result from external factors, such as collision, stranding (grounding), natural disasters, and sabotage, than from failure within the ship.

Considering the increases in LNG traffic that are projected, and the risks to the public and the environment, higher standards should be required by regulations for certain conventional ship systems to minimize the possibility of ship collisions and groundings.

The panel recommends that more stringent regulations for LNG ships be developed in the areas of navigation, steering, ship control, and continuity of electric and propulsion power by requiring, (a) high seas and coastal waters position-determining systems of a modern effective electronic type, (b) long-range and navigational radars of demonstrated reliability, (c) a collision-avoidance system that interfaces with both radars, (d) a Doppler log system, (e) dual power and control systems for the steering apparatus, extending from the wheel on the bridge to the rudder stock, (f) bridge control of speed and direction to minimize response time when maneuvering, (g) a bow thruster of adequate size to improve ship control and steering at low speed, (h) an arrangement that will prevent interruption in the operation of the steering apparatus upon loss of main electric power, and (i) an electric-power system that permits the ship to be operated and maneuvered at reasonable speed in case of malfunction of part of the main switchboard. (Many of these systems are incorporated in most recently built LNG ships, although not required by current regulations.)

b) Traffic Control and Berthing

Effective traffic control is the most significant factor for the elimination of the possibility of serious collisions and groundings in coastal and harbor areas. The Coast Guard recognizes the fact by employing traffic control in U.S. ports that receive LNG and LPG ships. However, present traffic-control procedures can be improved.

The panel recommends that the seaward extent of traffic-control lanes for LNG/LPG ships should be based on the dimensions of the vapor cloud expected to result from a large spill on water (See Section 2 below).

The panel recommends that the Coast Guard should, in its current efforts to provide comprehensive guidelines to local commandants for their port LNG/LPG Operating Plans, address more specifically:

- Maneuvering and control capability of the specific LNG-LPG ship
- Early off-shore control
- Effective escort during transit to the berth
- Exclusion area for other traffic during transit of the LNG-LPG vessel
- Speed regulations
- Protection of the LNG-LPG vessel from collision while at berth.

c) Crew Training, Human Error

While equipment failure has contributed to collisions and groundings, human error has been the major cause. The Coast Guard specifies the minimum number and rating, and requires special training for the crew and officers on U.S.-flag LNG ships. However, at present there is no formal program for monitoring the performance of officers and crew on LNG ships to insure that they remain competent, safety conscious, and vigilant. There are no uniform standards for crew manning and training on foreign-flag LNG ships.

The panel recommends that the Coast Guard continue its efforts to establish international standards for crews of LNG SHIPS.

The panel recommends that the Coast Guard analyze the crew- and officer-training programs and crew-selection methods used by various organizations for LNG ships and also examine the actual performance of the crews with respect to competence and safety practices. The officers and crew of LNG tankers should be especially trained for the proper responses to the specific types of accidents that may be experienced on such ships.

An increased use of simulators for training purposes should be considered. The necessary facilities exist in this country.

d) Loading and Discharge of Cargo

Loading and discharge, or transfer, of LNG are recognized as hazardous operations. The present systems are designed and constructed to high standards of reliability and safety, in accordance with Coast Guard and international regulations. Small spills occur, but since the beginning of marine transportation of LNG in 1959 only one large spill (of about 1000 m^3 from an onshore transfer line in Arzew, Algeria, during loading) has occurred in more than 9000 loadings and discharges.

It is the consensus of all who have studied the problem that a fire on an LNG ship will not result in tank overpressure and rupture.

A maximum credible spill of 100,000 to 500,000 gal (380 to 1900 m^3) of LNG resulting from failure of the main transfer line when discharging has been postulated in accident scenarios in the literature. The panel recommends that the effects of such a spill be analyzed, particularly in regard to:

a. The effect of fire and radiation on ship and crew;
b. The effects on the ship's structure of an unignited LNG pool on the water at the ship's side, and the effects of the LNG on the ship's deck

c. Practical prevention and mitigation measures that may be suggested beyond current practice.

2. Consequences of Containment Failures

In the event of a major rupture of an LNG container, the escaping LNG will evaporate and mix and move with the air surrounding the spill. The air-fuel mixture will ignite and burn if a suitable ignition source is present.

Mathematical models that attempt to describe these events have been developed, and predictions have been made of the expected consequences. The panel recognizes, however, the difficulties of predicting the precise behavior of such a complex system under a variety of initial conditions of rupture, meteorology, and terrain. No comparisons have been made of the predicted behavior with the actual results of large spills because of the lack of sufficient reliable observations from the few such accidents. An appropriate research effort to clarify these matters is presented. The panel believes that uncertainty exists in characterizing the blast and radiation fields that may follow the ignition of a large, very nonuniform, methane-air cloud at some distance from the source of the spill.

The panel recommends that, until better information is developed, the Germeles-Drake or Esso formula be used to define the dimensions of the vapor cloud resulting from a large spill on water, and that these dimensions be used to establish the seaward extent of the traffic-control lanes for LNG-LPG ships.

There is a very small, but still real, probability that, despite the use of all reasonable means to avoid containment failure, a large methane-air cloud will form and travel some distance from the source of a spill. The consequences of the ignition of such a cloud if it reaches a populated area or nearby industrial facilities would be unacceptable, so a secondary line of protection is desirable.

The panel recommends that efforts be made to define the conditions that would warrant deliberate ignition of the vapor cloud far enough from populated areas or valuable facilities so that blast or radiation would not damage them. It is recognized that the source of the leak--be it ship or storage facility-- may suffer serious damage.

A vigorous research program should be pursued on the design principles of such a secondary line of defense. In particular, the proper placement of an ignition source depends on thorough understanding of the formation, composition, and damage potential of methane-air clouds under a variety of spill scenarios and weather and terrain conditions. Since such a response may be applicable to spills of substances other than LNG, some of which may be toxic as well as flammable, the panel recommends that the proposed investigation be designed to include such chemical substances. The panel is concerned particularly about liquefied gases that enter commerce in large quantities. These gases include propane, ethylene, ammonia, and hydrogen, whose transportation and storage involve safety considerations similar to those for methane.

a) Dike Design and Performance

The containing dikes of land storage tanks are designed to hold the maximum amount of liquid that could be spilled, but their efficacy is questionable in the case of a catastrophic accident wherein the tank is emptied very rapidly.

The panel recommends that a more careful examination be made of the expected results of a catastrophic spill for the case of low dikes some distance from the tank. Methods are now available for designing dikes to limit vaporization rates.

The panel recommends that investigations be continued on inexpensive dike floor/wall insulations, such as corrugated aluminum.

For postulated spills of LNG into diked enclosures, it appears that simple Gaussian dispersion models will allow the average downwind concentration of methane to be estimated reasonably accurately, assuming that the vapor-flow rate from the dike can be estimated.

The panel recommends that research be done to:

1. Model LNG spills in diked enclosures for three major areas: the boiling rate on the dike floor and walls; the effect of dike geometry on the rate of vapor loss; and the downwind dispersion characteristics of vapor overflowing the dike wall.

2. Clarify the effect of high dikes on the dispersion process. Does dispersion begin at the top of the dike, or do the cold, heavy vapors fall to the ground before dispersing?

3. Clarify the effect of turbulence promoted by the tank, the dike, nearby structures, etc., on the dispersion of vapor.

4. Develop dispersion correlations for downwind points not far from the dike, where the Gaussian models are least accurate.

To implement the four recommendations, either LNG spill tests or appropriate wind tunnel simulation experiments are necessary to provide data to answer the questions raised.

b) Cloud Formation

Few experiments have been done to verify the theoretical models proposed for the boiling/spreading rates of spilled LNG. It is not at all clear how best to estimate the vapor-dispersion process following a large spill of LNG on water. No experiments have been large enough to verify the large, gravitational, vapor-spread phase that is predicted.

The panel recommends that research be done to:

1. Clarify the extension of existing models to very stable weather, as they have only been tested with LNG in neutral to slightly stable weather.

2. Evaluate carefully any further model development or experimental program to assure that the results would be meaningful and cost-effective. In particular, the degree of entrainment during the gravitational vapor-spread phase needs further study, but this work may be possible only in very large tests.

3. Determine experimentally the true boiling/spreading rates of unconfined spills of LNG on water; establish heat-transfer rates and clarify whether ice is formed.

c) Flameless Vapor Explosions

Flameless vapor explosions are an insignificant hazard relative to fires and combustion-supported explosions because:

a. The amount of cryogenic materials involved in flameless vapor explosions must be very small relative to the amount spilled

b. The energy yield of a flameless vapor explosion must be very small relative to explosions involving combustion reactions

c. The geometry of an unconfined spill provides for optimum dissipation of the energy of a flameless vapor explosion in the most harmless way.

The panel recommends that the assumption that a spill on water will be unconfined should be reviewed. With present ship design there are large internal spaces in close proximity or adjacent to the LNG tankage that might fill with water and LNG in the event of an accident. In such a partial confinement one must consider not only the short-duration pressure pulse of homogeneous nucleation, but also the heaving force of explosion-induced rapid vaporization.

d) Ignition and Flame Propagation

The incompletely mixed nature of a fuel-vapor plume may influence ignition and other burning characteristics. Experience indicates a wide range of ignition probabilities: most small hydrocarbon releases do not ignite, but, at the other extreme, releases caused by collision and penetration of an oil tanker almost always ignite.

Ignition occurs very easily in the right conditions: a methane/air mixture in the flammable range of composition; and a high-temperature source of ignition such as a flame or an electric spark. A source of ignition must be very hot to ignite methane; ignition by a heated surface requires a combination of high temperature and adequate surface area.

Flashback should generally be expected, once a plume is ignited. Flashback probably will occur more easily over land than over water, however, and may not occur at all over water at modest wind speeds.

The panel recommends that work be done to evaluate the combustion characteristics of incompletely mixed systems. Some important characteristics to be evaluated are: flame-propagation rate and conditions for flashback over land and water.

e) Effects of Flame Radiation to Nearby Structures

Irradiance at long distances from a fire associated with a major LNG spill can be determined with adequate accuracy from an estimate of the mass burning rate. Current data are unrealiable for computing irradiance near a moderate-size spill, which is of great importance for designing fire-protection equipment for use at LNG installations and on LNG carriers.

The panel recommends that data be obtained on fire geometry near structures in the presence of wind, including the possibility of the generation of fire whirls. Wind-tunnel model experiments should be considered for this purpose.

Vapor-cloud deflagration tests are needed on a scale large enough to determine whether the size of LNG fire balls has an upper limit of a few meters. The primary emphasis of further research on flame radiation should be on obtaining more accurate data for moderate-size LNG fires, preferably by careful laboratory experiments rather than by full-scale field tests. Measurements in large tests should be made to verify mathematical models of flame radiation, not to derive the primary empirical data used in such models. Spectroscopic measurements probably should be given relatively low priority in research, but if contemplated they should be performed with rapid-scan instrumentation.

f) Cloud Explosion and Blast

Blast-wave theory has been developed primarily out of concern over the yield of atom bombs, while the dynamic effects of high explosives, observed in large field tests, have been treated as an empirical science. However, most of the physical characteristics of explosions have been established by laboratory expriments. Today, blast-wave theory and its experimental background can be considered well founded.

The panel recommends that, with respect to the escalation of combustion to explosive magnitude, formation of deflagrations propagating fast enough to drive pressure waves ahead of them should be considered more important than the transition to detonation that so far has received the overwhelming share of attention. In particular, the question of whether a transition to detonation is possible leads to incorrect emphasis, since damage caused by a pressure wave generated by deflagration may be as serious as that caused by detonation.

Proper consideration should be given to certain unusual circumstances that so far have not been taken into account, as for example, a detonating vapor cloud of a more sensitive fuel supplied by an external source, initiating an explosion in an LNG cloud.

The experimental program on dispersion of LNG spills, formation of explosive clouds, and blast effects should be based on laboratory experiments, with supporting evidence provided by small field tests. Large field tests should be used only to check the validity of prediction when a predictive capability is at the last stages of development.

The primary objective of research on the explosion hazards of LNG clouds should be to devise rational means of predicting explosive yields. A major effort should be based on numerical analysis, which in turn would provide specific requirements for experimental data.

Research to provide rational background for assessing hazards should be associated with studies of preventive measures. Such studies should include work on strategies to be followed in case of a specified set of accidental spills. They should also include development of measures, such as a salt-water spray, for desensitizing the cloud by inhibiting the propagation of the flame so that the rate of combustion would be too small to generate a pressure wave.

3. Risk Assessment

The assessment of the risk of water transportation of LNG is a worthwhile undertaking, but the results of risk studies must be interpreted with care. Numerical estimates should not be taken literally, but can be useful in identifying possible weaknesses in the system and likely failure modes; as a guide for decision makers; and as a tool that can be used to scrutinize and criticize the decision maker.

The reliability of any risk analysis depends on the adequacy of the experimental or experiential data base, the validity of synthesized probability data (i.e., probabilities of events are modeled from similar systems, but not measured), the validity of subjective probability estimates (conjecture), and the accuracy of the physical models used in the analysis. The risk assessments reviewed for this report ranged from those that were based almost entirely on conjectural (unsupported) input data to those that provided considerable justification of input data. A major limitation of all the risk-assessment studies evaluated was that, even in the most detailed study, credible accident scenarios were overlooked.

There are significant differences in analyses that are called risk assessments. Some studies focus on the probability of an undesired event, such as a large LNG spill. Others focus on the consequences of the spill.

Still others concentrate on even narrower aspects of the problem of assessing risks. However, the broader definition of risk encompasses both probability and consequences.

Almost every LNG risk study emphasizes the low-probability, catastrophic event. Low-probability events are inherently difficult to assess to the degree of accuracy and level of confidence that are desired.

The panel recommends that:

- Risk assessments be periodically updated, because new knowledge or changing conditions during the lifetime of a project can affect the conclusions of the original assessment.

- Additional accident scenarios for high-consequence, low-probability events should be evaluated for risks. Risk assessments should be performed not only for the high-consequence, low-probability events, as is currently the practice, but also for the lower-consequence, high-probability events. Public acceptance of LNG can be adversely affected by less-than-catastrophic events, such as spills during transfer operations or shipboard fires.

- The risks associated with water transportation of LNG and with other hazardous materials should be compared. The Coast Guard in consultation with an advisory group should establish the basis for risk comparisons (e.g., cargoes and ports to be studied). The applicability of risk-benefit analysis should be evaluated.

- Better input data should be developed to increase the reliability of risk analyses. A worldwide incident-reporting system, including coverage of minor incidents and near misses, would help to provide relevant data. Data from "man-in-the-loop" trials at a ship-simulator facility should be collected. Such data will increase the reliability of synthesized probability data for ship collisions at specific sites. Risk assessments should provide confidence levels and discussions of uncertainties when probability data are used.

CHAPTER III

SAFETY ASPECTS OF LNG SHIP DESIGN AND OPERATIONS

A. CURRENT DESIGN PRACTICES

1. Codes

The rapid increase in sea transport of liquefied gases in bulk in the late 1960's created a need for international standards to insure their safe carriage with a view to avoiding or minimizing the risk to the ship, its crew, personnel at shore installations, and to the environment. Recognizing this need, the Inter-Governmental Maritime Consultative Organization (IMCO), adopted on November 12, 1975, the Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk. (Inter-Governmental Maritime Consultative Organization, 1976).

This code is a comprehensive document consisting of 19 chapters providing specifications for the ship, its cargo systems, safety systems, and related auxiliary systems. The Table of Contents on page 32 indicates the breadth of the requirements. A detailed review of the code and its development and background is given in Kime et al., 1977.

The Code was prepared by an ad hoc working group of the IMCO Subcommittee on Ship Design and Equipment. The group was composed of delegations from 16 of the leading maritime nations. The individual delegations included governmental and industrial experts on gas ship design, construction, and operation. Observers from the International Association of Classification Societies, the International Chamber of Shipping, and other international organizations participated in the work of the group. The U.S. delegation, under the leadership of the Coast Guard, contributed significantly to the Code, which reflects the U.S. position and practice in most areas.

The Code deals primarily with ship design and equipment. Other important facets of the safe transport of the cargoes, such as crew training, operations, traffic control, and handling in port, remain primarily the responsibility of the individual governments of the countries where the ships trade. However, IMCO is currently examining the possibility of establishing uniform minimum-crew and crew-training regulations.

The Coast Guard is currently drafting regulations to implement the IMCO Code (United States Coast Guard, 1976). While the Code is considered acceptable to the U.S. in almost all respects, more stringent requirements are considered necessary in a few cases (Kime et al., 1977).

The Code applies to ships for which the building contract was placed after October 31, 1976. For existing gas ships, IMCO developed a separate code that did not completely attain the U.S. objectives. Existing foreign-flag ships trading to the U.S. are reviewed under the Letter of Compliance program of the Coast Guard.

LNG ship technology developed over the preceding 20 years in worldwide trade was examined critically in developing the Code. There have been minor technical problems. However, as of January 1, 1980, no serious accidents had occurred during approximately 4600 voyages to deliver LNG to Europe, Japan, and the U.S. This statement applies only to the LNG ships. The shipping terminals have suffered two accidents. One occurred during construction (Libya) and one during operations (Arzew, Algeria). In the latter case, a valve ruptured probably due to faulty operation, and more than 1000 m^3 of LNG was spilled without ignition. Also, a receiving terminal (Staten Island) suffered a major fire during repair of an empty tank, wherein the exposed polyurethane insulation and Mylar lining were accidently ignited.

The consensus is that LNG ships are designed and constructed to high levels of reliability and safety. A General Accounting Office report states, "LNG ships are probably the least vulnerable of all the systems involved in LNG storage and transportation." (General Accounting Office, 1978, page 21). An Office of Technology Assessment report states, "No serious accidents have occurred and it appears that existing U.S. Coast Guard standards of design and construction are probably adequate to assure equally low risks of ship failures in the future" (Office of Technology Assessment, 1977, page 42). Other studies express similar conclusions. However, all recommend improvements to lessen risks in view of the significant increase in LNG traffic that is projected.

The IMCO Code concentrated on the safety of the LNG systems. It did not require higher standards for certain conventional systems, such as navigation, steering, ship control, and continuity of power. Considering the risk to the public and the environment, higher standards than for conventional ships should be required of such systems.

The integrated LNG system is extremely capital-intensive in all its parts (liquefaction, shipping, storage, and regasification) and to be competitive and profitable, it must be safe and reliable. Prudent shipowners and responsible designers recognized this fact from the beginning, and generally included features and equipment in excess of regulations to enhance reliability as well as safety.

2. Cargo Containment

The key element of safety with LNG ships is the cargo containment system. The Code's central theme is to provide maximum attention to cargo containment and to minimize the release of cargo in the event of a casualty. The Code defines various types of containment systems and specifies the requirements for each (Inter-Governmental Maritime Consultative Organization, 1976; Kime et al., 1977).

For some tank types, a secondary barrier must be provided to contain temporarily any envisaged leakage of liquid cargo through the primary barrier. For other tank types, which are suitable for rigorous stress analysis, a partial secondary barrier sufficient to protect the ship against a possible leak of predictable size is required. This is sometimes referred to as "leak before failure," since any crack would result in a detectable, controllable leak long before it grew long enough to cause catastrophic failure of the tank. The rigorous stress analysis and fracture mechanics analysis for one case have been described in detail (Glasfeld, 1976).

The foregoing design and construction standards and the operating experience of gas ships lead to the apparent consensus that a release of cargo large enough to be hazardous to the environment and the public is significantly more likely to result from external factors, such as collision, stranding (grounding), natural disasters, and sabotage, than from failure within the ship. From the beginning of the development of the design standards, it was recognized that a severe collision or stranding could lead to cargo tank failure. The results could include uncontrolled release and dispersion of the cargo, possibly brittle fracture of the ship's hull, fire, etc. The IMCO Code recognizes this risk and states, "the requirements of the Code are intended to minimize this risk as far as is practicable, based upon present knowledge and technology." Design and construction alone cannot eliminate the adverse results of a severe collision or stranding. However, some improvements in design, together with traffic control and adequately trained crews and responsible officers, can eliminate, or at least lessen by several orders of magnitude, the possibility in coastal or harbor areas of a collision or stranding of the magnitude that would result in a large release of LNG cargo.

B. CURRENT OPERATING PRACTICES

The Coast Guard regulates and controls ship traffic in U.S. ports that receive gas ships (currently, for LNG ships, Boston, Cove Point in Chesapeake Bay, and Savannah). The regulations are designed to avoid collisions and groundings and assure safe operations while the ship is in port and tranferring cargo. Traffic control is the most significant factor in preventing collisions and groundings in coastal and harbor areas. Statistics indicate that without traffic control, the probability of a serious incident is unacceptably high in certain harbors. In others, the growth of traffic may warrant such controls in the future.

The Coast Guard specifies the minimum numbers and ratings for crews on U.S.-flag LNG ships. The Coast Guard also requires special training for the crews, and shipowners/operators and the unions have developed special training programs, including the use of a simulator in at least one case. However, the adequacy of the training has not yet been proven in practice due to insufficient service time.

For foreign-flag ships, the IMCO, 1976, Code includes three general requirements, but sets no standards for minimum number of crew or crew training.

At present there is no formal program to monitor the performance of the officers and crew on gas ships to be assured that it is competent and safety conscious. Various reports indicate a need for improvement.

All areas of large spill prevention depend on the human factors. Ship systems cannot be designed to be foolproof or to operate safely in incompetent hands, as shown by some of the more serious collisions and strandings. However, maritime history has shown that ships can operate safely when manned by an adequately trained crew supervised by knowledgeable and responsible officers. For example, in the 138 years from 1840 to the present writing, covering 175 ships, the Cunard Line did not lose a passenger in a ship accident, excepting torpedoings and bombings. Cunard established this record in ships whose accommodations were made largely of wood and contained combustible furnishings and whose navigation, control, and communications equipment were rudimentary by present standards. However, the line's watchword was safety. Less safety conscious operators suffered passenger fatalities from fire and collisions with other ships and with icebergs.

The reliability and safety of LNG shipping operations have been discussed (de Frondeville, 1977; General Accounting Office, 1978; Office of Technology Assessment, 1977).

Port safety operations have been discussed (Patterson, 1978) and specific operating/emergency plans presented (U.S.C.G. Marine Safety Office, 1977; U.S.C.G. Fifth District, 1978). The port safety operational requirements are detailed and site-specific. The essential elements are:

- Adequate prior notice of the LNG vessel's arrival to the USCG and all concerned organizations and personnel.

- Examination and inspection of the ship at anchor before entering port for:

  Valid documentation.
  Inspection, primarily of the cargo systems including tanks, piping, equipment, controls, and alarms, as well as the material condition of the vessel, fire-fighting systems, communication, and personnel.

- Transit to the terminal:

  In daylight in good visibility.
  Escorted by USCG vessel.
  Other traffic may be excluded within a "moving safe area" around the LNG ship, depending on specific site.
  Assistance by tugs of adequate number and power.

- At the terminal:

  Detailed inspection prior to discharge of cargo.
  Depending on specific site, escort to warn off other traffic, safe speed limit for other traffic, LNG vessel moored to advantage for quick departure, etc. No other operations such as bunkering fuel, permitted during cargo discharge.

- Departure - after complete discharge of cargo:
  Similar to inbound transit, except that daylight is not required and fewer tugs may be used.

C. RUPTURE OF SHIP CONTAINER

1. Collision (See Chapter IV)

2. Grounding and Breakup

The IMCO Code requires that cargo tanks be protected from penetration in the case of minor damage to the ship resulting, for example, from contact with a jetty or tug. The Code also requires that the tanks be protected from collision or grounding damage by locating them at specified minimum distances inboard from the ship's shell plating, and by providing a double bottom and side tanks. This construction prevents penetration of the cargo tanks from all but the most severe groundings.

Thus it is expected that grounding in a harbor channel, when the LNG ship is being operated at a permissible speed, will not result in penetration of a cargo tank. The Coast Guard requires that the ship be designed to contain or consume the LNG boil-off for at least 21 days (Kime et al., 1977). That period allows time to float the ship or take other remedial action. If high winds and high seas are predicted, the grounded ship's ballast system may be used to fill ballast tanks, thereby adding weight to prevent working of the ship on the bottom.

Severe groundings of large, modern ships have resulted from equipment and human failure and combinations of the two. For example, the Argo Merchant grounding was apparently caused by selection of a dangerous course, failure of navigation instruments, and human error in the use of other navigational aids. The Amoco Cadiz grounding apparently resulted from following a course too close to the rocky shore considering the weather, steering-gear failure at a critical time, then anchor failure, and then inability to secure sufficient timely assistance from tugs. An LNG ship in either set of circumstances most likely would have suffered penetration of a cargo tank and loss of cargo. In the severe weather conditions that prevailed after these groundings, an LNG ship might have broken up and lost all cargo. Ships cannot be designed and constructed to survive the effects of severe groundings in bad weather. Measures designed to prevent groundings should be enhanced. (See Section D, Accident Avoidance).

3. Sloshing

Sloshing of LNG in partially filled tanks of the membrane type has caused the membrane lining to fail and allow LNG to leak into the interbarrier space. Such releases are readily detected. Means are provided for containing the leakage until measures can be taken to prevent further failure. It is improbable that sloshing would ever result in a situation that would be hazardous to the public. Also, see Appendix C.

4. Ship Fire Effects

Heat from a fire on or next to the ship might cause overpressure in an LNG tank. Overpressure is prevented by relief valves sized to accommodate the vapor generated by a specified heat flux (Inter-Governmental Maritime Consultative Organization, 1976; Kime et al., 1977).

The IMCO Code and Coast Guard regulations require four provisions for fire-protection/fire-extinguishing systems for gas ships:

Structural fire protection
Fire-water main system
Water-spray system
Dry-powder fire extinguishing system

The U.S. Coast Guard has been a world leader over the past 40 years in developing fire protection for ships. The consensus of all who have studied the problem is that a shipboard fire on an LNG carrier will not result in overpressure and rupture of LNG tanks. In the Yuyoh Maru collision, this LPG ship was carrying naphtha in its wing tanks and LPG in the center tanks, a dual cargo that the U.S. Coast Guard would not permit. The naphtha fire that resulted from the collision lasted for weeks, but did not cause an LPG tank to rupture (de Frondeville, 1977).

The generally accepted worst case of a severe collision, resulting in an almost instantaneous spill of 25,000 m^3 of LNG with ignition of the vapor, would produce an intense fire of short duration. Based on this case, a thermal analysis for one ship type indicated that there would be some local deterioration and melting of the cargo-tank insulation, but no overpressurization of the tank. A thermal analysis for the same type of LNG ship was made for a less intense fire of long duration (20 h) on an assumed burning oil barge abreast of the LNG ship. Again the results indicated some melting of the cargo tank insulation, but no overpressure.

D. ACCIDENT AVOIDANCE

As previously stated, the apparent consensus is that a large release of cargo is most likely to result from external factors, i.e., collision, stranding (grounding), natural disasters, and sabotage.

1. Design of LNG Ships

Prevention of serious collisions and strandings will be enhanced by stronger regulations on navigation equipment, collision-avoidance systems, steering apparatus, continuity of electric and propulsive power, and ship control. Many improvements in such gear are incorporated in most recently built LNG ships by action of prudent ship-owners and responsible designers although not required by current regulations. New requirements resulted from the International Conference on Tanker Safety and Pollution Prevention, held in London, February 6-7, 1978. The U.S. Coast Guard proposes to implement them June 1979 to June 1981 for new and existing gas ships. The requirements will include at least two radars, collision avoidance aids, and improvements to the steering gear and its control systems.

The following specific improvements are proposed:

1. Require a Position Locating System of the Loran C or equivalent type for accurate continuous determination of position in coastal waters, to assure that LNG ships are in the sea lanes designated for approaching and departing U.S. harbors.

2. Require long-range (10 cm) and navigational (3 cm) radars of demonstrated reliability.

3. Require a Collision Avoidance System (CAS), with manual and automatic monitoring of targets, which interfaces with both the 10-cm and 3-cm radars.

4. Require a high-seas position-determining system of a modern electronic type, such as Omega or a satellite navigation system (SNS).

5. Require a Doppler Log System for indicating ship speed for use with the CAS and SNS systems.

6. Strengthen the requirements for the ship's steering apparatus by extending the requirements for dual controls and power units to the hydraulic and mechanical equipment,

so that dual systems extend from the steering wheel to the rudder stock. Require that operation of the steering apparatus not be interrupted during the period between loss of main electric power and its replacement by emergency power. This could be done by requiring a source of temporary power, or by requiring that the emergency generator be operating when in maneuvering waters so it can provide power essentially instantaneously to the steering apparatus on loss of main electric power.

7. Require that the main switchboard comprise three sections interconnected by automatic circuit breakers, so that the ship can be operated and maneuvered at reasonable speed with any one section out of service.

8. Present regulations require that electric generating sets have sufficient capacity to carry the necessary sea load under normal operation with any one generating set in reserve. This is also a requirement for seaworthiness, so that a ship is not permitted to leave port without a set in reserve. This requirement should be extended to prohibit a ship from entering port under her own power unless she has in reserve one generating set capable of supplying the necessary electric load for maneuvering the ship at reasonable speed.

9. A bow thruster unit of a specified size should be required to improve control and steering at low speeds, as in channels, where the large sail area of LNG ships makes control difficult.

10. A centralized engine-control and monitoring system with bridge control of speed and direction should be required to minimize response time when maneuvering.

11. Small spills that occur when cargo is being loaded or discharged are controlled by the crew with the ship's wash-down and fire-fighting systems. Recent USCG-sponsored research indicates that the fire-fighting systems on new LNG ships are better than required by regulations, but that further improvement is possible with presently available equipment. Regulations should be amended to require the more capable systems that have been recommended (Welker et al., 1976), including increased capacity for the dry-powder system and containment areas on deck to limit the fire area.

12. Thought should be given to the location of the cargo control station, which in most recent designs is close to the loading and unloading connections where spills and fires are most likely to occur.

2. Operational Controls

The best way to avoid collisions and strandings in coastal and harbor areas, as noted earlier, is to regulate and control ship traffic, as is now done by the Coast Guard in U.S. ports that receive gas ships. These measures should be continued, and the following improvements should be considered.

1. LNG ships should be required to approach or leave U.S. ports in specially designated sea-lanes which will extend well out to sea, probably beyond the territorial limit. Until better information is developed, it is recommended that the Germeles and Drake or Esso formula be used to define the dimension of the vapor cloud resulting from a large spill on water, and thereby the seaward extent of the traffic-control lane. Also, LNG ships should never come closer to the coast than this safe distance. The sea, bay, and harbor lanes and channels to be used by LNG ships should be selected to maximize the distance between the ships and centers of population. When in these sea-lanes, it should be the responsibility of the LNG ship to avoid striking or being struck by another ship, through effective use of its high quality navigational and collision avoidance equipment. The Coast Guard should escort LNG ships from well outside the port sea buoy to the terminal and return. Before the LNG ship enters the sea-lanes from sea, the Coast Guard should be assured that all normal, standby, and emergency navigational, control, propulsion, steering, and electric-power systems are in operational readiness.

2. The Coast Guard should establish and enforce speed limits for ships passing a terminal where an LNG ship is berthed. The limits should be such that if a vessel veers from its proper course and rams the LNG ship, it will not have enough momentum to penetrate to the LNG tank. Permissible speeds would be 6 knots for craft displacing less than 10,000 long tons, 4 knots for ships displacing 10,000 to 40,000 long tons, and 3 knots for ships displacing 40,000 long tons or more (See Chapter IV, Figure 1).

3. A procedure should be developed in the LNG shipping industry for reporting to the responsible agencies all mechanical malfunctions and their correction, accidents and near misses, and any items pertaining to safety that were recorded in the ship's log. The Coast Guard, under its authority for monitoring the entry of LNG ships into territorial waters, should require and obtain such a record during the preentry inspection.

3. Personnel

The panel believes improvements are needed in manning, in crew and officer training, and in monitoring crew and officer performance.

As previously stated, owners/operators of U.S.-flag LNG ships are providing special training, and the Coast Guard has minimum manning requirements. However, the adequacy of the manning and training has not yet been proven in practice because not enough time has passed. The performance of the officers and crew on gas ships should be monitored formally to insure that they are competent and safety-conscious and remain so. While safety drills of various types are presently required their coverage and adequacy should be reviewed.

The officers and crew of LNG tankers should be especially trained for the proper responses to the specific types of accidents that may be experienced on such ships. The sequence of decisive and timely actions after a casualty is crucial in preventing more serious consequences. Casualty response manuals should be required, supplementing the presently required damage control manuals. These manuals should detail the step-by-step actions to be taken in the event of such accidents. This subject is covered more fully in the report entitled, "Responding to Casualties of Ships Bearing Hazardous Cargoes" (National Academy of Sciences, 1979).

With foreign-flag LNG ships that trade to U.S. ports, the authority of the Coast Guard is limited to determining that the manning is in accordance with international regulations, which do not specify minimum manning or crew training. Initial action on the international level on this subject started at an IMCO meeting in June 1978. The Coast Guard can observe the performance of the officers and crew during the preentry inspection, during transit to the terminal, and during discharge operations and can take appropriate action in cases of unsatisfactory performance.

E. RESEARCH RECOMMENDATIONS

Safe LNG operations do not depend on further research. However, the research suggested below should help to reduce both the probabilities and consequences of large spills.

1. Research proposed by others to define the vapor cloud resulting from a large spill on water should help to establish the desirable seaward extent of the traffic-control lanes for LNG ships.

2. Research proposed by others on the fire and radiation effects of a large spill on water should provide a basis for reexamining the adequacy of the LNG ship's fire protection.

3. Others have postulated that failure of the main transfer lines when discharging would result in a maximum credible spill of 100,000 to 500,000 gal (380 to 1900 m^3) of LNG. A spill of this size when discharging is much larger than now used for design. The effects of such a spill should be reviewed particularly in regard to:

a. Fire and radiation effects on the ship and crew.

b. The effects on the ship's structure of an unignited LNG pool on the water beside the ship, and of the unignited LNG on the ship's deck.

c. Practical prevention and mitigation measures beyond current practice.

4. It appears to the panel that significant ship collisions and strandings have not been analyzed systematically for causes and possible design or operational improvements. The foregoing discussion and recommendatons on accident avoidance include known design and operational improvements, but others may be possible. It is recommended that a technical review be made of the accident reports to determine if further improvements are justified.

5. Analyses should be made of the crew and officer training programs for LNG ships used by various organizations. Actual performance should be examined for competence, safety practices, etc. Contingency planning for casualty response should be examined for adequacy, completeness, and suitability for crew training purposes.

6. Requirements for LNG and other hazardous-cargo ships should be more exacting and stringent than for conventional ships. The IMCO Code is mute on the requirements for LNG ships after building inspection and surveys. The Coast Guard requirements are still being developed at the time of this writing. Present and proposed survey and inspection requirements for LNG ships, including both LNG systems and conventional ship systems, should be reviewed for adequacy. Also, while the Coast Guard observes the condition of LNG ships as they are entering port, it does not appear to monitor maintenance comprehensively. This point should be investigated and consideration given to

whether the Coast Guard or the American Bureau of Shipping (ABS) or both should monitor maintenance to assure continued safe operation.

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CHAPTER IV

COLLISION HAZARDS FOR LNG CARRIERS

A. INTRODUCTION

The possibility of LNG spillage caused by collision of the large LNG carriers (50,000 to 165,000 m^3) being used or planned for importing LNG into the United States is a major concern in public safety. The concern exists despite the fact that, since 1959, about 4600 LNG voyages have been made, using some of the busiest routes and harbors worldwide, without such an occurrence. The much larger LPG fleet also has a most encouraging record.

A key part of Environmental Impact Statements related to LNG terminals deals with the development of scenarios for collisions and spills, including probability of occurrence and proposed mitigating measures. Under the Ports and Waterways Safety Act of 1972, the U.S. Coast Guard is responsible for enforcing the necessary mitigating measures.

Spills of up to the full capacity of the vessel have been postulated. However, an almost instantaneous spill of 25,000 m^3 of LNG is generally accepted as the worst credible event. Slower and/or staggered release results in considerably less travel of the vapor cloud.

The consequences of a collision depend strongly on the magnitude, build-up time, and shape of the spill and on the extent and composition of the vapor cloud and its mode of ignition, if any. These factors are covered elsewhere.

This chapter will cover the following points:

- Critical speeds--the speeds at which impacting vessels may penetrate to the cargo tank of the LNG ship
- Probability of collision in transit
- Collision at berth and miscellaneous mishaps
- Mitigating measures

B. CRITICAL COLLISION SPEEDS

The critical collision speed of a vessel impacting an LNG carrier is calculated typically by applying the semi-empirical equation developed by Minorsky, 1959. This method is based on analyses of actual high-energy collisions, including correlation of the kinetic energy absorbed with the extent of structural damage. The method has been examined critically since 1959 by investigators in the U.S., Europe, and Japan, whose work has included the use of model tests. However, nothing better than the Minorsky approach has been developed.

Figure 1 shows the results of calculations made with the Minorsky equation for different types of LNG ships when struck at 90 degrees. The displacements of the impacting ships (tankers, bulk carriers, cargo liners, trawlers, tugs, naval vessels, etc.) range from less than 1000 to more than 100,000 long tons. With membrane tanks, the critical speed is that necessary to contact the LNG ship's inner hull, as it is assumed that membrane tanks have little resistance to tearing. Freestanding tanks (cylindrical, prismatic, or spherical) would have somewhat greater resistance, so the critical speed would be higher, as shown by the curve related to speeds necessary to penetrate to the spherical tank at its point closest to the outer hull.

At normal port and channel speeds--8 to 10 knots--vessels of more than 5,000 to 10,000 tons displacement constitute a potential hazard if they strike the LNG ship at its most vulnerable point at an angle of 90 degrees. Thus, traffic control and speed regulation are necessary in channels and harbors to avoid collisions of serious consequences.

Should the LNG carrier be the impacting vessel, minimum collision speeds of 12 to 15 knots have been calculated as necessary to breach the forward tank.

The Minorsky correlation has been criticized in particular because its data base does not reflect the double-hull construction of LNG carriers. Efforts are under way in the U.S. (USCG-SRC) and in Europe (Bureau Veritas) to develop better analytical tools. It does not seem probable, however, that the results will affect the major conclusion--that ships of more than 5,000 to 10,000 tons may significantly damage an LNG cargo tank under certain conditions of collision.

C. COLLISION PROBABILITY IN TRANSIT

More than 80 percent of ship collisions occur in coastal and harbor waters. A number of methods are used to evaluate the risk of collision and spillage associated with

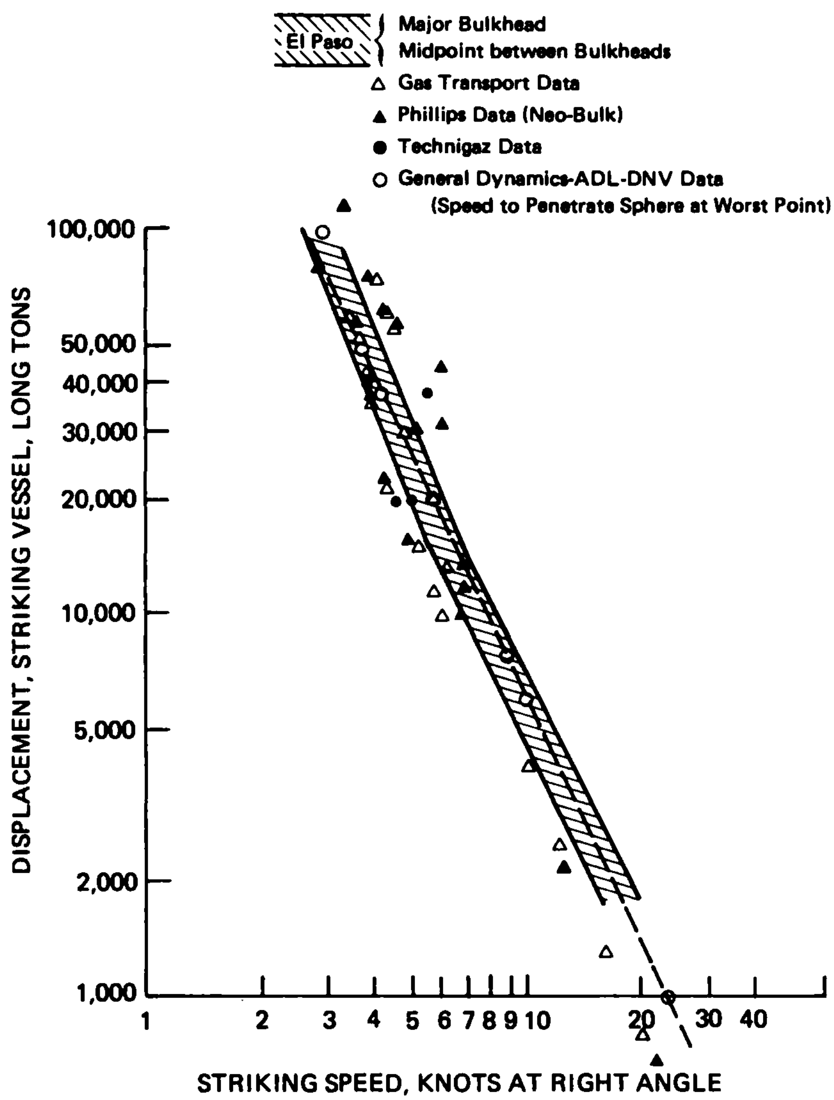

Figure 1 Striking Vessel Displacement vs. Normal Impact Speed to Reach the Inner Hull of Large LNG Carriers (71,500-130,000 m^3)

a given terminal. These methods all start in a similar way and diverge according to the degree of analytical detail (See also Chapter X, Section E).

First, the traffic patterns are analyzed and forecast over the life of the project by:

- Sources and traffic lanes (primary, secondary, tertiary in order of importance)
- Commodity flows and vessel types and sizes

Then, the LNG carrier is introduced and a collision probability calculated using either historical statistics, analytical or Monte Carlo simulations, or a combination of both. Historical approaches often rely on Bovet's analysis of Minorsky's data base (Bovet, 1971). The analytical methods involve selection of an encounter range (minimum distance: 1 or 2 nautical miles) and calculation of the probability that it will occur.

There are problems with each of these methods. The historical approach is often not site-specific because of inadequate local data. This approach also does not take into account the effect of Vessel Traffic System (VTS) or new operating procedures, except through a "VTS reduction factor" or other somewhat artificial reduction coefficients. With the analytical approaches there have been difficulties in proceeding beyond the encounter range, and attempts have been made to fall back on history. However, the recently available Ship Maneuvering Simulators, such as the Computer Aided Operations Research Facility (CAORF) at the Kings Point Merchant Marine Academy, provide further insight into what may happen in "potential collision situations," including human error, which has been found to play a role in about 80 percent of actual collisions.

The CAORF bridge simulator has been used recently (Reese and Grossman, 1978) to compare several alternative LNG-terminal sites on the California coast. In this study, a Monte Carlo simulation was used to develop the frequency, geography, and geometry of encounters, so that the most frequent situations could be modeled on the simulator. The approach provided an improved measure of the risk of collision and spillage. Also, it has led to the development of more specific mitigating measures: navigation aids aboard and outside the vessel and improved operating procedures. Another study (Mara, 1978) concentrated on collision-avoidance equipment in restrained channels. Here, the simulator showed substantial benefits from a navigation option which displays channel limits on the PPI scope of the Collision Avoidance System.

D. COLLISION AT DOCK

During berthing, a ship's approach speed is reduced substantially below the critical speed to avoid damage to the hull and the breasting dolphins. However, passing vessels may present a hazard to a ship at berth. The Methane Princess suffered a minor collision aft at Canvey Island and two near-misses occurred at Le Havre over the 15-20-year history of those two LNG terminals. Site-selection, exclusion areas, and enforced operating procedures for passing vessels can and must be designed to eliminate such risks.

Besides the potential for ship-to-ship collisions, impact from flying objects has been considered where warranted (under aircraft paths, within missile ranges). These considerations also have resulted in specific procedures.

E. MITIGATING MEASURES

The U.S. Coast Guard develops and enforces LPG-LNG Operation/Emergency Plans in each existing LNG terminal under the Ports and Waterways Safety Act of 1972. For new terminals, the Coast Guard is often asked to testify on the suitability of a given site in the course of certain permit applications.

1. Collision in Transit

The LPG-LNG Operation/Emergency Plan requires adequate notice so that the vessel may be boarded and inspected before entering port at the discretion of the Commandant. This inspection is compulsory at first entry (to confirm the Letter of Compliance) and at each subsequent entry in most harbors. The Coast Guard cutter that brings out the inspection party escorts the vessel during transit to the berth.

The collision problem is treated in site-specific fashion; good daylight visibility is required, traffic may be eliminated within a "moving exclusion area," etc. However, concern has been expressed by the public and by the General Accounting Office, 1978, over the fact that the Safety Inspection checklist is generally limited to cargo systems; fire-prevention and fire-fighting systems; and communications, including warning signals. For example, the checklist does not include detailed checks of navigational aids and maneuvering equipment, such as electric power, steering gear, and their backups.

Furthermore, only the most recent Operation/Emergency Plans have specified the level of specialized crew training as other than "sufficient": "Crews aboard foreign LNG vessels shall have specialized LNG related training or experience of a level comparable to or greater than that originally required of the crews of the dedicated U.S. flag LNG carriers calling at Cove Point, Md." (U.S. Coast Guard MSO, 1978).

Finally, the consequences of LNG spills may extend beyond several miles. The Coast Guard, therefore, may be required to "monitor" the vessel beyond the usual anchorage if offshore traffic and weather (wind direction) warrant special precautions.

2. Collision at Berth

The inoperative terminal at Staten Island is a controversial example of risk which includes possible collision of a berthed ship with a vessel proceeding down the adjacent channel. The use of "camels" or dumb barges alongside the berthed LNG carrier has been suggested as protection against such collisions. However, speed limits and an anchor watch for the passing vessel would appear to be more effective. Tug control (effective or immediately available through a slack tow at the bow) should be an additional precaution for a passing vessel whose displacement is large enough so that the lower acceptable speed limit may be incompatible with maneuverability.

3. Site Approval

The U.S. Coast Guard appears to have been reluctant to intervene in public hearings during processing of permits for new sites, although it conducts its own hearings in some cases. Public hearings can be a frustrating and imperfect process once the local opposition and the site developer have reached polarized and vested positions. It has been suggested, therefore, that early citizen participation in such matters be fostered, along the lines of the Japanese "Safe Entry Committee" (de Frondeville, 1977). The local Coast Guard Commandant customarily draws on local expertise (pilots, etc.) in developing his operating plan. But the currently sensitive political situation in inhabited areas appears to dictate more open and participative procedures, instituted as early as possible and before the official permit applications are made. Coordination with other cognizant and permit-granting state and federal agencies is important even at this early stage (National Academy of Sciences, 1979).

F. CONCLUSIONS AND RECOMMENDATIONS

Collision phenomena and consequences, such as critical speed of impact, shape and timing of the spill, and cloud travel and explosivity, are subject to some uncertainties. Research, planned or in progress, will be more useful in formulating contingency plans and guiding site selection than in eliminating collision and its consequences, which will remain of concern in all but minor collisions. The prevention of collision through operating procedures and design precautions is thus of paramount concern to the U.S. Coast Guard.

The importance of the "man in the loop," illustrated by the presence of human error in about 80 percent of known collisions, suggests increased use of simulators of the CAORF (Kings Point) and MSI (La Guardia) type in research and training. Such bridge-simulating systems are powerful instruments for refining estimates of risk and developing mitigating measures that are site-specific. Also, they offer opportunities, not yet fully exploited, in the areas of master and pilot decision-making analysis, effects of stress and fatigue, effectiveness of training programs or new equipment, efficient interaction between shore and ship, etc.

Besides human error, equipment failure is a major cause of collision. There is little statistical information on the probability of failure of critical navigation and maneuvering equipment on board ship. A reliability information bank would be a useful step toward filling this information gap.

In its current efforts to provide comprehensive guidelines to local Commandants for their LNG-LPG Operating Plans the U.S. Coast Guard should:

1. Address more specifically or quantitatively public concerns about:

   - Maneuvering and navigational capability of the vessel offshore
   - Early offshore control when warranted by traffic and weather conditions within the "cloud" safety zone
   - Effective escort during transit to the berth
   - Exclusion area for other traffic during transit of the LNG vessel
   - Speed regulations
   - Protection of the LNG vessel from collision while at berth

2. Encourage early and open participation by local specialists (not only pilots and harbor officials, but insurance people, etc.) as well as by affected or duly concerned citizens during the design and site-selection process for new terminals

3. Coordinate its actions closely with other permit-granting agencies, both federal and state

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CHAPTER V

VAPORIZATION AND DISPERSION OF LNG FOLLOWING A SPILL ON LAND OR WATER

A. INTRODUCTION

LNG accidents, postulated and real, involve a loss of a liquid that boils far below ambient temperature. The spilled liquid vaporizes, forming a flammable cloud that disperses downwind. This chapter summarizes a critical review and assessment of the literature dealing with LNG vaporization and dispersion rates related to possible LNG spills on land and water The chapter also identifies key research needs. Appendix B documents the assertions made and provides a comprehensive technical evaluation of previous work. Ignition and combustion are covered in Chapters VII and VIII.

The focus here is on accidents that involve a significant loss of LNG into the environment. Small leaks do not pose serious hazards either to plant personnel or to the general public.

In assessing the hazard posed by serious accidents in shore terminals, one assumes either a line failure at maximum flow or a catastrophic tank failure with loss of all liquid. In both cases, it is imperative to (a) contain the liquid within a diked area and (b) ascertain that flammable concentrations of vaporized LNG do not appear outside the property limits and jeoparidze the general public. Reasonable arguments may be made that catastrophic tank failure is not a credible accident, considering current U.S. technology, so that only the "linebreak" accident need be considered. However, this line of reasoning seems tenable only if it can be shown that the probability of the catastrophic event's ever occurring is sufficiently low and that, even if the event did occur, no extremely serious loss of life and property would result. Further, methods are now available, although often expensive, for reducing the risk from even rapid, complete failure of a full tank of LNG to an acceptable level (See Section B.1).

There is no convenient way to reduce the risks from a serious LNG spill on water. Large quantities of LNG are involved, and containing the spill in a small area is still an unresolved problem. A very large cloud forms rapidly and remains a hazard for a significant time. Methods, probably conservative, are available for estimating the maximum duration and extent of the cloud. The most important element is prevention. If an accident does occur, a disaster can result at considerable distances from the ship. Little can be done to prevent or modify the vaporization and dispersion processes.

B. SPILLS ON LAND

1. Accidents

Should an accident occur within a shore terminal, the spreading of LNG is expected to be limited by confining dikes. This would certainly be the case with line or tank failure within the primary dike that encloses the tank itself. While the containing dikes are designed to hold the maximum amount of liquid that could be spilled, their efficacy has never been tested in a catastrophic accident where the storage tank is emptied in a short time. Rather, hazard analyses are normally based on a "credible" accident as specified in the National Fire Protection Association 59A Code. Such an event assumes a piping failure and is called the "design" case. To be conservative, the largest pipe that penetrates the tank is the one chosen to fail. The leak is assumed to occur at the maximum rate possible with a full tank of liquid or with maximum flow in the line. There may or may not be a time limitation on this hypothesized leak. Dikes of current design will contain liquid from leaks of this kind.

The catastrophic accident assumes rapid and complete tank failure and is far more drastic than piping failure. Hazard calculations based on such an accident assume that the space inside the dike is filled "instantaneously" with liquid. However, it is not at all certain that the dike would retain a large flow of LNG from a collapsing tank. With relatively low retaining walls some distance from the tank, significant overflow may be expected. High close-in dikes would be preferable in case of a major accident as they are normally of stronger construction and would withstand greater stresses.

In any case, LNG lost into the diked area vaporizes, and vapor normally is lost over the dike wall. The rate of vaporization decreases with time, so the modeling of such accidents usually involves the assumption of a transient yet continuous source. The modeling of LNG spills into diked enclosures involves three major elements: the boiling rate on the floor and walls of the dike; the effect of dike geometry on the rate of vapor loss; and the downwind dispersion characteristics of vapor overflowing the dike.

2. Vaporization

All known boiling rates of LNG on soil, sand, and insulated concrete are well correlated by a one-dimensional heat-transfer analysis where

$$\frac{\text{Rate of vaporization}}{\text{Area of substrate contacting LNG}} = F/t^{\frac{1}{2}}$$

t is the time after the spill and F is a boiling parameter characteristic of the substrate contacting the LNG. Packed soil is normally used in the floors and walls of LNG dikes and F factors are relatively high. Significantly lower vaporization rates may be achieved with other dike-floor materials. Dycon and Zonolite insulating concretes, made by the Koppers Co. and W.R. Grace, respectively, have been tested and show much lower F factors than soil. Dry polyurethane slabs also are good insulations, but maintenance can be a problem. A new and quite promising and economical dike-floor insulation is corrugated aluminum or steel over packed soil. This concept deserves further study. The use of dike-floor/wall materials with low F factors is particularly important because the maximum rate of flow of vapor from a diked enclosure is proportional to F^2.

Rates of vaporization of LNG in dikes areas also are affected by the design of the dike. Sumps placed in critical zones are often beneficial for small spills, as they would collect the LNG in a localized area with minimum contact between the warm LNG and the substrate. Also, sloped dike floors have been shown analytically to reduce the heat-transfer area between the substrate and the boiling LNG for the design-case spill. The floors of essentially all LNG dikes are sloped downward from the tank to some degree to remove rain or melted snow. However, steeper angles ($\sim 3°$ to $5°$) will cause LNG to flow away from the tank and into zones near the dike wall where sumps could be placed. Compartmentalization of dikes has been suggested, but is not recommended because it may, in fact, increase the vapor-production rate. Vapor-holding techniques, such as solid or leaky fences on top of the dike wall, are not normally satisfactory for reducing vapor-generation rates.

With current knowledge, one can satisfactorily estimate the rate of generation of vapor from an LNG spill in a diked area if the thermal properties of the substrate are known and if the scenario of the spill is detailed. More importantly, methods now available allow the dike to be designed to limit vaporization rates. Dike-floor insulations, sloping dikes, sumps, etc., will--at additional cost--reduce the net vaporization rate for either the design or catastrophic accident.

Control of LNG spills and vaporization on land poses the following research needs:

- Continued investigation of inexpensive, effective dike-floor/wall insulations. The proposed use of corrugated aluminum is an example.
- More careful examination of the results expected from a catastrophic spill, especially for the case of low dikes some distance from the tank. Are such dikes effective? Should high, close-in dikes be used?
- Development of accident scenarios that involve a tank with a cryogenic inner tank but a carbon-steel outer tank. Under what conditions will a severe leak from the inner vessel lead to rapid cooling and failure of the the outer vessel? Should new LNG tanks be required to have both inner and outer tanks made from materials that retain their strength at LNG temperatures?

3. Dispersion of LNG Vapor

LNG boiling within a confining dike produces essentially pure methane vapor because the ethane and propane in the liquid are much less volatile at LNG temperatures. The methane vapor, at about 112°K, is denser than the surrounding air and tends to collect in the diked area until it overflows. Dispersion downwind then begins.

There have been a number of small-scale studies of how LNG vapor mixes with air, but most were not well instrumented and controlled. Significant data have come from only two test programs--those of Gaz de France at the FOS-SUR-MER terminal and the American Gas Association at San Clemente, CA. The largest spill--50 m³ of LNG spilled rapidly--was made in the AGA tests in a circular basin (470 m²) of packed earth with low dike walls. Because of test limitations and prevailing weather, essentially no data were obtained for stable weather or for spills contained within high dike walls. The Gaz de France tests were made at high humidity, whereas the absolute humidity for the AGA tests was relatively low.

A major qualitative difference exists between the dispersion behavior reported for land spills and water spills (See Appendix B, Section C). In the land spills to date, dispersion was rapid even vertically. In water spills, the vapor cloud was more stable, dispersed slowly vertically, and spread laterally.

Although there are few experimental data to support vapor dispersion models, many models have been proposed. In contrast to the rather diverse models suggested for water spills of LNG, almost all models that purport to yield downwind concentrations of methane after a spill in a diked enclosure are quite similar. Except for the model described by Van Ulden, each is in essence a variation of the Sutton Gaussian model modified for an area source. Even similar dispersion parameters were used. The differences lie in minor modifications to account for such items as turbulence caused by wind flowing over a tank or dike wall, by a plume "lift" where humidity is high, etc.

The British Gas Corporation compared the more common models with a standard spill case and found that all give similar hazard zones downwind. All yield good agreement with the few reliable measurements of downwind concentration following a spill of any reasonable size. The Van Ulden model assumes a dense cloud of vapor that spreads laterally with little dispersion or mixing with the atmosphere. It appeared to correlate well with limited data for a Freon-12 spill. Most of the models are derived so as to be applicable with both high or low dikes or when the atmosphere is quite stable. However, the predictions for high dike cases and for stable atmospheres cannot be confirmed because no experimental data are available.

A special case that has been little studied is dispersion of vapor upon serious failure of an in-ground tank. One might postulate failure of the liquid container and rapid boiling of LNG as the insulation and outer concrete wall cool rapidly. Another example is collapse of part of the roof into the tank. In both cases, if the cooling rate of the structures can be estimated and converted into an LNG vaporization rate, existing vapor-dispersion models can be used to predict potentially hazardous zones downwind. A vapor source at grade is probably the best assumption for an accident scenario of this type.

Suppression measures, such as water sprays or foam, have not been shown to change significantly the rates of vapor dispersion from large spills.

In summary, for postulated spills of LNG into diked enclosures, well-developed, simple Gaussian dispersion models appear to allow a reasonably accurate estimate of the average downwind concentration of methane, assuming the rate of flow of vapor from the dike can be estimated. However, important areas of uncertainty remain. The research needs are:

- Clarification of the effect of high dikes on the dispersion process. Does dispersion begin at the dike height or do the vapors fall to the ground outside the dike before dispersing?
- Clarification of the effect on dispersion by eddy shedding and turbulence caused by the tank, the dike, nearby structures, etc.
- Development of dispersion correlations for points not far downwind from the dike, where the Gaussian models are least accurate.
- Extension of existing models to very stable weather conditions. The models have been tested with LNG only in neutral to slightly stable weather.

These four problems might best be studied in wind tunnels, and work of this nature is in progress at Colorado State University.

C. UNCONFINED SPILLS ON WATER

1. Scenarios

Most scenarios for LNG spills on water assume the instantaneous release of a large quantity of LNG--about 25,000 m^3--on the surface to simulate the loss of a tank on a large LNG carrier. Accidents such as the breakage of a transfer line during unloading, deliberate jettison, etc., are not usually considered, since they are unlikely to affect public safety. In all but one scenario the spill has been assumed to be radial. Accidents leading to loss of LNG near the waterline might be expected to produce a pool which is skewed.

On water LNG is assumed to spread and boil. The vapor cloud is generated in a short time and behaves as an entity which spreads because of gravity, entrains air, and eventually, if not ignited, disperses downwind.

2. Vaporization and Spreading of the Liquid

Boiling rates of LNG on water have been measured mostly with the water in a fixed-area calorimeter. Ultra pure methane boils initially at a low heat flux, but the rate increases with time to a maximum near 100 kW/m^2. Thereafter the rate decreases. With LNG containing heavier hydrocarbons, the rate rises more rapidly to a maximum that often exceeds 150 kW/m^2 before dropping. With any significant amount (about 5 percent) of propane present, the flux is quite high--more than 200 kW/m^2--initially but soon decreases.

These phenomena usually are explained by assuming that initially the LNG film-boils on water. With very pure methane, about 40 s is required for ice to form and cool. Nucleate boiling can then occur with concomitant higher fluxes. If heavier hydrocarbons are present, less time is required to attain the maximum flux, and the maximum flux is significantly larger. If any significant amount (about 5 percent) of propane is present, the time required to reach maximum flux is so short that it is not normally observed. The later decrease in heat flux results from resistance to heat transfer across the growing ice shield. A computational scheme is available for predicting the variation of boiling flux with time for LNG boiling on water in a confined area. This technique also allows for variation in composition and boiling point caused by weathering of LNG.

Unconfined spills boil and spread simultaneously. Few experimental tests have been made to verify the theoretical models that have been proposed. Most analyses show that the spreading rate decreases with the square root of time and is proportional to the 0.25 power of the original volume of the spill. Constant boiling fluxes are assumed. In the few tests to date, little or no ice has been observed to form in unconfined spills. Thus there is a real question as to the value of the boiling flux. Some analysts use the confined-area fluxes (with ice), while others argue that the low film-boiling values would be more realistic. Since these fluxes differ by perhaps a factor of 10, the calculated rates of formation of the vapor cloud vary significantly.

3. Vapor Dispersion

Only two large test programs have been conducted with LNG spills on water. In the Shell Gadila tests, the LNG was jettisoned over the stern of the ship but essentially evaporated before striking the water. In the Esso Matagorda Bay tests, the LNG was discharged via nozzles and passed through a wide arc to the surface; even here significant evaporation probably occurred. LNG flow rates in the two cases were as high as 1140 m^3/h. Low, wide vapor clouds were observed in both cases. Only the visible cloud was tracked in the Shell Gadila tests; downwind methane concentrations and temperatures were measured in the Esso tests.

A number of theoretical models have been proposed for estimating downwind concentrations of methane following a large, essentially instantaneous spill of LNG on water. (See Table 1, Appendix A). All assume an initial period in which LNG spreads radially and boils. The computational methods differ, but the calculated values agree surprisingly well. The vapor cloud that is formed resembles a rather flat pancake whose diameter equals the maximum radius of the pool. The cloud is not very thick; for a spill of 25,000 m³ the values range from 10 to 20 m.

Following evaporation, most models incorporate a "vapor-cloud spread" phase in which the dense,cold methane vapor expands radially. The cloud's thickness or volume may increase or decrease depending on whether air entrainment is allowed. In most cases the cloud is assumed to warm by one or all of the following mechanisms: heat transfer from the seawater; heat transfer from the surrounding air; condensation of water vapor in the entrained air. Normally, this cloud-spread phase is terminated when the cloud has attained neutral buoyancy or when the radial velocity becomes equal to the local wind speed. Spreading is computed by very similar methods in all models. Calculations of heat-transfer rates do vary, but the most important difference among models is the allowance for air entrainment. For example, with a 25,000-m³ spill, if reasonable entrainment is allowed, the cloud contains only 20-25 percent methane after the cloud-spread phase of pure methane. Other models allow no entrainment and end with a very flat, wide, cloud of pure methane.

As a final step in modeling, the neutrally buoyant cloud is assumed to disperse. In some models, the cloud disperses instantaneously, in others it sheds vapor continuously. Also, dispersion coefficients chosen differ significantly. Some analysts pick low, instantaneous values quoted for very stable atmospheres. Others use the common Gifford-Pasquill coefficients for continuous plumes. The selection of the value of the source strength and dispersion coefficients effectively dictates the final results.

A model developed by Science Applications, Inc. differs appreciably from those described above. Essentially this technique is a numerical computer code that attempts to account for the vapor-spreading phase and the turbulent-mixing processes in a fundamental manner. The details of the code are embedded in a complex computer program, so it is difficult to assess the method. However, vapor dispersion predictions obtained with this model do differ--often significantly--from those obtained from simpler models. A different numerical code is being developed at

Lawrence Livermore Laboratory, but no details have been released.

It is not all clear how one can best estimate vapor dispersion following a large spill of LNG on water. No tests have been large enough to verify the gravitational vapor-spread phase that is predicted. (The largest spill was about 200 m³ in eight minutes in the Shell Gadila tests.) The difficulties and costs of experimentally simulating very large spills are enormous, and the time and effort might better be spent in examining ways to lessen the probability of an accident.

Research needs in unconfined spills of LNG on water are the following:

- Examination of the scenarios possible if the inner tank of an LNG tanker were broken by ramming or grounding. In particular, clarify the results expected from mixing LNG and water in the space between the inner tank and hull. Determine if flameless vapor explosions are possible and, if they are, their effect on the ship's integrity (See Chapter VI).

- Careful evaluation of any further model development or experimental program to assure that the results would be meaningful and cost-effective. In particular, the degree of entrainment during the vapor-gravitational-spread phase needs further study but this may only be possible in very large tests.

- Experimental determination of the boiling/spreading rates of unconfined spills of LNG on water. Establish heat-transfer rates and clarify whether ice forms or not.

D. CRITERIA FOR PEAK-TO-AVERAGE CONCENTRATION

The vapor-dispersion models discussed here can be used to estimate average methane concentrations downwind of an LNG spill. Concern has been expressed that these average values are inadequate for determining distances downwind at which hazard exists. The argument is that concentrations in major portions of the cloud could be above the lower flammable limit while the average concentration was below the limit. It is necessary, therefore, to establish criteria for the ratio of peak-to-average (P/A) concentrations of methane that can be expected in a real accident.

Analyses show that P/A values are complex functions of many variables. In most experiments, small, continuous sources have been used. Relatively high P/A ratios have been observed because of fluctuations in concentration caused by lateral eddying and dispersion at the edges of the cloud, combined with lateral movement of the cloud back and forth across the sensors. In a wide LNG cloud, lateral mixing would occur at the edges, but P/A ratios in the bulk of the cloud should be much lower than observed in experiments. Sampling time is another important variable--P/A values increase with a decrease in sampling time. Transient sources also affect P/A values because the average concentration at any point downwind also varies with time. Rough terrain and other sources of atmospheric turbulence increase P/A values; the lowest values occur in stable atmospheres. P/A values for gusty weather should not be coupled with analyses in which dispersion coefficients are based on stable weather.

In large LNG clouds dispersing in stable weather, the P/A ratio would be expected to be near 2 in the center of the cloud about 10 percent of the time. The ratio would increase to 3 about 1 percent of the time. These values agree with the results of the AGA land tests and the Esso water spills.

There are no pressing research needs for establishing criteria for P/A ratios.

CHAPTER VI

FLAMELESS VAPOR EXPLOSIONS

A. INTRODUCTION

During the early years of LNG technology there were numerous incidents in which LNG poured onto water produced noisy, unexpected pops and bangs--flameless vapor explosions. Usually this LNG was the heel from a storage tank or the residue from some large experiment. The incidents were irrelevant to the normal operation of an LNG installation, so accounts of the phenomenon understandably did not appear in the technical literature.

The first publicized experience with flameless vapor explosions of LNG-water occurred during Coast Guard-sponsored research at the Bureau of Mines in 1970 (Burgess et al., 1970a). The spreading rates of LNG spills on water were being studied on a pond that normally was used for underwater testing of explosives. Seventy gallons of LNG were being poured when there were two noisy explosions, the first coming 1/8 s after the LNG first contacted the water. Since the incident was unexpected, overpressures were not measured. However, two motion picture cameras preserved the scene.

Lacking a quantitative measure of the magnitude of the explosions, the research team canvassed the witnesses. They offered the observation that the noise was comparable to the explosion of a stick of dynamite. This unfortunate analogy was included in the news release that accompanied the Bureau's Report of Investigations (Burgess et al., 1970b) and triggered an intense effort by industry to understand and quantify this new possibility of hazard.

Many lines of inquiry--impurities in the pond water, impurities in the LNG, hydrate formation, etc.,--proved unfruitful. But a team at the Shell Pipe Line Company went directly to the tenable explanation that the explosions resulted from superheating of the cryogenic liquid (Enger and Hartman, 1972). The team studied the compositions of hydrocarbon blends that produce explosions when spilled onto water (Figure 2) and determined that an LNG mixture containing more than 40 percent methane, should not explode on water. In the euphoria of this reassuring result, other investigators turned their attention to the more serious hazard of flammability.

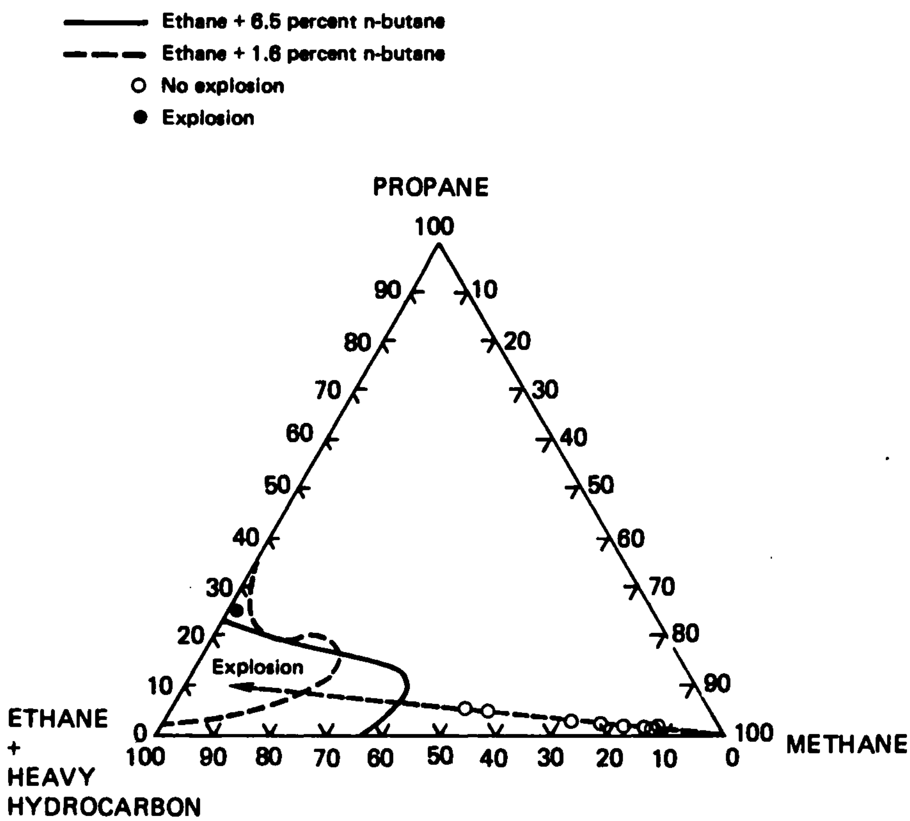

Figure 2 Aging Curve for LNG in Relation to Zone of Vapor Explosions (Enger and Hartman, 1972)

A second incident--anomolous in terms of the Shell conclusion--occurred during vapor dispersion experiments by an American Petroleum Institute (API) group at Matagorda Bay, Texas (Feldbauer et al., 1972). Some 1880 gal of LNG (nominally 85 percent methane) were spilled onto seawater over a period of 25 s. Seventeen seconds after the spill ended a flameless explosion occurred which was followed by three more within 2 to 3 s. These explosions, too, were unexpected, so again the overpressures were not measured.

These two incidents, at the Bureau of Mines and at Matagorda Bay, comprise the experience that has received most attention. However, another aspect of the problem was the subject of considerable research. The Japanese evidently had experience with explosions when LNG was added to heavy hydrocarbons (Kitagawa, private communication). This phenomenon was discovered independently by Esso Research and Engineering Co. (May, private communication). As a result of these studies, reviews of LNG hazards sometimes have included warnings against the use of LNG vessels for dual service, that is, to transport also LPG.

B. CONCEPT OF A LIMIT OF SUPERHEAT

A physical description of flameless vapor explosions was achieved within a few months after the problem became know (Enger and Hartman, 1972; Nakanishi and Reid, 1971; Katz and Sliepcevich, 1971). This work was a quite remarkable application of basic research to a safety question. Following is a condensation of the consensus of investigators in 1971.

When LNG contacts a warmer liquid such as water, its contact surface is raised momentarily to a temperature above its boiling point. If ice crystals or other nuclei for boiling are present, vaporization begins quickly to return the system to a stable state. But if no nuclei are present--normally a difficult condition to assure--the surface liquid continues to warm to a limiting temperature at which vaporization develops suddenly and spontaneously. This "homogeneous nucleation" produces a local pressure disturbance which can disperse LNG at hundreds of feet per second.

The limiting temperature, T_{sl}, can be estimated from kinetic theory or from thermodynamics and can also be measured in the laboratory. For most liquids, T_{sl} lies in the range 0.88 to 0.90 T_c where T_c is the liquid's critical temperature in degrees Kelvin.

Normally, if the temperature at the interface of the two liquids, T_i, is less than T_{sl}, vaporization may be rapid (nucleate boiling) but not explosive. If the interface temperature is more than about 1.10 T_{sl}, a vapor film develops between the liquids before any appreciable amount of cold liquid can achieve "homogeneous nucleation" (film boiling). The necessary condition for explosion

$$T_i \sim (1.00\text{-}1.10)\ T_{sl} \qquad (1)$$

was illustrated by the Shell Pipe Line finding that propane explodes violently on water but only when the water is at 327° to 343°K. The significance of Figure 2 is that only the compositions at the lower left of the triangular diagram can safisfy Equation 1. When liquid methane is spilled on water, $T_i \sim 1.76\ T_{sl}$ and explosions have never been observed.

Such was the consensus of 1971, and the anomolous API explosion of LNG (85 percent methane) on water was rationalized as follows:

In a small spill of LNG on water, the spreading pool is never very thick. Before its methane content has fallen to 40 percent through vaporization, the pool becomes too thin to remain coherent. Thus the pool breaks into small patches which do pop and crackle harmlessly in their final stages of disappearance. But in a sufficiently large spill, it is possible for most of the methane to have vaporized while the pool is still thick enough to remain coherent (the limiting thickness for breakup is said to be about 1.7 mm). Based on this reasoning, the API team calculated the curve of Figure 3; methane contents and spill sizes to the left of the curve make the LNG susceptible to vapor explosion (Feldbauer et al., 1972).

The Bureau of Mines explosion could not be rationalized on the foregoing basis because it was maintained that the LNG in question was close to 95 percent methane and the delay to explosion was only 1/8 s. This small controversy may have sustained some interest in vapor explosions. But subsequent research on superheat limits was stimulated mainly by extension of the concept to other industrial hazards.

Many explosions have occurred with water as the cold, volatile liquid in contact with molten steel, aluminum, or titanium or various molten salts. Such explosions have led to extensive damage and even to fatalities. However, it must be recognized that water can be much more energetically superheated than LNG and also that most industrial accidents involve some kind of confinement. The premise in assessing the hazards of LNG spills is that the cryogen is spreading in a thin layer on a broad, flat surface.

A recent review attempts to synthesize the observations relating to all types of flameless vapor explosions (Reid, 1978). One particular new factor appears when pure liquid

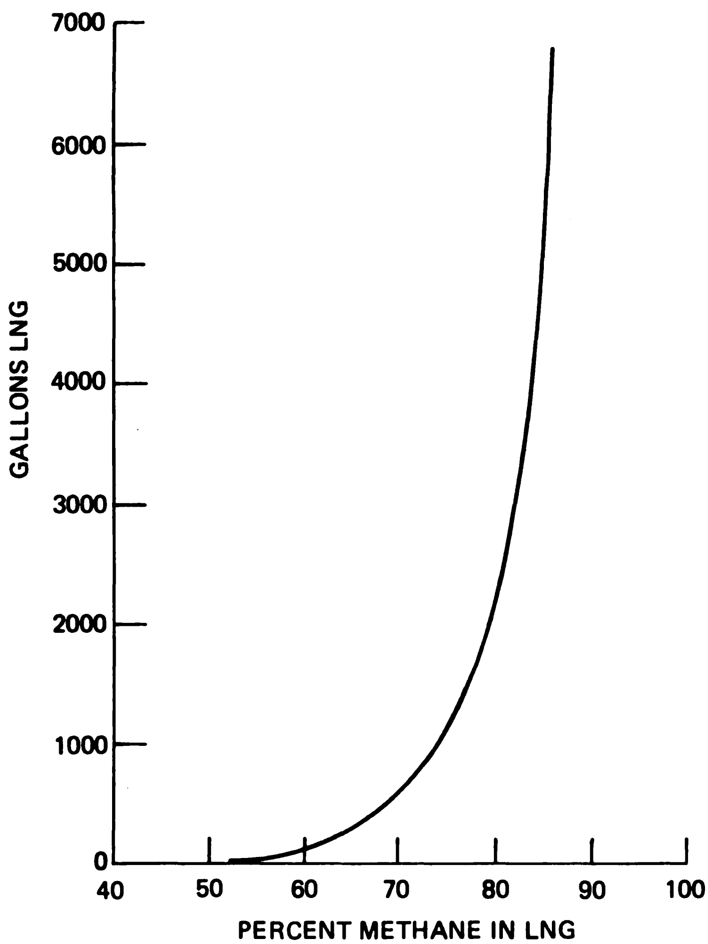

Figure 3 Calculated Minimum Spill Size for "Explosion" (Feldbauer et al., 1972)

methane or ethane strikes water at velocities such as 10 to 20 m/s; interactions and explosions occur that are not observed on pouring the liquids together (Porteus and Reid, 1976).

C. RATIONALE FOR DOWNGRADING THE HAZARD OF VAPOR EXPLOSIONS

In reports and briefings of 1972 vintage, the point that vapor explosions are an insignificant hazard relative to fires and combustion-supported explosions was argued in three general ways:

1. The amount of cryogenic materials involved in vapor explosion must be very small relative to the amount spilled
2. The energy yield of a vapor explosion must be very small relative to explosions involving combustion reactions
3. The geometry of an unconfined spill provides for optimum dissipation of vapor-explosion energy in the most harmless way

It is worthwhile to amplify these arguments somewhat. If one begins with an LNG containing 95 mole percent methane, 90 mole percent of the mixture must vaporize to reduce the heel to 50 mole percent methane; even further vaporization must occur to reach the explosive range of Figure 2. Also, the top surface of the pool of LNG on water will be at the boiling point while the LNG-water interface approaches T_{sl}; at any conceivable temperature gradient, only a tiny fraction of the cryogen can be within a few degrees of T_{sl}. Finally, in a spreading pool of perhaps 100-m diameter, the composition and temperature of a volume element at the edge must differ sharply from the composition and temperature at the center; it is inconceivable that any large fraction of the pool could approach T_{sl} at any one time.

When a volume element of liquid is subject to "homogenous nucleation," the maximum pressure developed is the vapor pressure of the liquid at T_{sl}; this is of the order of 20 atm for LNG--comparable to a gas explosion involving a very thin layer of gas. The energy release cannot exceed the energy of superheat, which is of the order of 25 cal/g of methane; this compares with 330 cal/g for a lean-limit explosive gas mixture and with 1100 cal/g for TNT.

If the accident under consideration is a broken transfer line or a gash in the side of a ship, we are indeed thinking of a spreading pool; the center of gravity of any large mass of vapor-exploding LNG must necessarily be at some distance from the hull of the ship or any other target. And since the LNG-water interface is "capped" by only a thin layer of LNG, most of the explosion's energy will be dissipated in blowing LNG into the atmosphere. Finally, the major concern expressed about vapor explosions was that the shock might ignite a flammable hydrocarbon-air mixture in the vicinity. This possibility seems to be negated by the absence of ignition in any of the thousands of "bangs" that have occurred in experimental programs.

D. NEED FOR ADDITIONAL RESEARCH

In the opinion of the panel the judgments on small hazards resulting from flameless vapor explosions reinforce the views generally accepted in the early 1970s. However, the following research is recommended to clarify several additional issues:

1. The assumption that a spill on water will be unconfined should be reviewed. With present ship design there are large spaces between the outer hull and the LNG tankage which might fill with water and LNG; with such partial confinement one must consider not only the short-duration pressure pulse of "homogeneous nucleation" but also the heaving force of rapid vaporization induced by the explosion.

2. The new finding that methane and ethane can explode on impact with water should be clarified. Research on the phenomenon is in progress (Reid, 1978); the findings presumably will be matched with candidate scenarios for accidents.

3. It seems to have been assumed that hydrocarbon-water and hydrocarbon-hydrocarbon interactions are entirely comparable, and this assumption bears further scrutiny. A difference in scale might arise from the mutual solubilities of hydrocarbons as opposed to the very low solubility of hydrocarbons in water. This bears on the possibility that LNG may sometimes be added to the liquid heel of LNG or LPG that had been carried in the same containment.

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CHAPTER VII

IGNITION OF LNG

A. IGNITION REQUIREMENTS

It is often assumed in hazard analysis that a cloud of flammable vapor and air will be ignited. This assumption is based in part, at least, on laboratory experience that mixtures in the flammable range of composition are in fact very easy to ignite. Nevertheless, most accidental releases of flammable vapors disperse in the air without igniting. The probability that such releases will ignite depends on several factors.

1. Flammability Limits

Combustible gas-oxidant systems normally will ignite only within characteristic, observed limits of composition. The concept of flammability limits has proved a useful and reliable tool in hazard analysis. This is true despite the fact that the limits are not a fundamental property of the gases involved, but depend on how the measurements are made. Many factors affect the experimental measurements. They include temperature, pressure, nature of the diluent, heat and mass transport, etc. There is probably a considerable difference between the observed limits and any possible fundamental limits (Lewis and Von Elbe, 1961; Linnett and Simpson, 1956).

Reported flammability limits show some variation attributable to convection effects. Thus, the reported limits for methane/air depend on whether the flame, once started, propagates up, down, or horizontally, as shown in Table 1.

Table 1 Flammability Limits, Methane/Air

Propagation	Lower % CH_4	Upper % CH_4
Upward	5.35	14.85
Horizontal	5.40	13.95
Downward	5.95	13.95

The limits can also be influenced by induced mixing. The lower limit for methane/air, measured in a 4-l globe, was found to be 5.6 percent; if the mixture was stirred slightly, however, the limit dropped to 5.0 percent. Very rapid stirring raised the lower limit above the quiescent value of 5.6 percent. The flammability limits generally quoted for methane/air are 5 to 15 percent methane. These are conservative values in that they are the outside limits measured in the laboratory.

The presence of an inert gas narrows the range of flammability, and if enough is present ignition is impossible. Nitrogen is the inert gas used as a rule in the holds of LNG ships. Addition of 40 percent to the air will achieve the nonflammability condition. This limit corresponds to a reduction of the oxygen content in the air to about 13 percent. The effect of inert dilution mainly compresses the flammable range by lowering the upper limit.

2. Ignition Energy

A minimum threshold energy is required to ignite a flammable mixture. This ignition energy is a function of experimental variables, in particular the characteristics of the energy source, the composition of the mixture, and rate of flow of the gas. Energy measurements where the source of ignition is a spark obtained by discharging a capacitor bank between two electrodes have been described (Lewis and von Elbe, 1961). Results for methane/air are shown in Figure 4, which illustrates two critical points in terms of safety analysis:

1. With a high-temperature source, such as a spark, the energy required for ignition is extremely small--less than 1 mJ for a stoichiometric mixture.

2. Near the flammability limits the energy requirement rises steeply.

In effect, as long as the mixture is well within the flammable range, the ignition energy is very small. Only at the edges of the flammable range, where the likelihood of ignition is low, does the ignition energy required become significant.

Temperature is also an important criterion for judging ignitability. Methane/air can be ignited by a surface whose temperature exceeds some minimum value. Ignition temperatures which have been suggested as safety guides are shown in Table 2 (National Fire Protection Association 325M, 1977):

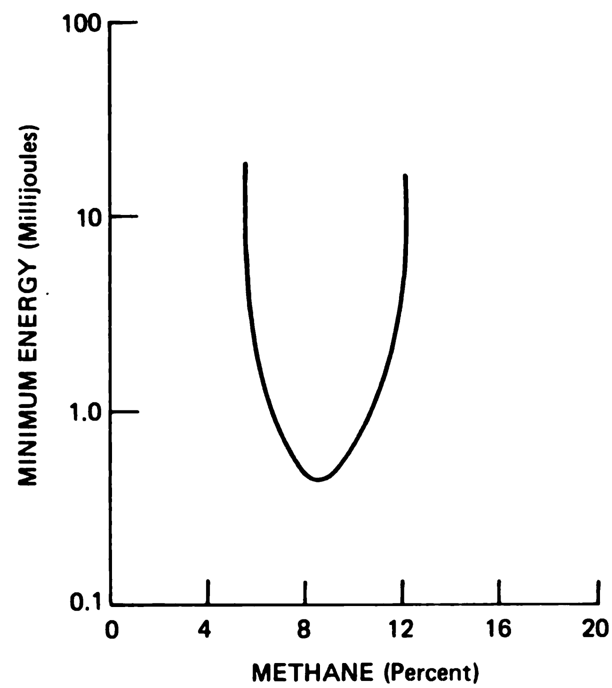

Figure 4 Minimum Spark Ignition Energies for Methane/Air

Table 2 Ignition Temperatures for Various Flammable Materials

Flammable Material	Ignition Temperature in Air* °C	°F
Methane	537	999
Propane	432	842
Benzene	498	928
Methyl Ethyl Ketone	404	759

*Negligible flow rate of gas over surface.

Safe operating practice requires that equipment--light fixtures for example--operating in potentially combustible mixtures be below these temperatures (e.g. 20 percent below).

3. Fluid Flow and Ignition

Ignition requires that a minimum volume of fuel/air mixture be heated to some critical temperature at which chemical reaction liberates heat faster than it can be drained away. Analysis suggests that the required minimum volume and critical temperature are about the same for a flowing system as for a quiescent one, at least within order-of-magnitude (Lewis and von Elbe, 1961, page 435). The ignition energy for a flowing system is usually given as the energy-release rate required to anchor a flame. For an open flame, this energy-release rate (flame size) is so small that almost any open flame will cause ignition so long as the combustible gas is well within flammable limits. For example, a hydrogen/air pilot flame liberating a total of about 150 cal/s (1/3 g of H_2 per min) is sufficient to ignite a stoichiometric natural gas/air mixture flowing at about 52 m/s.

The temperature required for ignition by a hot surface increases substantially with the rate of flow of the combustible gas. In fact, the surface temperatures required to ignite flowing methane/air mixtures are so high that experimenters have preferred to work with more easily ignited fuels.

Surface temperatures of 1100°C or more were required to ignite heptane/air flowing over a heated rod at more than about 18 m/s (Mullen et al., 1949). In other experiments, pellets of 1 to 6 mm diameter were shot at about 4 m/s into the combustible gas to simulate flying sparks, etc., (Silver, 1937; Patterson, 1939, 1940). Ignition of methane/air (near stoichiometric) was obtained with a 6.5-mm platinum sphere at about 1200°C (Silver, 1937). Data reported for other fuels show that surface temperatures required for ignition increase substantially (e.g. by 200°C) for smaller pellets and for higher velocities.

It appears, therefore, that the surface temperature required for ignition is highly variable. For methane/air, with large surfaces and negligible flow rate, the temperature suggested by the National Fire Protection Association--537°C--propably applies. But with moderate velocity past the surface, or with small particles, incandescent surface temperatures (e.g. 1200°C or more) will be required.

4. Ignition By Friction and Impact

Ignition by friction or impact has been investigated extensively because of its importance to mine safety (Powell, 1969).

Impact accompanied by friction can produce temperatures that approach the lower of the melting points of the two materials involved. Impact may embed one material in the other or project fragments as sparks into the surrounding atmosphere. A surrounding flammable mixture may then be ignited in any of several ways.

- The sparks produced may oxidize on contact with the ambient atmosphere and so grow hotter (as do cerium sparks produced by lighter flints, for example). Aluminum, magnesium, and titanium produce reactive sparks that cause ignition under impact conditions where steel will not. Ignition may be caused by very small reactive particles--burning particles of titanium as small as 10 μg, have been shown to ignite methane.

- Nonreactive particles are usually cooler than reactive ones and therefore must be larger to cause ignition. An example is the 6.5 mm-diameter platinum sphere that ignited methane/air at 1200°C (Silver, 1937).

- Hot surfaces produced by friction can ignite methane, depending on the area of the surface, the force applied (which affects temperature), etc. For example, with mild steel on mild steel, methane was ignited under the following conditions:

  Area: 1 in.^{2} steel cube pressed against a steel wheel
  Wheel speed: 4.6 m/s
  Force: 450 lb (pressure of 450 psi).

These conditions undoubtedly would be exceeded in serious ship collisions involving penetration of one of the hulls.

- Embedded material may react with surrounding material--in particular, the thermite reaction between aluminum and rusty steel (iron oxide) is known to occur and can produce very high temperature (e.g. 3000°C). Other metals than aluminum, such as magnesium, also can cause the thermite reaction.

- Friction involving rocks of various types has been extensively investigated. In the largest study of ignition by rubbing rock surfaces, quartzitic rock was found to be necessary for ignition.

B. IGNITION AND FLASHBACK

It is usually assumed that if a vapor/air plume is ignited, the flame will spread to consume most of the plume that is richer in combustible material than the lean limit. (Mixtures that exceed the rich-limit composition will burn by introduction of surrounding air.) It is expected that the flame will flashback--will travel upwind toward the source of the plume; if the plume is still attached to its source, the flame eventually will stabilize there. Experimental data on LNG-plume fires are meager, but support the view that flashback will occur. Small LNG plumes have been ignited and have flashed back to the source (Burgess et al., 1972; Humbert-Basset and Montit, 1971; Lind and Whitson, 1977). Presumably, however, there will be atmospheric conditions (wind speed) where this will not occur.

The laminar burning rate of methane/air mixtures is quite low (about 35 cm/s for a stoichiometric mixture). Flames will propagate at much higher rates, however, because of the gas expansion that occurs on combustion, and possible turbulent mixing. Nonetheless, flame propagation upwind against a high wind probably depends on a zone of low wind speed in the boundary layer at the surface of the plume. The situation is somewhat analogous to flashback in gases flowing through cylindrical tubes. In this case, flashback has been shown to depend on the velocity gradient near the surface as well as on factors such as flame speed and pressure fluctuations caused by the flame itself. Data on methane/air mixtures are shown in Figure 5. Flashback can occur only when (a) the gas velocity somewhere near the wall is low enough to permit it, and (b) the wall is still far enough away that it doesn't quench the flame.

Similar criteria might be expected for flashback along the earth's surface. Differences in flow over land and water, however, probably would exert significant influence:

- The surface of the land is always dynamically rough (Monin, 1970). That is, roughness elements always exceed the thickness of the viscous boundary layer. Consequently, the current near the surface consists of vortices formed by flow past the roughness elements. Flashback would be expected to occur readily in this kind of flow.

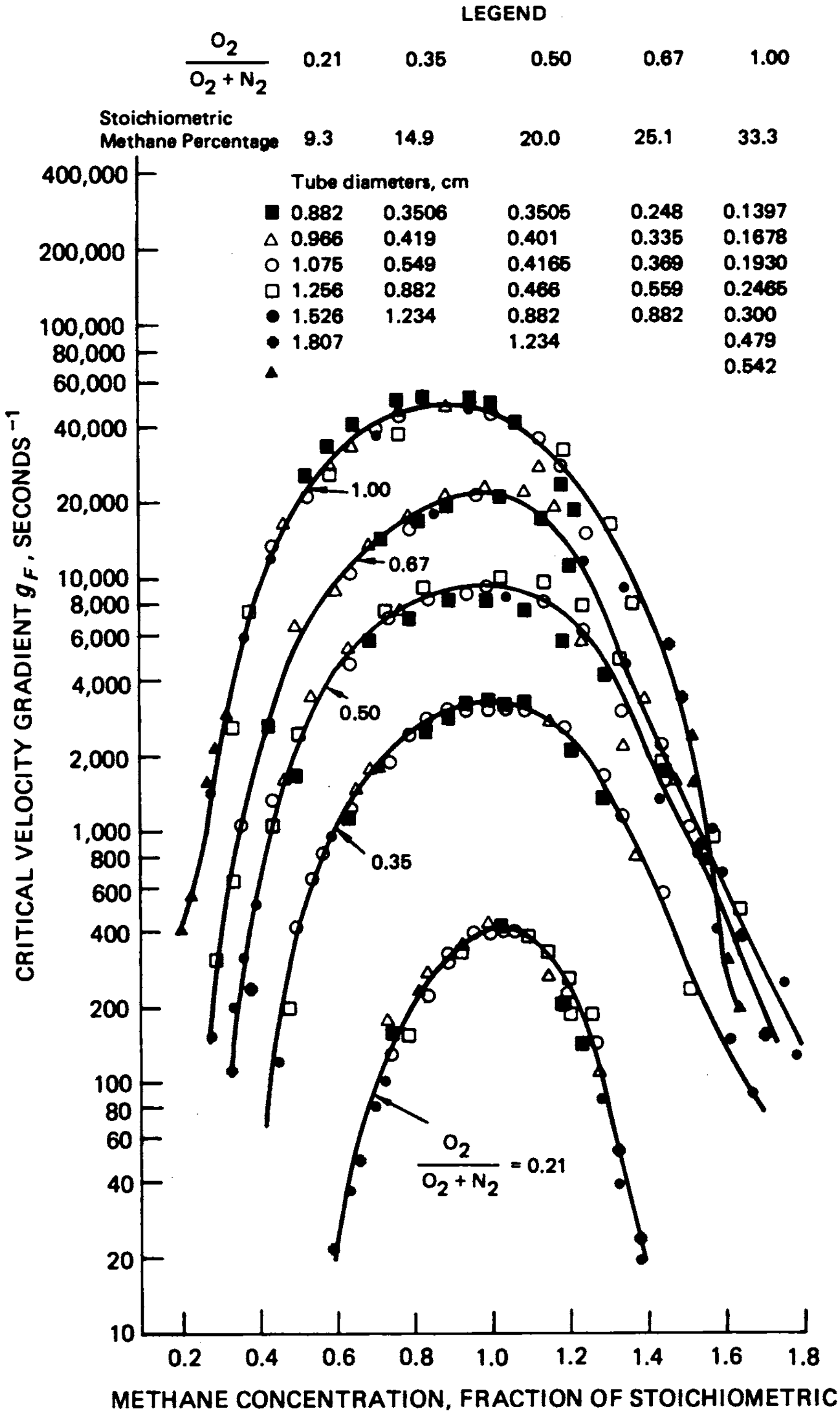

Figure 5 Critical Boundary Velocity Gradients g_f for Flash-back in Cylindrical Tubes of Different Diameters. Methane-Oxygen-Nitrogen Mixtures at Room Temperatures and Atmospheric Pressure (Harris, Grumer, von Elbe, and Lewis, 1949)

- By contrast, the surface of the sea is dynamically smooth for low wind speeds (e.g. 1 m/s) (Monin, 1970). For this condition there are no roughness elements acting to anchor the flame as there are over land. Flashback would require the right combination of low speed and closeness to the surface, without surface quenching. Moderate or strong winds change the surface of the sea in a manner that depends on wind duration or fetch. One result can be fully developed waves, which represent a rough surface.

Calculations suggest that there will be a range of moderate wind speeds (a few meters per second) where flashback can occur over land but not over water. Flashback is expected to occur over both at low enough wind speed and over neither at high enough wind speed; the limiting speed would be higher over land than over water. However, quantitative data on the effective ranges of wind speeds are lacking.

The data in Figure 5 indicate that flashback depends on gas composition and becomes much less probable as the rich or lean limits are approached. Near the edges of flammability (e.g. $<$ 6 percent and $>$ 12.5 percent), flashback would be possible only at very low wind speeds.

C. INCOMPLETE MIXING AND FLAME PROPAGATION

Laboratory data on combustion characteristics usually are obtained on completely mixed systems. An LNG plume, by contrast, is quite heterogeneous. Experimental evidence of this incomplete mixing was developed from Esso data on LNG spills (Feldbauer et al., 1972). The visible fog formed when cold methane vapor mixes with air was found to persist much farther than equilibrium would indicate, and the effect was assigned to incomplete mixing. Peak concentrations equal to 2.7 times the measured average values were calculated from the thermodynamics of the fog formation. (These peaks were not measured by the analytical instruments used because of inadquate response times.)

An analysis of the effect has been presented (Harris et al., 1975) in terms of the following concepts:

1) Large deviations from average composition will occur only in very small eddies; large eddies must necessarily have compositions close to the average.

2) Large deviations from average will occur at a given point for only a small fraction of the time; small deviations will occur for larger fractions of the time. The results of this analysis appear in Tables 3a and b.

Table 3a Concentration (C) Variation in Eddies

Eddy\Size, ft	C Eddy/C Average
20	1
10	1.3
5	1.5
1	1.8
0.01	1.9

Table 3b Frequency of Higher-Than-Average Concentration

C Exceeds	% of Time
C average	50
1.4C average	32
1.8C average	18
2.7C average	2.3

Similar data and analysis have been presented elsewhere (Csanaday, 1969). The frequency shown above matches fairly closely Csanaday's results for incomplete mixing under "Neutral or Stable Weather, Rough Terrain." It is probable that the unmixed nature of LNG plume will affect ignition and flashback. The point has not been studied, however.

D. EXPERIENCE WITH IGNITION OF FLAMMABLE CLOUDS

A combustible cloud will certainly ignite in the right combination of circumstances--composition well within the flammable range and contact with a suitable ignition source, such as an open flame or an electric spark. Although experience indicates that most flammable clouds in fact do not ignite, there is no well-organized body of statistical data on ignition experience. However, a certain amount of information is available.

The Office of Pipeline Safety requires pipeline leaks to be reported, whether ignition occurs or not. Following is an analysis of the resulting data (McDermon, private communication):

YEAR	TOTAL LEAKS	TOTAL FIRES	% FIRES
1973	122	7	5.7
1974	107	14	13.1
1975	110	17	15.5
1976	85	6	7.1

In 1975, Engineering Computer Optecnomics (ECO) reviewed oil-tanker accidents for the preceding 25 years for El Paso LNG Company. The data were taken from reports of the Coast Guard and the National Transportation Safety Board. In ship accidents involving penetration, ignition occurred with only one exception, which involved two ships carrying heavy fuel oil of high flash point (Porricelli, private communication). Invariably ignition occurred when the liquid was volatile enough so that the outside temperature exceeded the flash point. The major source of ignition was believed to be friction heating, but other sources, such as broken electric cables may also have been involved. (In one instance--the Alva Cape in New York Harbor--the source of ignition is believed to have been an accompanying tug external to the accident.) This importance of frictional heating would agree with a conclusion of the Naval Research Laboratory (Affens and Lange, 1979). For metal rupture and leakage not caused by penetration, ignition was not as frequent.

LNG tankers differ in design from other tankers. The walls of the LNG tanks are 1 to 3 or more feet from the ship's double hull, and the atmosphere in the surrounding hold space is generally made inert by adding nitrogen. Combustible mixtures should not form inside the hold, even in severe accidents. The product is so volatile, however, that penetration of the cargo tank would lead to rapid expulsion of vapor and probably liquid. The probability of ignition under such circumstances can only be guessed; it is probably high, but not 100 percent.

Experience and opinions on the frequency of ignition in industrial accidents have been given recently (Kletz, 1977):

- In polyethylene plants, experience shows that only about one leak in 10,000 ignites. The leaks are mostly very small.

- In a series of plants handling a hot mixture of hydrogen and hydrocarbons at 250 bar, experience shows that about one leak in 30 ignites. Again, the leaks are mostly small.

- In any plant, the probability of ignition will increase with the size of the leak, because larger clouds are more likely to reach a furnace or other source of ignition. For leaks larger than 10 tons, the probability of ignition is higher than 1 in 10 and perhaps as high as 1 in 2. (Note that these probability ranges represent an opinion; firm data are lacking.)

The probability of ignition varies with the location of the leak--within a plant, in a city, in the countryside etc.--but no statistics appear to be available. It has been stated that, "There is no reported case of a cloud drifing a significant distance in a factory before exploding" (Kletz, 1977). The statement may be misleading, however, because many large vapor clouds probably have not been reported. And there has been at least one case reported of a cloud that did not ignite (LNG tank rollover, La Spezia, Italy, 1971).

In summary, experience suggests a wide range of ignition probabilities:

- The probability of ignition is very low for small leaks, even in plant or factory areas.

- The probability of ignition for oil-tanker accidents involving penetration has been high, close to 100 percent. The probability might be lower for LNG ships because of their special design features.

- The probability is expected to vary widely with the locale because of wide variation in the available sources of ignition.

E. CONCLUSIONS

1. Ignition occurs readily in the right conditions: a methane/air mixture in the range of 5 percent to 15 percent methane and a high-temperature source of ignition such as a flame or an electric spark.

2. Ignition of methane by a heated surface requires a combination of adequate surface area and high temperature (537° to 1200°C depending on the surface).

3. Flashback should generally be expected, once a plume is ignited. Flashback probably will occur more easily over land than over water however, and may not occur over water at modest wind speeds.

4. The incompletely mixed nature of a flammable plume may influence ignition and other burning characteristics.

5. Experience indicates a wide range of ignition probabilities: most small hydrocarbon releases do not ignite; at the other extreme, releases caused by collision and penetration of an oil-tanker almost always ignite.

F. RECOMMENDATION

Work is recommended to evaluate the combustion characteristics of incompletely mixed systems. Important characteristics to be evaluated are: energy requirements for ignition; flame propagation rate; conditions for flashback over land and water.

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CHAPTER VIII

THERMAL RADIATION FROM LNG FIRES

A. INTRODUCTION

The emission of thermal radiation is one of the most important and potentially most highly destructive effects of an LNG fire. Thermal radiation is present regardless of whether LNG burns relatively slowly as a pool fire or the fire spreads either slowly or explosively through a vapor cloud. Moreover, since thermal radiation can ignite flammable materials at considerable distances from the site of the primary fire, it can cause the fire to propagate far beyond the confines of the original spill.

Although we need to know more of thermal radiation from LNG fires, highly accurate data on radiation from very large fires do not seem necessary for estimating the radiation damage from a major spill. Currently available data, despite their uncertainties, appear to be adequate for this task. It seems far more important to obtain accurate data on radiation from relatively small and moderate-size fires, because such data are needed to design fire protection systems for use at LNG terminals and on board LNG carriers.

Fire radiation has been studied extensively in recent years and, despite its complexity, considerable progress has been made in deriving quantitative predictions from simplified models. Reviews dealing with flame and fire radiation are available in the literature (Hottel and Sarofim, 1967; Siegel and Howell, 1972; de Ris, 1979). Moreover, several reviews dealing specifically with LNG fires have been published (Burgess and Zabetakis, 1963; Raj, 1977; Department of Transportation, 1976; Department of Energy, 1978). This discussion will emphasize primarily those areas of the subject that require further research.

Models of fire radiation are discussed and currently available data on LNG fires are presented in Section B, which follows. Since such models apply to a variety of fire geometries, the geometric aspects of pool fires and vapor-cloud fires are discussed separately in Sections C and D, respectively. Thermal-damage criteria are reviewed briefly in Section E, and subjects for further research are suggested in Section F.

B. MODELS OF FIRE RADIATION AND CURRENT DATA ON LNG FIRES

The two sources of thermal radiation in flames and fires are gaseous combustion products, principally water vapor and carbon dioxide and submicron-size particles of soot (Hottel and Sarofim, 1967; Siegel and Howell, 1972). The gaseous species emit infrared molecular-band radiation, while the soot emits a continuum in the visible and near-infrared spectrum. In general, the concentrations of these species, as well as the temperature, vary in space and in time within a flame. However, to compute thermal radiation from a flame using a detailed model of species concentrations and temperature distributions would be prohibitively complex. Primarily during the past decade, therefore, research on fire radiation has been concentrated on the development of greatly simplified models that permit radiative transfer to be estimated with acceptable accuracy.

Only the two simplest models have been applied to LNG fires. One of these, the total-radiation model, regards the fire as a point source that emits an empirically determined fraction of the total rate of heat release as radiation. This model thus requires for a given spill only an estimate of the total mass burning rate, which can be obtained from the models of vaporization and dispersion discussed in Chapter V. The model's great simplicity is offset by the fact that it cannot be used to compute irradiance at distances from the fire that are not large compared to the fire's dimensions.

The second type of model, for computing irradiance relatively close to the fire, must express the irradiance as an integral of the contributions from all volume elements of the fire. Therefore, in addition to mass burning rate, information on flame geometry is needed. The simplest model of this nature assumes that the fire radiates as an isothermal gray emitter (i.e. with spectrally flat emissivity). Despite the drastic simplification, this model has been found adequate for sufficiently large luminous flames whose radiation is dominated by the soot continuum.

These two alternative models are described below:

1. The Total-Radiation Model

Under the assumption of spherically symmetric emission from an equivalent point source, the irradiance, q, received by a target at a distance R from the fire is given by the inverse square law (Burgess and Zabetakis, 1963; Raj, 1977):

$$q = Q_r/4\pi R^2 \qquad (1)$$

where Q_r is the total radiant power of the fire. (An atmospheric attenuation factor, $\tau(R)$, may have to be included in actual computations of q.) Measurements on a variety of fires have shown that, at least under some conditions, Q_r may be expressed as a nearly constant fraction, x, of the total rate of release of thermal energy:

$$Q_r = \chi \Delta H_c \dot{m} \tag{2}$$

where ΔH_c is the combustion and $\dot{m}$ is the mass burning rate. With pool fires, x appears to approach an asymptotic constant value for sufficiently large diameter (Burgess and Hertzberg, 1974). With buoyancy-controlled, turbulent jet diffusion flames of gaseous fuels, χ remains constant over a wide range of flow rates (Markstein, 1977).

However, indiscriminate acceptance of the constancy of x has been justifiably criticized. Measurements on flares (Brzustowski et al., 1975) showed that aerodynamic effects, particularly a crosswind, can cause x to vary considerably. A recent study of hydrogen diffusion flames (Fishburne and Pergament, 1979) has further substantiated the variability of x.

The use of the x fraction for estimates of irradiance at sufficiently large distances from a fire nevertheless has considerable merit, so long as one is aware of its limitations. The effect of fuel-jet velocity (Brzustowski et al., 1975) is of little interest in fires, which normally are entirely buoyancy-controlled. Moreover, this velocity effect reduces x, so that one is on the safe side by using the maximum value of x measured for low jet velocities. For methane-jet flames, a maximum value of 0.20 with no crosswind has been reported (Brzustowski et al., 1975); a value of 0.233 has been measured for natural-gas (95 percent methane) flames at the largest burner diameter of 40.7 cm (Burgess and Hertzberg, 1974). With a crosswind, an upper limit of 0.26 has been determined (Brzustowski et al., 1975). Measurements on LNG pool fires (95 percent methane) show somewhat greater variation. Fractions ranging from 0.15 to 0.34 have been obtained with pools in the range of 30.5 to 610 cm diameter (Burgess and Zabetakis, 1963; Burgess and Hertzberg, 1974), but these results are somewhat uncertain because of the presence of natural winds. For much larger, irregularly shaped LNG pools, an x value of about 0.20 (based on the lower heat of combustion) was obtained (May and McQueen, 1973). Finally, measurements of x (Lewis, 1977) for small vapor-cloud fireballs (Fay and Lewis, 1977) led to values for methane of about 0.10; these values decreased slightly with increasing fuel-vapor volume (volume range 20 to 200 cm^3).

Thus, with the exception of one measurement of low reliability that yielded a value of 0.34, x values for pool fires of LNG and for jet-diffusion flames of methane fell in the range of 0.15 to 0.27, and a lower value of about 0.10 was determined for methane fireballs. Moreover, it seems that for any fuel, values of x exceeding 0.40 are unlikely (Burgess and Hertzberg, 1974). Estimates of irradiance from LNG fires (for distances large compared to the fire's dimensions) based on x = 0.40 are therefore conservative and may include a safety factor of about two. For distances less than about nine times the characteristic dimension of the fire, however, such estimates of irradiance may be erroneous (Raj, 1977), and an alternative model must be used for near-field calculations.

2. The Gray-Emitter Model

Computation of irradiance levels in the vicinity of a fire caused by a moderate-scale LNG spill is of great importance for the design of fire-protection equipment at an LNG installation (Wesson et al., 1972; Closner and Parker, 1978; University Engineers, 1977) or on board an LNG carrier (Welker et al., 1976). The isothermal gray-emitter model has been used extensively for this purpose. Apart from the assumptions of isothermal and gray emission, the customary formulation of this model implies that scattering of radiation by the soot particles is negligible (extinction coefficient equal to absorption coefficient). The radiant power emitted by unit surface area of the flame, regarded as an isothermal gray emitter of absolute temperature T_f, absorption-emission coefficient k, and path length D, is then given by:

$$q_s = q_{s\infty} (1 - e^{-kD}) \tag{3}$$

with

$$q_{s\infty} = \sigma T_f^4 \tag{4}$$

where σ is the Stefan-Boltzmann constant. [For a gaseous emitter, formulation in terms of radiance $N = q_s/\pi$ (i.e. radiant power per unit surface and unit solid angle) is more appropriate (Nicodemus, 1971). However all data on LNG-fire radiation have been reported in terms of q_s.]

The determination of $q_{s\infty}$ (or, equivalently, T_f) and k requires a two-parameter fit to experimental radiation data, with the further implied assumption that the two quantities are constant throughout the flame and independent of flame scale and geometry. Moreover, while measurements with narrow-view-angle radiometers can be evaluated directly in terms of eq. (3), evaluation of total irradiance measurements with wide-view-angle radiometers requires a knowledge of flame geometry. Considering the drastic simplifications of the model, the uncertainties of flame geometry (Section C), and possible deficiencies of radiometric technique (Appendix to this Chapter), it is perhaps not surprising that different groups of investigators (Duffy et al., 1974; Welker, 1974; Attalah and Raj, 1974) have derived discrepant values of the basic quantities $q_{s\infty}$ and k (Table 4).

Table 4 Values of Blackbody Radiant Power, $q_{s\infty}$, Equivalent Flame Temperature, T_f, and Absorption Coefficient, k, for LNG-Pool Fires Proposed by Various Authors

$q_{s\infty}$ (kW/m^2)	T_f (°K)	k (m^{-1})	References
177	1328	0.16	Duffy et al., 1974
142	1258	0.18	Welker, 1974; Brown et al., 1974
100	1150	0.49	Attalah and Raj, 1973, 1974

It should be noted that, apart from other differences of interpretation, atmospheric absorption was neglected in one derivation (Welker, 1974), but not in others (Duffy et al, 1974; Attalah and Raj, 1974). Obviously, the measurements performed during the American Gas Association LNG program, Phase II (American Gas Association, 1974), did not provide a clear-cut choice among these values, which were proposed by the three participating groups partly on the basis of earlier work. The publication of one of the groups (Duffy et al., 1974) contains a critical evaluation of the contributions of the other two (Welker, 1974; Attalah and Raj, 1974) and arguments in favor of their larger value for $q_{s\infty}$. It should be also noted that, even for this value, the corresponding flame temperature is appreciably lower than the temperatures determined elsewhere for pool fires of other fuels (Burgess and Hertzberg, 1974).

One must thus conclude that gray-emitter data on LNG pool-fire radiation, although used extensively for engineering calculations (Wesson et al., 1972; Closner and Parker, 1978; University Engineers 1977; Welker et al., 1976), are of questionable reliability. Careful laboratory measurements on moderate-scale fires are expected to yield more reliable data than were derived in the past from larger-scale tests (see Section F). Radiation measurements in large-scale tests should be used to verify existing models, rather than to derive the primary data used in such models.

The gray-emitter model also has been applied to radiation from LNG fireballs. One group (Hardee et al., 1978) measured a radiant flux of 123 kW/m² for a stoichiometric methane-air fireball of 1.67 m diameter, and, with an absorption coefficient of 0.18 m^{-1} (Brown et al., 1974), arrived at a $q_{s\infty}$ of 469 kW/m². This value, corresponding to a temperature of 1700°K, appears high, and the application of the absorption coefficient determined for pool-fire diffusion flames to a stoichiometric fireball is questionable. In another work (Fay et al., 1978), evaluation of measurements on small fireballs (Lewis, 1977; Fay and Lewis, 1977), assuming constant temperature, led to unreasonably low values (T_f = 630°K for methane). These workers propose an alternative interpretation in which T_f, for methane, decreases with time from an initial value of about 2000°K during fireball combustion.

The very limited existing data on fire ball radiation appear inadequate to permit reliable estimates of radiative transfer by the gray-emitter model. The unsatisfactory state of current knowledge on LNG-fire radiation is demonstrated further by the fact that two drastically different values for $q_{s\infty}$, 100 kW/m² (Raj, 1977) and 489 kW/m² (Hardee et al., 1978), are both claimed to be compatible with the radiation damage incurred in the Cleveland LNG fire.

3. Spectroscopic Radiation Measurements on LNG Pool Fires

The only published spectral data on LNG fires were obtained during the American Gas Association (AGA) Phase II tests (Carpenter and Shackleford, 1974). These tests, although carefully planned, yielded data of limited reliability, owing partly to the inherent difficulty of obtaining spectral data in field tests on windblown pool fires and partly to added experimental difficulties encountered. Nevertheless, some interesting conclusions are derived (American Gas Association, 1974). Among these are the following:

1. With 1.8-m diameter pool fires, flame-brightness temperatures ranged up to 1400°K. This value is much closer to diffusion-flame temperatures reported elsewhere (Burgess and Hertzberg, 1974) and casts further doubt on the data of Table 4.

2. The soot continuum was estimated to contribute 40 to 60 percent to the radiation from the 1.8-m diameter fires and 60 to 80 percent to that from the 6.1-m diameter fires.

3. The molecular-band contributions are strongly attenuated by atmospheric absorption and appear in emission only in the wings of the bands.

4. Results obtained with a 24.4-m diameter fire were limited and unreliable because of experimental difficulties. They showed, however, that radiant emission increased by a factor of 1.9 about five minutes after ignition, owing to transition from methane to heavier-hydrocarbon combustion (See Section B, part d). The maximum emissivity was about 0.8.

5. The slow-scanning spectrometer used in this work is ill-suited to measurements on highly fluctuating turbulent diffusion flames, and the authors recommend use of rapid-scan equipment in future work.

Conclusions 2 and 3 confirm the general experience in fire research that the gray-emitter model provides a fairly good approximation to fire radiation for sufficiently large fires. The difficulties of performing spectroscopic studies on LNG fires and of evaluating the results for predicting fire radiation quantitatively indicates that such studies should be given low priority in future research.

4. Effects of Heavier Hydrocarbons in LNG on Fire Radiation

A discussion of LNG-fire radiation would be incomplete without considering the influence of the (normally small), fraction of heavier hydrocarbons in LNG. During vaporization of LNG, methane evaporates preferentially, and the heavier hydrocarbons are released only after almost all the methane has been consumed. Thus, in an LNG-pool fire the flame changes suddenly from clean-burning to sooty or smoky burning (American Gas Association, 1974; Carpenter and Shackleford, 1974) near the completion of the burn. Information on the quantitative effect of this change on fire radiation is almost nonexistent, except for the conclusion that for the 80-ft diameter pool fire the irradiance increased by a factor of 1.9 during the transition to sooty burning (Carpenter and Shackleford, 1974).

This conclusion is in agreement with measurements on arrays of laminar diffusion flames (Markstein, 1975) which showed that the radiance for higher aliphatic hydrocarbons is larger than that for methane by factors in the range of 2.0 to 2.4. There is little doubt that this result can be extrapolated at least to turbulent diffusion flames of moderate size, so that, with small spills, of LNG, one may expect fire-radiation intensity to increase suddenly to more than twice the initial value when almost all the methane has been consumed. In large spills the increase may be reduced by the concurrent increase of radiative-energy loss, causing a reduction of the temperature in the outer layer of the flame. However, even for large fires, the assertion that the fires of the heavier fractions of LNG will radiate less energy than the methane fire (Raj, 1977) should be regarded with considerable skepticism and has been proven to be erroneous for moderate-size fires in the AGA tests (Carpenter and Shackelford, 1974).

Although the increase of radiation intensity caused by combustion of heavier hydrocarbons occurs only for a short period toward the end of burning of an LNG spill, it should not be disregarded in the assessment of radiation damage in contingency planning, site layout and design.

C. POOL-FIRE GEOMETRY

The computation of irradiance from a pool fire at a given target on the basis of the gray-emitter model (Section B, part b) requires knowledge of a geometric view factor, derived from a simplified model of fire geometry. The model used by the participants in the AGA Phase II series consists of a cylinder of circular cross-section with its axis tilted from the vertical to account for wind effects. View factors for this model have been published (Raj, 1977; Rein et al.,1970).

There is disagreement among the participants (Duffy et al., 1974; Welker, 1974; Attalah and Raj, 1974), however, on the expressions for flame length and tilt angle that correlate the experimental data.

The Thomas, 1978, expression for flame length-to-diameter ratio

$$L/D = 42 \left(\dot{m}''/\rho_a\sqrt{gD}\right)^{0.61} \tag{5}$$

is used by Welker, 1974, where $\dot{m}''$ is the mass burning rate per unit area, ρ_a is the density of ambient air, and g is the gravitational acceleration. Attalah and Raj, 1974, arrive by dimensional analysis and least-square fits, at the relationship

$$L/D = \begin{cases} \left(\dot{m}''/\rho_a\sqrt{gD}\right)^{-0.19} u^* & \text{for } u^*>1 \\ \left(\dot{m}''/\rho_a\sqrt{gD}\right)^{-0.19} & \text{for } u^*\leq 1 \end{cases} \tag{6}$$

Here,

$$u^* = U/\left(\dot{m}''gD/\rho_v\right)^{1/2} \tag{7}$$

where U is the wind velocity and ρ_v is the density of saturated fuel vapor at the boiling point. For the tilt angle ϕ, Welker, 1974, uses the expression

$$\tan\phi/\cos\phi = 3.2\ Re^{0.07}\ Fr^{0.7}\ (\rho_v/\rho_a)^{-0.6} \tag{8}$$

where Re and Fr are the Reynolds and Froude numbers, based on wind velocity and flame diameter, while Attalah and Raj, 1974, use

$$\cos\phi = \begin{cases} (u^*)^{-\frac{1}{2}} & \text{for } u^*>1 \\ 1 & \text{for } u^*\leq 1 \end{cases} \qquad (9)$$

It should be noted that the two groups also use different relationships for the mass burning rate as a function of pool size. This may account in part for the different models of flame geometry. A review of these relationships (Duffy et al., 1974) questions the validity of eq (6) and favors the Thomas expression, eq (5), but shows that there is no clear-cut preference between the expressions for the tilt angle, eqs (8) and (9).

Thus, considerable uncertainty exists on the choice of a geometric model for an LNG-pool fire. Moreover, recent tests at China Lake (Lind and Whitson, 1977) have indicated L/D ratios as large as 5, considerably in excess of those encountered in the AGA tests, casting further doubt on the existing models.

The combined uncertainties of the model of pool-fire geometry and of the parameters of the gray-emitter model (Section B, part b) make the validity of current predictions of irradiance levels highly doubtful.

D. VAPOR-CLOUD FIRES

Vapor clouds and vapor-cloud fires have been reviewed, primarily qualitatively (Slater, 1978). Vapor-cloud explosions that involve significant gas-dynamic effects are discussed elsewhere in this report, while this section deals only with vapor-cloud deflagrations in which such effects are negligible. Two contrasting modes of vapor-cloud deflagration are considered. These are the fireball (Lewis, 1977; Fay and Lewis, 1977; Hardee et al., 1978; Fay et al., 1978) and the two-dimensional spreading fire (Raj and Emmons, 1975) (see also Raj, 1977).

1. Fireballs

From dimensional arguments, an entrainment hypothesis, and a momentum balance, the following expressions have been derived for the flame height, z_p, and combustion time, t_p, of a spherically burning vapor cloud (Lewis, 1977; Fay and Lewis, 1972):

$$z_p = 1/\beta\ (3V_p/4\pi)^{1/3} \qquad (10)$$

$$t_p = [14\rho_p/g\beta(\rho_a - \rho_p)]^{1/2}\ (3V_p/4\pi)^{1/6} \qquad (11)$$

where β is a constant entrainment coefficient, ρ_p is the density of the combustion products and ρ_a that of the ambient gas, and V_p is the volume of the combustion products. The latter, for a hydrocarbon of composition C_nH_m, is given by:

$$V_p = \frac{m\phi + 4.762(4n + m)}{4\phi}\ (T_p/T_r)\ V_f \qquad (12)$$

where ϕ is the equivalence ratio, T_p is the adiabatic flame temperature of the products, and T_r is the ambient temperature of the reactants. Since the ratios ρ_p/ρ_a and T_p/T_r are determined by ϕ, the only unknowns in these expressions that have to be determined experimentally are β and ϕ.

Experiments were performed over the initial volume range from 20 to 190 cm³ with methane, ethane, and propane. The following results were obtained for methane: $\beta = 0.315$ $\phi = 0.215, T_p = 870$ °K, $z_p = 10.0\ (V_v)^{1/3}$, $t_p = 0.271\ (V_f)^{1/6}$. The results of radiation measurements on these flames are discussed in Section B, parts a and b.

Others have derived a similar model and estimated the radiative flux from LNG fireballs (Hardee et al., 1978). Their experiments extended to much larger quantities of methane (maximum 10 kg) than those of Fay et al., 1978, and included both pure methane and premixed stoichiometric methane-air fireballs. Their reported radiation data indicate much larger radiant fluxes than determined either by Lewis, 1977, or in pool-fire measurements (see Section B, part b). The authors propose that test series in the range of 100 to 1000 kg should be performed and also a test in the optically thick region of 5000 to 10,000 kg.

Raj, 1977, has argued that beyond a critical size, of the order of the product of turbulent flame velocity and burn time, t_p, a vapor cloud cannot burn as a fireball. He states that this critical diameter may be at most a few meters. Verification of the existence of such a critical size is clearly an important subject for future experiments.

2. Spreading Vapor-Cloud Fires

The analysis of the spreading vapor-cloud fire by Raj and Emmons, 1975, starts with the observation, in a rather limited number of tests, of fire propagating from a downwind ignition source against the wind through a spreading LNG-vapor cloud. The spreading velocity, S, relative to the cloud (Raj, 1977; Raj and Emmons, 1975) was observed to range from a minimum of about 1.8 m/s for low wind velocity to about 14 m/s for a wind velocity of 6 m/s.

The simplified model of Raj and Emmons, 1975, considers a fire of two-dimensional geometry spreading from a line ignition source through a horizontal vapor cloud of constant thickness, δ. Other assumptions include buoyancy-controlled burning; constant spreading velocity, S, known from experiments; linear variation of vapor depth underneath the flame base of width W in the spreading direction; and steady-state correlations for flame height-to-width ratio, H/W. For the latter, a simplified correlation based on results obtained elsewhere (Steward, 1964) is used. The analysis showed that the base width, W, increases with time, but approaches an asymptotic steady value, W_∞, given by:

$$W_\infty/\delta = 20(H/W)\ (S^2/g^\delta)\ (\rho_o/\rho_a)^2\ [\omega(r + \rho_a\omega/\rho_o)^2/(1 - \omega)^3]^{1/3} \tag{13}$$

where ρ_o is the density at the plume base and ρ_a that of ambient air, ω is the inverse volume-expansion ratio of the gases resulting from combustion, and r is the stoichiometric air-fuel mass ratio. The authors report reasonable agreement between theory and the limited experimental data on flame-base width.

E. THERMAL DAMAGE CRITERIA

A fairly detailed review of thermal-damage criteria is included in Raj, 1977. The two types of criteria considered are ignition of wood and cellulosic materials and burn injury. On the basis of literature ignition data (Lawson and Simms, 1953; Lawson, 1954; Simms and Law, 1967). Raj, 1977, recommends an irradiance of 31 kW/m² as the lowest for spontaneous ignition of wood (Simms and Law, 1967). The lower value of 12.5 kW/m² for piloted ignition (Lawson, 1954) is regarded as inapplicable because of the absence of firebrands in LNG fires. It is also suggested that, for fires of short duration, a criterion based on total energy input to the wood should be used. It should be noted that

Slater, 1978, quotes 12.5 kW/m² as a safe-distance criterion, while Hardee et al., 1978, used 13.2 kW/m² (Wesson et al., 1972) in their analysis of the Cleveland LNG fire. Note also that an irradiance of 31 kW/m² agrees closely with the limit of 31.55 kW/m² at the property line stipulated in National Fire Protection Association Code 59A(14).

The burn-injury data reviewed in Raj, 1972, include results obtained without protective clothing (Buettner, 1951; Moritz and Henriques, 1946) and with protective clothing (Seaman, 1967; Stall and Chianta, 1970; Heskestad et al., 1971; Mehta et al., 1973). The data of Buettner, 1951, are correlated by the expression

$$t = (35/I)^{4/3} \qquad (14)$$

where t in seconds is the time for feeling severe pain and I is the irradiance in kW/m². Criteria based on skin-surface temperature and on total energy absorbed as well as the effect of protective clothing are also discussed by Raj.

It is stated that at an irradiance of 3 kW/m², severe pain would be felt after 26 s and bare skin would be damaged irreversibly in about 90 s. The lowest irradiance quoted in Raj, 1977, for evaluating the distance for thermal hazard to people is 1.47 kW/m², attributed to Fay. An irradiance of 4 kW/m² as damage threshold for short-time exposure is quoted in Slater, 1978.

One may conclude that damage criteria are still somewhat uncertain, but work in this area probably should not be included in plans for LNG research.

F. SUGGESTED SUBJECTS FOR FURTHER RESEARCH

From the preceding review, one may conclude that the thermal-radiation damage caused by a major LNG spill at distances large compared to the dimensions of the fire can be estimated with acceptable accuracy on the basis of the total radiation model (Section B, part a). It thus appears that the greater need is for research on LNG-fire irradiance levels near a moderate-size spill, since accurate data are required to design fire-protection equipment for use at LNG terminals and on board LNG carriers. Existing data have been used to perform such engineering analyses (Wesson et al., 1972; Closner and Parker, 1978; University Engineers 1977; Welker et al., 1976), but the reliability of these data is questionable (Section B, part b).

Experience in other areas of fire research has shown that while full-scale tests may be needed to verify mathematical models, they are not well suited to obtaining the empirical data that enter into these models. Such data can be obtained with far better accuracy and reliability in relatively small-scale laboratory experiments.

In particular, the modified Schmidt method that has been used recently to measure gray-emitter temperatures and absorption coefficients for plastics-pool fires (Markstein, 1979) could be applied easily to small-scale LNG-pool fires or simulated pool fires of methane gas burning on a porous metal slab. Briefly, this method consists of measuring the radiance seen by a narrow-view-angle radiometer that views the flame against a background of blackbody radiation of known temperature. By repeating the measurements over a range of background temperatures that includes the anticipated flame temperature, T_f, both T_f and the emissivity, ϵ, of the flame can be determined. If one also determines the effective path length, D, through the flame, as by averaging flame photographs, the emissivity can be converted into an emission-absorption coefficient

$$k = - \frac{1}{D} \exp(1-\varepsilon) \qquad (15)$$

Undoubtedly, values more reliable than those now available (See Section B, part b, and Table 4) could be obtained in this manner.

With respect to pool-fire geometry, laboratory experiments in addition to larger-scale tests would also be of great value. In particular, wind effects on pool fires could be modeled in small-scale, open-jet, wind-tunnel tests of the type used elsewhere (Brzustowski et al., 1975) to study flares. For example, it has been pointed out (Raj, 1977) that there are no data on the effect on flame tilt--including potential spilling of flame over low dike walls--caused by wind flow around structures within or near the fire. Such effects, which may increase the radiation hazard over current estimates, probably could be studied successfully in wind-tunnel model tests, as has been done for oil tanks (Lois and Swithenbank, 1979). Wind-tunnel tests also may be addressed to the possibility that wind shear may cause substantial increases of flame height and burning rate (Emmons and Ying, 1967; Lee and Garris, 1969; Garris and Lee, 1973; Lee and Otto, 1975). This effect--fire whirl--is mentioned elsewhere (Raj, 1977) as a subject for future research.

Data on fire geometry in laboratory as well as large-scale tests will continue to be obtained primarily by photographic methods. Alternative techniques, such as use of scanning radiometers or video-tape recording with pyroelectric vidicons, should be considered, however. In past work on LNG, fire-geometry data have been evaluated in terms of a simple mathematical model. Workers in other areas of fire research have used an alternative approach: flame photographs were digitally averaged, and polynomial fits to the average flame contours were used to compute fire radiation (Markstein, in press; de Ris et al., 1976; Modak, 1977). This method may provide a more accurate fit to the actual fire geometry than the use of a fixed-geometry model, and should be considered in future studies of LNG-pool fires.

Experiments on fireballs at larger scale than in the past seem indispensable to resolving the question of whether there exists a critical size, of the order of the product of turbulent-flame velocity and burn time, above which a fireball cannot be produced (Raj, 1977). Scaled-up experiments of the type performed by Lewis, 1977; Fay and Lewis, 1977; and Hardee et al., 1978 should be the primary approach for obtaining data on fireballs, including fire radiation. However, in view of the concern about transportation of LNG in tank trucks that has been triggered in part by recent accidents involving LPG tank trucks, it appears desirable also to perform realistic full-scale tests of simulated LNG tank-truck accidents. It is not likely that accurate scientific data can be obtained from such tests, even when properly instrumented. Their primary purpose should be to resolve the question of whether the disastrous type of Boiling Liquid Expanding Vapor Explosion ("BLEVE") (Slater, 1978) that occurs with LPG can also take place with LNG.

Spectroscopic measurements probably should be given relatively low priority in research, owing to the great difficulty of obtaining meaningful data and the marginal additional information that they provide as compared with spectrally integrated radiometry. If spectroscopic work is contemplated, however, it should be performed with rapid-scan instrumentation, as has been recommended (Carpenter and Shackleford, 1974).

Finally, in both laboratory and large-scale tests on LNG fires, careful attention should be given to radiometric technique. Pertinent suggestions are presented in the Appendix to this chapter.

G. CONCLUSIONS

From the preceding discussion, it is concluded that:

1. Irradiance at large distances from a major LNG spill can be estimated with reasonable accuracy (perhaps within ± 30 percent) from an estimate of the mass burning rate.

2. Current data are unreliable for computing irradiance near a moderate-size spill, which is of great importance for designing fire protection equipment at LNG installations and on board LNG carriers, as well as for site design and building layout.

H. RECOMMENDATIONS

1. The primary emphasis of further research should be on obtaining more accurate data for moderate-size LNG fires, preferably by careful laboratory experiments rather than by full-scale field tests.

2. Measurements in large-scale tests should be made to verify mathematical models, not to derive the primary empirical data used in such models.

3. Vapor-cloud deflagration tests are needed on a sufficiently large scale to determine whether LNG fireballs are limited to a maximum size of a few meters.

4. Data are needed on fire geometry near structures in the presence of wind, including data on the possibility of the generation of fire whirls. Wind-tunnel model experiments for this purpose should be considered.

APPENDIX

RADIOMETRIC TECHNIQUE

It has been stated that "radiometry enjoys the dubious distinction of relatively poor attainable precision and accuracy" (Nicodemus, 1971) and that "radiometric measurements are among the most difficult measurements to make" (Kostkowski, 1977). Even with careful work in near-ideal conditions, accuracies of not better than a few percent are common (Nicodemus, 1971). Far larger errors can be expected with measurements on turbulent, highly fluctuating, and wind-driven diffusion flames. It is imperative, therefore, that at least those systematic errors that the experimenter can control be kept to a minimum.

Unfortunately, in past work on LNG radiation, this has not always been the case. The effective radiation temperatures for LNG-pool fires shown in Table 4 are rather low, and even lower temperatures have been reported for fireballs (Lewis, 1977; Fay et al., 1978). Valid, spectrally integrated measurements for such sources require radiometers with flat spectral response from the visible to at least 10 μm . Two conditions must be satisfied to ensure adequate spectral response:

1. The window material of the sensor must transmit as uniformly as possible over the specified spectral range.

2. The absorptance of the coating of the sensitive area of the sensor must be as spectrally flat as possible over the specified range.

Various window materials are available that satisfy the first condition, and sensors with such window materials are commercially available. Among materials suitable for flame radiometry are calcium fluoride, zinc sulfide (Kodak Irtran 2), and thallium bromo-iodide (KRS 5). Used in the past, but unsuitable, are sapphire (cutoff wavelength $\sim$ 5 μm) and quartz (cutoff wavelength $\sim$3 μm). Windowless sensors are not recommended because errors may result from convective cooling of the sensitive area.

The second condition generally implies a compromise between spectral response and time constant. If fast response is not needed, good spectral response can be achieved, e.g. with a coating of 3M paint, which is available with commercial sensors.

To test the spectral response of a radiometer, calibrations with a blackbody source should be performed over a range of source temperature of about 900° to 1500° K. Reliance on factory calibrations of radiometers, often performed with a tungsten source at much higher temperature and with quartz (or even glass) windows, is unacceptable. Radiometers with internal electrical calibration are now available and would be particularly advantageous for large-scale tests, where calibration in the field is undesirable. Even with these radiometers, however, calibration should be checked periodically with a blackbody source.

Another feature of radiometers that is often overlooked is their angular response characteristic. In particular, the angular response of wide-view-angle radiometers should be calibrated.

Finally, wide-view-angle measurements should be evaluated in terms of the total radiation model (Section B, part a) and narrow-view-angle measurements in terms of gray-emitter model (Section B, part b). The purpose is to avoid combining the uncertainties of geometric models of the fire with the uncertainties of radiometry.

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CHAPTER IX

CLOUD EXPLOSION AND BLAST EFFECTS

A. INTRODUCTION

Cloud explosion is the ultimate hazard of LNG. It cannot be disregarded, no matter how small the probability of its occurrence. Critical factors in cloud explosion are the composition of the cloud, which is governed by the mechanism of formation, the way combustion is initiated -- the mechanism of ignition, and the propagation of the flame. Thus, although cloud formation and ignition are considered elsewhere in the report, those aspects of them that bear in particular on cloud explosion are included here.

The following general features of cloud explosion should be taken into account. The phenomenon is influenced primarily by the history of its development. This involves a significant number of elementary events that can interact synergetically. As a consequence, a program of large-scale experiments cannot be expected to reproduce the variety of conditions that could be encountered in a practical situation. At the same time, however, a significant amount of research pertaining to this problem is going on throughout the world. Thus knowledge of the elementary processes has become well established, facilities have become available for simulating them under laboratory conditions, and attainment of the computational capability needed to predict the outcome of an actual event under a prescribed scenario of accidental causes is only a matter of time.

Under such circumstances, the use of large-scale experiments should be considered solely for proving the validity of prediction, once the computational capability is developed. Meanwhile, work to attain this capability should be given first priority. This review is slanted toward that goal. The review is by no means comprehensive. It covers highlights selected to convey a feeling for the types of problems encountered and the methods used to solve them.

B. INITIATION

The process of cloud explosion, as noted earlier, depends crucially on the history of its development, including the way it is initiated. An explosion is manifested by a pressure wave. Such a wave can be generated by a detonation or a deflagration. However, the structure of the resulting flow field differs radically in the two cases.

Deflagration is a flame front that, in the flow field of a pressure wave, behaves as a gasdynamic discontinuity propagating at a subsonic velocity. Deflagration is initiated by mild ignition -- an event leading to the establishment of a self-sustained exothermic process. Since combustion is basically a chain reaction, ignition depends critically on the rate at which chain carriers are generated. This rate is controlled mainly by chain branching steps which usher in the exothermic recombination steps. The establishment of the latter is slowed by heat losses in the combustion system. The theory of thermal ignition, where such losses play a dominant role, is well developed (Merzhanov and Averson, 1971; Semenov, 1958; Frank-Kamenetskii, 1955).

Detonation is a deflagration associated with a shock front. In a gaseous medium it can be generated in two fundamentally distinct ways: (1) by transition from deflagration to detonation starting with a weak ignition, and (2) by direct initiation using a sufficiently strong ignition source. In the first case, all the energy required for the development of detonation is derived internally from the combustible mixture itself; in the second, it is provided by the external ignition system. Current knowledge in this field has been reviewed (Lee, 1977).

1. Transition to Detonation

The crux of the mechanism of transition from deflagration to detonation is the generation of pressure waves by the flame. Basically, this process is governed by the rate at which exothermic energy from combustion is deposited in the medium -- the exothermic power. The process is enhanced greatly by flame acceleration, which is caused first by the breakup of the flame front into a turbulent structure and subsequently by the increased intensity of turbulence resulting from flame folding (Abdel-Gayed and Bradley, 1976). These effects can produce a significant increase in the flame propagation speed (Lee, 1977).

In this respect recent progress made in the development of a deterministic theory of turbulence, associated in particular with its large scale structure, should be of particular importance. The phenomenological aspects of this progress has been described by Roshko, 1976. The analytical facilities to treat such flows have been greatly enhanced by the Random Vortex Method developed by Chorin, 1973, 1978. The method provides a grid-free numerical technique that is capable of following the convoluted, typically nonsteady flow pattern characteristic of turbulent mixing, and of adjusting itself automatically to the full spectrum of scales for the various elements of the flow field.

The essential feature of the Random Vortex Method is the representation of flow in terms of a set of vortex blobs--elements of the flow field specified by functions that vanish outside of a small region (or blob) around its center point. The blobs are expressed in terms of stream functions of a point vortex, while the generation and dispersal of vorticity is governed by a set of random numbers simulating the effects of diffusion. The behavior of each blob is affected by all its neighbors, and the aggregate motion of the blobs can be traced by the computer without too much strain on its memory. The blobs, in effect, act as moving computational grid points depicting the convoluted turbulent motion as it occurs in the actual flow field--a task that could not be accomplished by a finite-difference technique.

Flame acceleration as a rule is associated with the generation of a pressure wave, which takes the form of a two-fronted blast wave. One front propagates into the unburned medium ahead of the flame, raising its temperature. The other front propagates into the burned medium toward the center of the flow field, where it is reflected and then interacts with the flame front, increasing both its turbulence and folding (Markstein, 1957, 1964).

The cumulative effects of interactions between the flame and the pressure waves generated by its acceleration impart a bootstrap nature to the development of the process. The effectiveness of obstructions in promoting the process has long been known, and their use is well established in detonation research (Zeldovich and Kompaneets, 1960). Recently the effect has been exploited to induce transition to detonation in an unconfined environment by placing hemispherical grids in the path of a hemispherical flame kernel (Dorge et al., 1976). Numerical analysis of the development of the process under such circumstances showed the importance of pressure waves generated by the accelerating flame and, in particular, their reflections at the center of symmetry (Kurylo et al., 1977).

The eventual detonation is not the result of a gradual transition from flame to detonation. Detailed experimental observations show that the transition invariably occurs in a localized region ahead of a highly turbulent flame brush which is generating a train of intense shock waves. Since the explosion in this localized region is much faster than anything that occurs previously, while the overall process is highly explosive, the initial transition was first termed "explosion in the explosion" (Urtiew and Oppenheim, 1966; Oppenheim, 1970). Later the phenomenon was identified with an explosive autoignition, or strong ignition, a process that could be studied most conveniently in shock tubes using the reflected-shock technique, as described in the next section.

To sum up, flame acceleration, associated with escalating turbulence and the ensuing pressure waves, accompanied by multireflection and interaction phenomena, play a crucial role in the transition from deflagration to detonation. However, self-initiation of a detonation wave occurs eventually when release of exothermic energy rises to a critical rate -- i.e., energy is deposited in the medium so rapidly that an intense blast wave is produced and triggers the detonation wave.

2. Strong Ignition

Strong autoignition is attained conceptually, if the induction period terminates at the same time over a sufficiently large volume in the reacting medium. The exothermic energy from combustion is deposited within this volume coherently in time, so that the rate of deposit becomes extremely high. As pointed out above, the process can be studied using shock tubes and the reflected-shock technique. The exothermic reaction starts after an appropriate induction time, following shock relfection from the closed end of the tube. The effects may be of two types: distinct flame kernels; or a fully developed blast wave -- headed by a shock front -- which appears just a few millimeters from the closed end and propagates at virtually constant velocity until it merges with the reflected shock. The first of these two modes is referred to as mild ignition and the second as strong ignition. This phenomenon was first observed by Saytzev and Soloukhin, 1962, and its fundamental significance was pointed out by Voevodsky and Soloukhin, 1965.

The demarcation line between the two regimes of ignition, on the plane of pressure and temperature for the thermodynamic state at which the chemical induction process takes place, is a locus of constant partial derivative of induction time with respect to temperature at constant presssure. It is referred to as the strong ignition limit. From the study of this limit, the condition of the time-coherent termination of the induction period necessary for strong ignition -- the key to the "explosion in the explosion" -- has been established (Meyer and Oppenheim, 1971a, 1971b; Vermeer et al., 1972). The most important factor in this respect is a sufficiently high and uniformly distributed temperature, which is achieved best by an adequately strong shock wave.

Experimental records indicate that strong ignition produces blast waves which, at an initial temperature on the order of 1000°K, correspond to energy deposition at a power density from a few kW/g to a number of MW/g. At a pressure of 1 atm the strong-ignition limit is primarily a function of temperature. For an argon-diluted, stoichiometric mixture of hydrogen and oxygen, this temperature is on the order of 1100°K. For methane, under corresponding conditions, it is 2200°K, the highest for any hydrocarbon.

The high temperature for methane can be explained as follows. Recent studies of ignition chemistry (Creighton, 1977) have shown that the kinetic processes of hydrocarbon combustion are dominated by methyl radical. The radical is derived mainly from collisions involving fuel molecules. Since carbon-carbon bonds are weaker than carbon-hydrogen bonds, methyl radical is formed from methane at a given temperature at significantly slower rates than from higher hydrocarbons. For this same reason methane exhibits other peculiarities, such as the remarkably nonuniform structure of the self-sustained detonation wave (Strehlow, 1968, 1969).

3. Direct Initiation

The essential purpose of an igniter used to generate detonation is to create conditions commensurate with strong ignition. As it is clear from the previous section, the central role is played by a shock wave. Thus, detonative igniters are, in effect, shock generators. The most popular detonative igniters are high explosives. Results of experimental tests of such igniters with methane-air mixtures have been reported in the open literature (Kogarko et al., 1966; Bull et al., 1976, 1978; Benedick, 1978).

Kogarko et al. claimed that detonation in an unconfined methane-air mixture at normal temperature and pressure could be initiated by a 1-kg charge of TNT. This conclusion was challenged by Bull et al. who pointed out that the detonation observed by Kogarko et al. was still under the influence of the explosive initiator when it reached the boundary of the enclosure, so that its subsequent decay could not have been observed.

The tests of Bull et al. were performed with oxygen diluted by nitrogen in smaller proportions than in air. By extrapolating the data, they concluded that 22 kg of tetryl is required to initiate a spherical detonation in air. However, Boni and Wilson, 1978, demonstrated by numerical analysis that this extrapolation did not take into account a sharp change in the slope of the line delineating the detonability limit that, according to calculations, occurs at the composition corresponding to the maximum dilution that Bull et al. employed. Boni and Wilson estimate critical charge at as high as 1 to 10 tons.

In more recent investigations, Bull et al., 1978 demonstrated that higher hydrocarbons in natural gas enhance the sensitivity to detonation. This observation essentially agrees with expectations based on the previously noted role of methyl radical in hydrocarbon ignition.

Other field tests have produced more conflicting results. Vanta et al., 1974, using 1 kg of explosive, observed detonation-like waves in natural gas-oil mixtures contained in plastic-film enclosures measuring 1.2 m x 1.2 m x 6 m. However, the measured speed of the wave front was below the Chapman-Jouguet velocity for a stoichiometric mixture. In a series of carefully conducted field studies, on the other hand, Lind and Whitson, 1977, using more than 2 kg of composition B booster, were unable to detonate a stoichiometric methane-air mixture contained in a hemisphere of 5 m radius.

Finally, Benedick, 1978, reported detonations in natural gas-air mixtures contained in 2.4 m x 2.4 m x 12 m polyethylene-film enclosures, using as initiators 1 m x 2 m rectangular layers of Detasheet, a Dupont explosive containing 65 percent pentaerythritol tetranitrate (PETN) and 8 percent nitrocellulose. The total weight of the explosive was on the order of 4 kg. Since in this case the initiating shock is planar rather than spherical, the result virtually agrees with the estimate of Bull et al. However, the length of travel over which experimental observations could be made was much too short to insure that the waves were self-sustained detonations.

Meanwhile, laboratory experiments using explosive gas mixtures (other than LNG) with a variety of initiators have provided much information on direct initiation of detonations under essentially unconfined conditions. Of particular interest is the work of Lee and his associates, using a variety of ignition sources: focused laser beams (Bach et al., 1969); exploding wires (Lee and Matsui, 1977); electric spark discharges (Lee, 1977); gaseous (linear) detonation waves (Matsui and Lee, 1978); and hot turbulent gas jets (Knystautas et al., 1978).

The conclusions reached from these studies can be summarized as follows:

(1) For a given explosive mixture and igniter, the threshold for direct initiation of detonation can be expressed in terms of a critical energy. Below this critical energy one obtains a flame that behaves as a

deflagration which, as time progresses, lags more and more behind the decaying shock created by the igniter. Above the critical energy one establishes an overdriven detonation that eventually decays to the steady Chapman-Jouguet state. The critical energy leads to the onset of an "explosion in the explosion."

(2) For a given fuel and igniter, with the same geometry of the system (i.e., spherical, cylindrical, or planar), the variation of critical energy with mixture ratio is expressed by a U-shaped curve with a minimum near stoichiometric composition and tending to infinity at both the lean and the rich limits.

(3) Critical energies determined for the same mixture at the same initial conditions using different types of igniters cannot be correlated because of the differences in specific power at which the energy produced by the igniters is deposited in the reacting medium.

(4) The initiation process is affected only the the energy released during the rising part of the power pulse.

(5) For a given igniter, critical energy for the same mixture can differ by as much as three orders of magnitude when the temporal characteristics of energy discharge are varied -- demonstrating the importance of the power of energy deposition, the parameter that controls the strength of the shock generated by the igniter.

(6) Critical energy decreases with the duration of its release down to a minimum value that is unaffected by further reduction of the duration of discharge. This minimum critical energy can be considered a source-independent threshold for the initiation of detonation in a given explosive mixture.

These conclusions have been confirmed in principle by experiments using a gaseous detonation wave as an igniter. The detonation was generated in a small-diameter tube and the wave ejected into a larger vessel where the onset of an unconfined detonation was observed. Such ignition systems have been used in the past by a number of investigators (e.g. Zeldovich et al., 1956; Soloukhin and Ragland, 1969).

This approach has been used to develop a technique for systematically measuring critical energies for direct initiation of spherical detonations (Matsui and Lee, 1978). The value of the energy is deduced from the diameter of the smallest tube capable of initiating spherical detonation. The magnitude of critical energy is determined by postulating that it is equal to the work of an effective piston moving at a velocity of flow behind the plane (initiating) detonation wave, while its size is confined within a cone created by rarefactions emanating from the periphery of the orifice at the exit of the tube. In this way, critical energies for initiating unconfined detonations were determined for a variety of hydrocarbon mixtures with oxygen and with air. These energies can be expressed in terms of a relative parameter: the ratio of critical initiation energy for a given fuel to that for a stoichiometric acetylene-oxygen mixture (3.83×10^{-4} joules). Table 5 gives examples of these characteristic ratios; all are for stoichiometric mixtures. The relatively low sensitivity of methane, especially in a mixture with air, is apparent and in agreement with the peculiar nature of its oxidation kinetics pointed out earlier.

Table 5 Relative Critical Initiation Energies for Various Fuels

Fuel	Relative Critical Initiation Energy — With Oxygen	With Air
Hydrogen (H_2)	4.1×10^3	1.1×10^{10}
Methane (CH_4)	1.3×10^5	5.9×10^{11}*
Propane (C_2H_6)	2.8×10^3	1.3×10^{10}
Butane (C_3H_8)	1.5×10^3	6.6×10^9

* Obtained by extrapolation of data on nitrogen-oxygen mixtures.

It should be borne in mind that the foregoing results are from a single investigation. They should not be considered definitive until verified by different experiments and provided with a rational theoretical background. Of particular interest to the main objective of this report is the fact that the necessary work should be relatively inexpensive and fruitful.

Of particular significant to explosive cloud ignition in the presence of fire at the site of an accident, is a recent study in which the initiation of detonation by hot, turbulent, gas jets was observed (Knystautas et al., 1978). The jets were produced by the use of a bomb where spherical flame was ignited at the center. The flame had access to a larger detonation vessel through an orifice fitted with a turbulence-generating grid. To maintain the apparatus at a size convenient for the laboratory size, the time and length scales of the processes under study were minimized by the use of undiluted acetylene-oxygen mixtures maintained initially at subatmospheric pressures.

The results demonstrated that turbulent jets trigger detonation by producing a blast wave resembling the "explosion in the explosion" -- the trigger of transition to detonation in the case of self-initiation. It appears, therefore, that conditions required for strong ignition can be achieved by the action of turbulent jets without much shock compression -- at least in the extreme case of the oxygen-acetylene system used in this study. In fact, the authors point out, the entrainment and mixing mechanisms in a turbulent eddy may be ideal in that they produce an induction-time gradient from the center outward. A blast wave originating at the center can thus be furnished with exothermic energy at the right time, in accord with its own motion, to result in its amplification. Although such a mechanism is quite unlikely to actually trigger detonation in an explosive cloud of natural gas, it could certainly enhance initial flame acceleration. The scale of obstructions required to produce effects similar to those produced by the grid used in the laboratory study should be commensurate with the size of objects one can expect to encounter at the site of an accident.

4. Scale and Unconfinement

The experimental studies described in the previous section provide good examples of how phenomena associated with the development of detonation can be scaled down for laboratory investigation. In such investigations the process perforce must be confined. Traditionally, experiments on the development of detonation in a gaseous medium have been performed using long tubes to confine the process, so that the wave front could be regarded as virtually planar. The concern over explosive clouds raised interest in unconfined explosions and, for laboratory purposes, the effects of confinement.

Since the wave front is essentially restricted to the confined space, confinement principally affects geometry. In any geometrical configuration the extent of the frontal area, A, is a function of the radius R -- the distance from the center of explosion. Thus

$$d \ln A/d \ln R = j$$

where j = 0, 1, 2 for planar, cylindrical, and spherical geometry, respectively.

From straightforward dimensional considerations it follows that a blast wave resulting from the deposition of energy in a gas can be characterized by an explosion length

$$R_o \equiv (E_j/P_a)^{1/(j+1)}$$

where Ej is the source energy per unit area, per unit polar angle and axial length, or per steric angle, for planar, cylindrical, and spherical geometries, respectively, while P_a is the pressure of the ambient atmosphere into which the wave front propagates.

As a consequence, one has a very simple relationship:

$$E_{spherical}/E_{cylindrical} = E_{cylindrical}/E_{planar} = R_o.$$

The validity of this relationship is well supported by experimental data on critical engergies for direct initiation of detonation (Lee, 1977). The relationship permits critical energies for direct initiation of unconfined spherical detonations to be estimated from corresponding energies measured for the planar case, the simplest and least expensive to study in the laboratory. Thus expensive, large-scale field tests can be replaced by much simpler laboratory experiments, using tubes for confinement and permitting much better insight into the details of the process than could possibly be achieved in the field.

There are, of course, various effects of unconfined explosions that cannot be modeled by experiments using tubes. The interest in exploding clouds spurred the development of an impressive array of ingenious techniques for laboratory investigations of such effects. Among studies of particular interest are those directed by Lee in Canada (viz. e.g. Knystautas et al., 1978; Lee, 1977; Matsui and Lee, 1978), Edwards in England (viz. Edwards et al., 1976), Manson in France (viz. Desbordes and Manson, 1978; Girard et al., 1978; Brossard et al., 1978), Wagner in Germany (viz. Dorge et al., 1976), and Nicholls in the U.S.A. (viz. Nicholls et al., 1978).

C. BLAST EFFECTS

The rapidly increasing use of huydrocarbon fuels has been reflected by the escalating number of accidental explosions. These provided some data on blast effects and promoted significant growth in investigations of their evolution. This work has been described in a number of survey articles and reports. Among these of particular relevance are: Strehlow, 1973; Strehlow and Baker, 1976; Coevert et al., 1974; Anthony, 1975; Eichler and Napadensky, 1977; Stull, 1977; Slater, 1978; Snellink, 1978. The Snellink publication is concerned explicitly with LNG.

A blast wave is a nonsteady flow field bounded by a shock front or a detonation wave. Its dynamic character is due to the combined effects of pressure and velocity. Upon encounters with solid objects the wave is diffracted -- a subject that was studied at some length, mainly using shock tubes, in the 1950s (viz. Emmons, 1958). In practice, all this has been of lesser importance and even the effects of dynamic pressure have been found to be negligible (Baker, 1973; Strehlow and Baker, 1976). The sole effect that is taken into account in assessing blast effects under practical circumstances is that of static pressure. The full spectrum of damage is expressed in terms of two parameters: the maximum relative overpressure,

$$P \equiv (P_{max} - P_a)/P_a$$

which usually corresponds to conditions immediately behind the front, and the static impulse,

$$I \equiv \int_0^{\tau} [P(t) - P_o]\, dt$$

evaluated at the position of the object affected by the wave. The integration is taken only over the period, τ, of the positive portion of the pressure pulse, a quantity that depends on the distribution of pressure within the wave. An isodamage response curve on the P-I plane takes the form of a rectangular hyperbola; the high overpressure side corresponds to high frequency, expressing the dynamic effects, and the high impulse side to low frequency, expressing static loads.

Most of the blast-damage criteria are expressed in terms of the overpressure alone. This is justifiable under the supposition that such criteria apply only to blast waves of essentially similar structure -- a condition which is indeed satisfied by waves formed by high explosives, which, as a rule, are negligibly small in comparison to the distance at which the observations are made. Following are examples of thresholds for damage (Strehlow and Baker, 1976): in 10^{-2} bars (or kPa)

Type of Damage	Threshold 10^{-2} bars (or kPa)
Total destruction	67
Reinforced concrete building	27
Serious damage	13
Nonreinforced concrete building	8
Earthworks damage	7
Minor structural damage	3
Glass failure	1

For a decaying blast wave, the maximum overpressure, P, plotted against the distance from the source, R, has a negative slope,

$$d \ln P/d \ln R = -\lambda/(1 - y)$$

where

$$\lambda \equiv d \ln y/d \ln R$$

is the so-called decay coefficient, while $y \equiv 1/M^2$ where M is the Mach number of the front.

For decaying blast waves, the variation of λ with y is expressed by a curve which is in the general vicinity of, but always below, the straight line $\lambda = (j + 1)(1 - y)$.

For such waves, therefore, logarithmic plots of the overpressure as a function of the radius appear as practically straight lines whose slopes are of an order of at most $j + 1$ (i.e. 3 for spherical and 2 for cylindrical geometry, the actual case lying somewhere between).

To compare the effects of different explosions, the distance is scaled with respect to the energy of explosion, i.e. the sum of the internal and kinetic energies in the flow field of the blast wave. For a decaying wave that resulted from the deposition of a certain amount of energy in the medium, this sum is equal to the wave's source energy, E_j. As pointed out in the previous section, this leads to the definition of a reference radius, R_o. For spherical waves, the geometric factor $j = 2$, so that the scaled radius is in this case expressed as

$$\xi \equiv R/R_o = R/(E_j/P_a)^{1/3}$$

Yields of explosions usually are expressed in terms of TNT equivalents. These parameters are defined either on the energy or mass basis, i.e. as

$$\alpha_e \equiv E_{TNT}/E_E = q_{TNT}W_{TNT}/q_E W_E$$

or

$$\alpha_m \equiv W_{TNT}/W_E$$

where q is the specific exothermic energy (or heating value) and W is the mass of the explosive. For a given threshold level of the maximum overpressure, it follows from the above that

$$\alpha_e = (\xi_E/\xi_{TNT})^3$$

In the case of hydrocarbons the ratio q_{TNT}/q_E lies within quite a narrow range, from 8.37 percent for methane to 9.17 percent for isobutane, so that $\alpha_m = \epsilon\alpha_e$ where ϵ is in the range from 11.95 to 10.9.

On this basis Eichler and Napadensky, 1977, analyzed the effects of five major accidental vapor-cloud explosions, none, incidentally, involving LNG. Adopting a threshold value of 6.8×10^{-2} atm (1 psi) for the maximum admissible overpressure around nuclear power plants, they estimated that the permissible stand-off distance from the center of an explosive cloud should be

$$R_s(\text{ft}) = 101.5(\alpha_e W_E)^{1/3}$$

where W_e is the weight of fuel (in pounds) consumed in the cloud, while α_e is estimated to be somewhere between 20 percent and 40 percent. According to the correlation provided by Napadensky, for a cloud where the full 11.8 ktons of fuel vapor obtainable from 25,000 m^3 of LNG is consumed, the above formula, using $\alpha_e = 0.4$, yields R_s = 6.54 km. This value corresponds to R_s = 11.1 km for an overpressure of 3×10^{-2} atm, for which Snellink, 1978, estimated a stand-off distance of 11 km.

D. ANALYSIS

Blast waves usually are considered geometrically symmetrical, nonsteady flow fields of a compressible medium bounded by gasdynamic discontinuities. Their behavior is governed by spatially one-dimensional, time-dependent equations expressing the conservation of mass, momentum, and energy, subject to appropriate boundary conditions at the center and at the front for the particular problem under consideration.

Based on the pioneering work (von Neumann, 1947; Sedov, 1946; Taylor, 1941), self-similarity variables have been formulated that transform the governing equations of certain of certain classes of problems into ordinary differential equations, thus making them amenable to simple analysis. Such self-similar problems are characterized, as a rule, either by a constant front velocity, or by a negligible (essentially zero) counterpressure, causing the Mach number of the wave to remain infinite irrespective of its actual velocity. In most actual cases, however, expecially in the interpretation of experimental records, self-similarity solutions are not applicable. One must take into account the dependence of gasdynamic parameters of the flow field on changes in conditions at the front. It thus becomes necessary to deal with a nonlinear, coupled, nonhomogeneous set of partial differential equations.

The properties and solutions of these equations applied to explosions and implosions became known as the blast-wave theory. The theory's fundamental features have been presented in texts (Courant and Friedrichs, 1948; Sedov, 1957). Further progress has been recorded in a number of comprehensive papers (viz. Sakurai 1965; Korobeinikov, 1971; Oppenheim et al., 1971, 1972; Lee, 1972) and books (viz. Korobeinikov et al., 1961; Zeldovich and Raizer, 1963; Korobeinikov, 1973).

In relation to exploding clouds, basic problems treated by the theory are as follows:

(1) Decaying blast waves, i.e., classically, waves resulting from instantaneous deposition of a finite amount of energy at a point

(2) Piston-driven waves

(3) The Riemann problem of bursting diaphragm or exploding high-pressure vessel

(4) Waves associated with flames or deflagrations

Of major interest to the subject at hand is the structure of the wave in each case, as reflected especially by the pressure profile and the motion of its front. In the first case pressure is maximum immediately behind the front and drops quite rapidly to a plateau of roughly one third the maximum at about half the front radius. In the second case, on the contrary, pressure is maximum at the surface of the piston around the center and, except for the trivial case of planar flow where it is uniform throughout the flow field, it increases gradually from the value attained behind the shock front toward the maximum. Blast waves driven by flames are essentially of this kind (Kuhl et al., 1973). Moreover, as a consequence of relatively low flame speed, the flow field of the wave can be quite extensive, the front being far away from the flame. Under such circumstances, the dynamic effects of the wave arising from the overpressure become very small, while the static load the wave can exert, as expressed by the impulse, can become appreciable (Oppenheim et al., 1978).

To deal with more complex configurations, the essential aspects of exact solutions for simpler cases had to be simplified. This was done first by Strehlow, 1975, and later, in a more detailed analysis, by Cambray and Deshaies,

1978. The approximate approach was generalized ingeniously by Williams, 1976, for the development of a qualitative theory of cloud explosions. This approach, as Williams emphasized, may provide a good feel for the problem, but cannot yield a quantitative solution.

Interest in atomic explosions provided one of the major incentives for the development of computational analysis and, in turn, of a variety of finite-difference techniques. One of the earliest of these techniques was used (Goldstine and von Neumann, 1955) to obtain a numerical solution of conservation equations for decaying blast waves expressed in terms of Lagrangian coordinates. At about the same time, more detailed solutions for this problem were obtained using the same technique (Brode, 1955; Okhotsimskii et al., 1957). The most important device employed in this connection was the so-called artificial viscosity introduced by von Neumann and Richtmyer. This device permits sudden changes in gas-dynamic parameters at the shock front to be distributed among a finite number of computational grid points. Its main virtue is that it protects the solution from uncontrolled numerical oscillations that are generated when variables undergo finite jump and, at the same time, guarantees that the width of the zone where the change takes place will not grow.

Further noteworthy refinements in finite-difference techniques (Godunov, 1959; Lax and Wendroff, 1964) concern primarily the increase in the order of approximation. Useful background on this subject is available (Richtmyer and Morton, 1967).

For exploding clouds, a simple code has been constructed (Cohen et al., 1975) on the basis of a finite-difference technique developed (Wilkins, 1969) to solve blast-wave equations formulated in Lagrangian coordinates. This code has been used by Strehlow and his associates (viz. Strehlow and Baker, 1976) and by others (Oppenheim et al., 1978) to evaluate some prominent features of exploding clouds. A more elaborate code developed (Hirt et al., 1974) to solve nonsteady flow problems formulated in arbitrary Lagrangian and Eulerian coordinates has been used (Boni and Wilson, 1978) to analyze the transition to detonation in unconfined clouds of methane-air mixtures.

All the numerical techniques described above employ some form of artificial viscosity to deal with discontinuities. This device smears out the effects of discontinuities and, in particular, obscures their mutual interactions -- the processes that decisively influence the escalation of the flow field in, for example, the transition to detonation. A way to treat the effects of discontinuities and their interactions sharply has been developed recently (Kurylo et al., 1977). This method, in effect, is a generalization of a shock-fitting technique developed (Moretti and Abbett, 1966) to treat internal discontinuities in steady flow. The technique is based on an implicit control of the solution obtained at a number of grid points around a discontinuity and its interaction partners (the influence zone) to make sure that the change of state they cause is well fitted to the continuous portions of the flow field.

Finite-difference techniques are fundamentally deficient for three reasons:

1. They produce fuzzy results because they are obtained as a rule by interpolating between computational grid points, which has a smoothing effect

2. They generate numerical diffusivity, propagating the round-off error inherent in the technique and thus obscuring the effects of transport phenomena

3. They are incompatible with singularities, which must be artificially excluded from the flow field to assure convergence of the numerical scheme.

The situation can be remedied in two ways:

(1) Development of analytical techniques

(2) Development of numerical techniques that do not use finite differences.

The first analytical technique to be developed was based on the truncated expansion of the dependent variables in terms of the front coordinate (Korobeinikov et al., 1961; Korobeinikov and Chushkin, 1963; Korobeinikov et al., 1963; Sakurai, 1965). With self-similar solution providing the zeroth-order step, only the first- and second-order approximations were thus evaluated. The results were found to be valid only for flow fields in the immediate vicinity of the self-similar limit, i.e. in the hypersonic range of front velocities.

Another approximate solution (Oshima, 1962) used the so-called quasisimilar method, whereby all the terms containing the front coordinate are taken equal to their values at the front. With this assumption, the method gave satisfactory results close to the self-similar limit and just behind the front, but the accuracy deteriorated fast toward the center. Consequently, the integral relationship expressing global conservation of mass could not be satisfied. In an alternative approximate method, the density was expressed as a power law of the field coordinate (Mel'nikova, 1966; Bach and Lee, 1970). Here the mass integral relationship was satisfied automatically. However, one was handicapped basically by the *a priori* assumption concerning the density profile. The continuity equation and the momentum equation yielded respectively, the velocity and pressure profiles, while the energy equation became superfluous -- a feature leading to a significant error in the energy integral relationship. As it turned out, this technique gave a satisfactory solution for the case of an adiabatic point explosion. However, in addition to the inherent error in the energy balance, the method's applicability was fundamentally restricted by the artificial nature of the approximation on which it was based.

The most advanced analytical technique (Korobeinikov and Chushkin, 1966; Korobeinikov et al., 1969) resulted in a set of tables of blast-wave parameters for adiabatic point explosions under conditions of planar, cylindrical, and spherical symmetry. A detailed description of this technique and its results is available (Korobeinikov, 1973).

The analysis is based on the method of integral relationships first proposed by Dorodnitsyn, 1956a, 1956b, and later refined by Belotserkovskii and Chushkin, 1965. With this method, the flow field is integrated along strips with respect to one of the independent coordinates, while the other is used to provide the compatibility conditions between them. By using the front coordinate as the independent variable, and integrating along strips starting from the front, the analysis avoids the problem raised by the existence of a singularity at the center.

A novel computational technique particularly well suited to the problem at hand was developed by Chorin, 1976. The technique can be used to evaluate the evolution in time of the nonsteady flow field governed by the typically hyperbolic set of blast-wave equations. It is based on the existence proof of Glimm, 1965, and is called the Random Choice Method. In essence, conditions at each grid point are evaluated from the solution of a Riemann problem obtained for two grid points at a previous time, while the time interval is controlled so that the new point is within the characteristic domain of the two old points. The crux of the technique lies in the manner in which the dependent variables at the new point are determined. Instead of interpolating, they are simply assigned a value obtained from the solution of the Riemann problem at an intermediate point in space whose position is fixed by a set of random numbers drawn from an equidistributed sequence. The results at each point are thus evaluated sharply. At any time interval the evaluation is associated with a finite error, but the proof of Glimm guarantees that, as time progresses, the error will decrease, and the solution, being stable and compatible, is definitely convergent.

The method of Chorin is still in the early stages of development. Although it has been used successfully for reacting gas flows (Chorin, 1977), it has yet to be applied to problems involving exothermic reactions whose rate is high enough to generate pressure waves, as in the case of exploding clouds. However, the technique should be considered particularly promising for the problem of exploding clouds. Besides its inherent ability to generate solutions devoid of numerically induced diffusion, and the concomitant ability to treat wave-interaction processes with sharp resolution, its main virtue is that it is fully compatible with the Random Vortex Method, which, as mentioned earlier, is ideally suited to the analysis of large-scale turbulence governing the early states of cloud explosion. Thus, the Chorin method may be instrumental in the development of a predictive capability for the problem at hand.

E. CONCLUSIONS

1. The subject of explosions and blast effects has a rich heritage of scientific background -- a body of knowledge that must be taken into account in research on LNG hazards.

2. Major impetus for the development of blast-wave theory has come from concern over the explosive yield of atom bombs, while the dynamic effects of high explosives, observed in large-scale field tests, have been treated as an empirical science with a modicum of rational background. It should be noted particularly, however, that most of the physical characteristics of explosions have been established by laboratory experiments.

3. The current significant interest in exploding clouds is manifested by publications on work in western Europe, Japan, and the United States. They cover not only LNG, but the full spectrum of hydrocarbon fuels.

F. RECOMMENDATIONS

1. With respect to the escalation of combustion to explosive magnitude, the formation of deflagrations propagating fast enough to drive pressure waves ahead of them should be considered more important than the transition to detonation, which so far has received overwhelmingly the most attention. In particular, the question of whether such

a transition is possible imparts the wrong emphasis, since damage produced by a pressure wave generated by deflagration may be as serious as that incurred by detonation.

2. Proper consideration should be given to certain unusual circumstances which so far have not been taken into account, as for example, explosion of an LNG cloud initiated by a detonating cloud of a more sensitive fuel vapor, emanating from an external source.

3. The primary objective of research required to assess explosion hazards of LNG clouds should be the attainment of rational means of predicting explosive yields. The major effort in this direction should be based on numerical analysis, which in turn, would provide specific requirements for experimental data. Of particular importance in this respect should be:

(a) study of the mechanism of flame acceleration, especially in connection with large scale turbulence and its escalation by obstacles in the flow field.

(b) investigation of two- and three-dimensional blast wave effects, permitting assessment of the influence of field geometry on explosion hazard.

4. The experimental program carried out to assess explosion hazards should be centered around laboratory studies, with supporting evidence provided by small-scale field tests. Large-scale tests should be used only to check the validity of prediction when a predictive capability is at the last stages of development.

5. Research to provide rational background for assessing hazards should be associated with a study of preventive measures. This study should include work on the establishment of strategies to be followed in case of a specified set of accidental spills. It should also include the development of actual means of prevention -- for instance, a saltwater spray to desensitize the cloud by inhibiting the propagation speed of the flame so that the rate of combustion would be too small to generate a pressure wave.

6. The program of research should be planned for at least three years. One cannot expect useful results based on reliable data to be obtained in a shorter time.

7. The research should cover all liquefied fuels, not just LNG. Comprehensiveness is important for scientific reasons and also because, by the time the results are

available, most of the political problems involving LNG will have had to be settled, while the hazards associated with the transport of fuels will not only remain, but most likely will have escalated.

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CHAPTER X

LNG RISK ASSESSMENT

A. INTRODUCTION

This report reviews the state of the art of assessing the risk of water transportation of LNG. The reports and papers selected for review are representative of the various approaches that appear in the literature. The purpose of this report is to:

- Describe the approaches that have merit
- Discuss the limitations of some of these studies
- Evaluate the validity of risk-assessment methods

B. RISK ANALYSIS (RISK ASSESSMENT) DEFINED

"Risk analysis is a systematic effort to quantify uncertainties associated with undesirable events" (National Academy of Sciences, 1976). The generally accepted definition of risk is that it is the probability that an undesired event will occur and the consequences of that event. The purpose of risk analysis for a given activity is to identify all the undesired events that could occur, estimate the probability that each will occur, and estimate the damages that would result from each. The damages may be expressed, for example, in terms of the numbers of deaths or injuries or the dollar value of property damage.

Risk can be assessed in many ways. The method used depends on the information available, the technical knowledge of the investigator, and the purpose of the analysis. Each of these factors leads to different levels of detail and sophistication in the analysis. For example, if risk is assessed for several sites in conjunction with an evaluation of economic and other site-suitability factors, the analysis may be a worst case evaluation or at least may not be very detailed. If the several sites had vastly different ship-traffic densities and quite different population densities in the surrounding areas, these factors, too, would tend to favor an order-of-magnitude or worst-case analysis, to rank the risk levels associated with the sites. On the other hand, if a specific site is desired for an LNG terminal, the risk assessment for the site should use the best possible data and go into as much detail as the available information and state of knowledge permit.

Because different levels of detail are associated with the various types of analyses, the results of different analyses cannot readily be compared quantitatively. One can meaningfully compare neither the results obtained for the same site nor the risks associated with several sites. This limitation would not exist if investigators included an indication of the uncertainty, confidence levels, or error bands associated with the risk value.

These cautionary and explanatory statements are made because casual readers or users of risk assessments who find quite different results in two studies performed for the same site may come to erroneous conclusions. They may decide arbitrarily that the analysis that gives the most pessimistic results is the correct one, or they may simply come to distrust all risk assessment studies. The user of risk assessment studies must be sensitive to the purpose of the analysis being reviewed and must not take the numerical values of risk literally. This point will be treated in more detail later.

C. TYPES OF RISK ASSESSMENT FOR WATER TRANSPORTATION OF LNG

The titles of a wide range of studies contain the words "risk analysis" or "risk assessment." However, not all of these studies address the determination of the two terms needed to express risk: the probability of occurrence and the consequences of an undesired event. Some studies focus on the probability that an LNG release will occur, others on the consequences of a release. For example, several "risk" studies assess only the probability of a collision between two ships, resulting in the release of LNG. Nevertheless, studies that evaluate probabilities alone or evaluate consequences in detail (or where consequence and vulnerability models are developed) are obviously necessary and useful in assessing risks.

Risk assessments at a variety of levels of sophistication and detail have been performed for federal and state agencies and for private organizations such as owners of LNG terminals. "For each LNG import terminal at least eleven federal agencies and twice as many state and local bodies are involved in the approval process" (Van Horn, 1976). However, very few of these agencies perform risk assessments. The majority of the risk studies for specific sites have been performed by (or for) the Federal Power Commission (FPC) in support of environmental impact statements and by terminal owners. The purpose of these site-specific risk assessments is to obtain approval for the site.

Other important safety studies or non-site-specific risk studies have been supported by agencies that include the Coast Guard, the U.S. Maritime Administration, the Department of Energy (and its predecessor, the Energy Research and Development Administration), the Santa Barbara County (Calif.) Office of Environmental Quality, and the Council on Environmental Quality. Many of the LNG safety and risk studies funded by these agencies have been performed to assist them in their decision-making and regulatory roles in general, rather than in the site-approval process.

This review discusses not only studies addressing the delivery of LNG to U.S. coastal ports, but related studies as well. These include several LNG risk-assessment studies done in Europe and some general studies that bear on LNG risks. The general studies include those on risk acceptability and risk perception.

The types of studies considered here are:

- Site-specific risk assessments

- Site-specific evaluations of the probability of an accident leading to the release of LNG

- Site-specific evaluations of the consequences of an LNG release

- Non-site-specific safety studies for the water transportation of LNG (generally these are models, such as the vulnerability model)

- Non-LNG safety and risk studies relevant to LNG transportation

- Acceptability-of-risk, risk-perception, and risk-benefit studies of a general nature

D. SUMMARY OF REPORTS REVIEWED

Highlights of the types of information found in the reports that were reviewed appear in Tables 6 and 7.

Table 6 Summary of Factors Considered in Site-Specific Studies

Reference	Scenarios	Data Base*	Were the following factors considered? Specific Causes of Accidents**	Risk-Reduction or Mitigating Factors	Future Traffic (All Cargoes) and Accidents	Consequences or Effects of a Release
Ligthart, 1976	Collisions, groundings	1963-1974 harbor reconstruction, resulting in reduced accident frequency, in this time period was taken into account	Yes	Yes, but qualitatively	No	No
A. D. Little, Inc., 1974	Collisions, rammings, groundings (both while moving and at dock)	1962-1970 accidents at east coast ports 1969-1973 barge and big ship accidents 1969, 1970 and 1972 traffic (a confusing mix of traffic and accident time periods).	Yes, for 1969 and 1970	Yes	Yes	No
Snellink, 1978	Collisions, groundings, rupture of transfer line, second tank damage after pool fire resulting from first tank rupture, LNG in empty spaces between outer and inner hull of tank after initial piercing above water line, also brittle fracture causes collapse of second tank	1963-1974	Not mentioned in this summary paper. May have been treated in supporting studies.	No	No	Yes, fatalities to LNG crew, colliding ship crew, terminal personnel, neighboring population, also property damage outside terminal.

Table 6 (cont'd.) Summary of Factors Considered in Site-Specific Studies

Reference	Scenarios	Data Base*	Were the following factors considered? Specific Causes of Accidents**	Risk-Reduction or Mitigating Factors	Future Traffic (All Cargoes) and Accidents	Consequences or Effects of a Release
SAI, 1975	Equipment failure (tanker ship and transfer line), collision, ramming, while at dock, aircraft crash, space debris, meterorite strike	1969-1974 accidents (for LA and six comparable areas), 1968-1973 traffic (1973 traffic by ship size and type)	No	No	Yes - estimated (judgement)	Yes - fatalities to the public
SAI, 1978	Collision, ramming while at dock, aircraft crash, striking fixed object	1969-1975 Chesapeake Bay area accidents and traffic. Seven other areas (from SAI, 1975) 1969-1974.	No	Yes	No	Yes - fatalities to the public
Reese, 1978	Collisions - encounter situations studied in detail	Six year period for seven major U.S. port approaches and world-wide accident statistics. Santa Barbara Channel 1969-1977.	Yes	Yes - but qualitative.	Yes - detailed evaluation.	No
Kenney, et al., 1978	Collisions, ramming, aircraft crash, meterorite impact	Not given - no reference to supporting studies	No	No	No	Yes - fatalities.

Table 6 (cont'd.) Summary of Factors Considered in Site-Specific Studies

Reference	Scenarios	Data Base*	Were the following factors considered? Specific Causes of Accidents**	Risk-Reduction or Mitigating Factors	Future Traffic (All Cargoes) and Accidents	Consequences or Effects of a Release
Booz Allen Applied Research, 1973	Collisions, rammings, groundings (not separately evaluated)	1971-1973 accidents at eight ports, 1969-1970 traffic, (accidents: over $100,000 damage to vessel or $150,000 damage to vessel and cargo. Also considered all incidents).	No	No	No	No
Simmons, 1974	Collisions, groundings	1966-1972 petroleum tankships accidents resulting in spills in U.S. waters, 1971-1972 traffic	No	No	No	Yes - fatalities to the public
A. D. Little, Inc., 1978	Collisions, unloading operations, missiles from Vandenberg AFB, aircraft crash, tornadoes offshore	Not given in this report, reported elsewhere	Not mentioned in their report, may have been treated elsewhere.	No	No	Yes - fatalities and burn injuries to the public. Presented profile of number of casualities as a function of probability.

Table 6 (cont'd.) Summary of Factors Considered in Site-Specific Studies

Reference	Scenarios	Data Base*	Specific Causes of Accidents**	Risk-Reduction or Mitigating Factors	Future Traffic (All Cargoes) and Accidents	Consequences or Effects of a Release
			Were the following factors considered?			
Welker, et al., 1976.	Cargo transfer operations, onboard cargo handling	Spills of other flammable liquids in marine transfer operations. Process industry failures, other industrial experience.	Yes	Yes	N/A	Fatalities as a function of spill size.
Locke, et al., 1978.	Engine room explosion leading to cargo tank failure, grounding, collision, berthing contact, external fire while ship is at berth, failure during transfer operation leading to embrittlement of deck plating and high local stresses	1965-1976	No	No (but evacuation effectiveness was considered)	No	Yes (casualties, injuries, and fatalities)

* Accident data are generally for the fiscal year (FY), whereas traffic is generally for the calendar year.

** By cause is meant the primary cause. For example, if a collision occurred, was it caused by human error (and why), by lack of certain equipment, failure of equipment to function as intended, etc. Only by knowing the cause of past accidents can one estimate the effects of implementing mitigating or risk-reduction measures.

Table 7 Summary of Non-Site Specific Studies Relating to Risk Assessment

References	Summary
Murrat et al., 1976	Overview of state of knowledge of risk assessments for LNG spills. List of 50 references plus a bibliography of 189 reports and articles.
United States Department of Energy, 1978	Review of past and present research in LNG safety and environmental control. Major areas evaluated were (1) effects of LNG releases and (2) release prevention and control, and (3) instrumentation needs to enhance the quality of data from experiments. Additional research needs were identified and discussed.
General Accounting Office, 1978	Review of safety issues and critical evaluation of present and planned research on transporting and storing liquefied energy gases--including LNG. Recommendations given.
See references marked *	Articles and reports on risk-benefit analysis, risk acceptance, and risk perception
See references marked #	Reviews of USCG programs (past and current) on risk analysis and LNG safety.
de Frondeville, 1977	Summary of safety and reliability experience in LNG shipping
Van Horn and Wilson, 1977	Summary of safety issues and LNG risk estimates.

E. VALIDITY OF DATA AND ASSUMPTIONS

Data for establishing the probability of an LNG spill are based most often on past accidents. In some instances the accident data that are used are for a specific port and the approaches to it. Often, the sizes of the ships involved in past accidents are taken into account in determining ship-to-ship collision probabilities. In this way, impacts by ships too small to cause damage to an LNG ship are not counted. (However, if these smaller ships carry hazardous cargo which could burn or explode as a result of the collision, then not considering them may result in underestimation of the possible hazards resulting from the accident.) In some studies, accident data are acquired for several major U.S. ports and all U.S. waters for ships above a certain size. Such data provide additional support for the frequency of collisions as a function of ship traffic.

The range of times for which accident data are acquired varies widely from report to report. Some investigators consider only the two years preceding the study; others gather accident data for about 10 years. Obviously, the longer period is better, even if there have been major changes (such as a vessel traffic system) in a harbor or port during the preceding 10 years, in part because it is desirable to assess the effects of new operating rules, procedures, or equipment on accident rates.

The major shortcoming of most studies is failure to estimate future traffic patterns (i.e., projected ship sizes and traffic density) that may affect the predicted accident rates. It is generally assumed in these several studies that LNG traffic will increase in some specific way over the next 20 or more years. However, future traffic in other kinds of ships using the same waterways is rarely mentioned. Obviously, accident probability estimates for LNG shipping facilities that are expected to have a lifetime of at least 20 years ought to account for traffic, ship sizes, and other hazardous cargoes expected during the same period.

The studies reviewed here include two exceptions to these limitations in probability estimates. They are the work by Reese, 1978, of J.J. McMullen and Associates, Inc., and by Ligthart, 1976, of the Netherlands Maritime Institute. Although the J.J. McMullen study has the words "Maritime Risk Assessment" in its title, it addresses only the question of accident probabilities leading to a spill. However, this very creative study is a more valid evaluation of the probability of accidents than any of the other U.S. studies reviewed. The study was done by people familiar with ships and their performance and special capabilities. It includes the results of using the ship-simulator facility at the Maritime Administration's National Maritime Research Center, (NMRC), Kings Point, N.Y., to examine the effects of the responses of the ship's master or pilot to situations that could end in a collision.

An example of the thoroughness of the McMullen study is that it considered current traffic generated by each of several ports, anchorages, routings, and traffic make-up by ship type and projected the results through the year 2000 for the Santa Barbara channel area. The data were used to simulate by computer the traffic conditions expected around proposed LNG sites. The most probable encounters, heavy-traffic encounters, difficult encounters, and the closest point of approach were determined for the pertinent geographic areas in the channel. The analysis determined the types, frequency, and location of exposures and the routes, aids to navigation, equipment, etc., required to reduce these exposures. High-frequency and difficult encounters were the basis of further, in-depth examination on the NMRC's CAORF (Computer Aided Operations Research Facility) ship simulator. Pilots and masters used as test subjects on the CAORF simulator were representative of those expected to operate LNG carriers.

The McMullen approach to estimating probabilities of accidents involving LNG ships and the effects of mitigating factors on accident frequency should be a model for other investigators. All too frequently in other studies the estimates of accident probabilities are little more than exercises in the manipulation of data, with no understanding of which data are meaningful and which questions to ask. It is clear that people who understand the behavior of ships and their differences and special features, as well as crew performance under normal conditions and under stress, can much better evaluate past accident data. Such people know which data are relevant and are better qualified to estimate the effects of possible accident reduction measures.

The work of the Netherlands Maritime Institute (Ligthart, 1976) does not appear to be as comprehensive as the J.J. McMullen study. However it does show familiarity with ships, including LNG ships, and their special characteristics and performance. The study does a very credible job of utilizing past accident records.

In contrast to a few very thorough investigators and to the majority who treat past accident data in a less sophisticated way, there are, unfortunately, several investigators whose input "data" are based on sheer speculation. The values are clearly arbitrary, and no basis is given for picking a certain value. The results of such analyses clearly should be rejected. In reading reports on risk assessments one should be sensitive to whether a basis or a source is given for the data presented.

The United Kingdom report on Canvey Island (Locke et al., 1978) handles the problem of the validity of input data in a unique way. The report uses one of five categories (a, b, c, d, or f) to describe the degree of uncertainty of each probability number, as follows:

(a) Assessed statistically from historical data.

(b) Based on statistics but with some missing figures supplied by judgement.

(c) Estimated by comparisons with previous cases for which fault tree assessments have been made.

(d) "Dummy" figures - likely to be always uncertain, a subjective judgement must be made.

(f) Fault tree synthesis, an analytically-based figure which can be independently arrived at by others.

1. Selection of Accident Scenarios

The number of accident scenarios considered by the many risk studies is quite limited. Most of the investigators consider only ship-ship collisions, with the LNG ship being the one struck. A few studies consider the LNG ship being struck by an airplane. The cargo of the striking ship was not taken into account in any of the studies reviewed, although past accidents have shown that if both ships, for example, contain flammable cargos, both cargos may become involved. Studies generally consider tanker ships credible striking ships that could cause a release of LNG, and tanker-ship traffic enters into the determination of the probability of a collision leading to an LNG release. However, when the consequences of a collision are considered, only the LNG ship is treated as having a hazardous cargo. Considering only the effects of an LNG release, if the other ship contains flammable, toxic, or other hazardous materials, clearly underestimates the consequences of the accident.

All risk studies seem to focus on the low-probability, high-consequence events that could affect nearby population centers. High-probability, lower-consequence events are not considered. The high-consequence events (catastrophes) are generally associated with involuntary risks assumed by people who live near the LNG terminal, but it is shortsighted (and underestimates the risk) to ignore the effects of an accident on the crews of both struck and striking ship. Other points not treated in risk studies are the effects on other ships at dock or in transit in the vicinity of a spill and on the LNG terminal and other shore-side facilities.

The assessment of risk should include as complete a spectrum of undesired events as possible, since total risk is the sum of individual risks from each possible undesired event. Neglecting potential accidents and their consequences leads to understating the risk. All possible accidents and their consequences cannot always be anticipated, so one can argue that risks are always understated. However, one should not knowingly neglect possible accident scenarios.

2. Treatment of Mitigating Factors

Many of the risk studies evaluated considered mitigating or risk-reduction factors that could contribute to reducing the probability of an accident leading to an LNG spill. "Credit" is often given for such things as (1) expectations of better training of the crews of all types of ships, (2) improved navigation and communication systems, (3) new safety-related operating rules, etc. Arbitrary multiplying factors (each less than one) are assigned to each of the mitigating factors. For example, in one detailed study (SAI, 1978), better training of all crews was credited with reducing the number of collisions to 0.2 of its former value -- if 10 collisions per year had been predicted prior to improved training, after training one should expect only two collisions per year. Yet the same report quotes several studies that show that human errors account for about 80 percent of all collisions. It is certainly not conservative to imply, by the use of a risk-reduction factor of 0.2, that improved training alone will eliminate the majority of collisions caused by human error (National Academy of Sciences, 1976a, to be published.)

An additional inaccuracy is at least as significant as overstating the effects of risk-reduction measures. It is that mitigating factors are often treated as being independent of one another, and the effects of several mitigating factors are multiplied to give the overall reduction in the number of collisions. For example, in one study, the three mitigating factors cited previously are assigned multipliers of 0.2, 0.5, and 0.5, respectively. It is then claimed that these factors will reduce the number of collisions by 0.05 (0.2 x 0.5 x 0.5 = 0.05). However, no justification is given for multiplying the factors together. It is clear that they interact -- they are not independent.

Most of the probability calculations reviewed were based on past accidents. They did not take into account the primary or underlying causes of the accidents. The risk assessor, therefore, cannot know if mitigating factors in fact will reduce risk. On the other hand, the J.J. McMullen study (Reese, 1978) evaluated the effect of risk-reduction measures on the NMRC-COARF simulator for the geographical area of interest. Thus the effects of risk-reduction measures were arrived at by other than arbitrary means.

3. Validity of Consequence Estimates

The state of the art in predicting the effects of an LNG release are discussed elsewhere in this document. Once the effects of the release (and subsequent ignition) are determined in terms of size of cloud or pool, radiation and/or overpressure as a function of distance, etc., it is necessary to calculate the damage or impact on exposed populations. These impact or damage evaluations have been performed in a number of vulnerability studies supported by the Coast Guard (Schneider, 1978). The vulnerability model seems to be under good control, and work is in progress to improve or refine it still further.

4. Summary of Studies Reviewed

In the large majority of the studies, reports, and papers evaluated in this review, the determination of the probability of a release of LNG is based on less than optimum use of historical accident data. In a few instances there was only a marginal attempt, at most, to use readily available information. The exception cited earlier (Reese, 1978), not only used historical accident data in a knowledgeable way, but predicted future traffic of all cargos and used the NMRC-CAORF simulator to obtain data not available by other means.

Another limitation of the many risk assessments that were reviewed is that they consider very few accident scenarios. Generally, only the worst case is treated. However, since the probability of its occurence is very low, the risk is also found to be low. What is lacking is a study that considers the wide spectrum of possible undesired events with their probabilities of occurrence and associated consequences. All possible events must be considered to determine the total risk -- the sum of the individual risks.

We must conclude that the numerical values of risk must not be taken too literally. This subject is discussed in greater detail in the next section.

F. VALIDITY OF RISK-ASSESSMENT METHODOLOGY FOR WATER TRANSPORTATION OF LNG

In spite of its shortcomings and limitations, assessing the risk of water transportation of LNG is a useful activity. Many of the shortcomings can be overcome.

The numerical values of risk presented in the many studies reviewed are not valid indicators of the actual risk, for the following reasons:

- Credible scenarios are omitted

- Future ship traffic (all cargoes) is not considered (with one exception)

- Too much credit is given, and the values are arbitrary, for future risk reduction factors when even considered

- Human error is not usually accounted for in these analyses. When it is accounted for, event sequences which are initiated by human error are usually treated as independent. Experience (such as Three Mile Island) shows that human errors are not independent of one another. Further, human errors are often assumed not to occur because they are presumed to be eliminated by safety devices.

- Data on ship traffic and accidents often are not used properly

- Confidence limits or error bounds for the probability of a spill are never given

- The total risk, as a sum or integral of individual risks from all the possible undesired events, is not calculated. Thus, the "true" risk is underestimated

- Differences in the various dispersion models for predicting cloud size lead to very large differences in consequence estimates

- Very low probability values (values ranging from 10^{-10} to 10^{-50}/yr are often cited in reports) have virtually no meaning. They arise from assuming that a number of conditional probabilities that enter into the evaluations are independent and so can be multiplied together to arrive at the final number

Risk-assessment studies rarely discuss accuracy or uncertainties of the input data or the results. Instead, the elements in the analyses are presented as facts. In so doing, the analyst implies greater accuracy in the results than is warranted by our current state of knowledge.

"However, whatever flaws the LNG risk assessment may have, they are clearly superior to less systematic approaches" (Fischhoff, 1977). The following quotation (Green, 1975), although directed toward risk-benefit assessment, applies as well to risk assessment alone. "Even the most scientifically effective assessment is useful only as another input of factual data, along with data from myriad other sources, interested and disinterested, informed and uninformed, rational and irrational, into the decision-making process. The object of risk-benefit assessment should be to produce data for use in political discussion and debate, to evaluate the level of such discussion and debate, and to inform and enlighten, but not control, those who are charged with responsibility for making decisions in the public interest."

G. ACCEPTABILITY OF RISK

The acceptability of risk is generally treated in the studies evaluated in the context of other societal risks. Comparisons are made frequently with motor vehicle fatalities (probability of a fatality per person exposed), fires, electrocution, natural disasters (tornado, lightning) etc. An obvious problem with this comparison approach for water transportation of LNG is that, unlike motor vehicle accidents, for example, the risk is involuntary. People who live near an LNG receiving terminal may not use natural gas and so may not benefit directly from the facility, but they are exposed to the hazard anyway. Further, individuals can control -- or at least think they can control -- many societal risks. For example, a nonsmoker may have smoke detectors at home and also may have the most up-to-date electrical wiring system with electrical appliances in perfect condition, etc. That person is much less likely to die from fire or electrocution than the average person -- in fact we know that deaths by fire are not distributed uniformly through all socioeconomic groups.

Comparing the risks to the public from LNG accidents with voluntary risks (e.g., auto driving) and controllable risks (e.g., fires, electrocution) helps to give a feel for the magnitude of the estimate. But such comparisons do not and should not imply in any way that the LNG risk is necessarily acceptable or comparable to the other risks.

Starr, 1969, who has done the pioneering work in risk acceptability and risk-benefit analysis, argued originally that the acceptable risk for a new technology would be the same as the risk associated with existing activities having similar benefits to society. Most risk assessors use Starr's original concept of acceptability. However, the public is willing to accept much greater risks from voluntary activities (e.g. skiing) than from involuntary activities. Also, Starr's original concept assumes that what was considered acceptable in the past will be considered acceptable in the future. The risk assessor may show that the risk of water transportation of LNG is much lower than many other risks society currently accepts. But this demonstration does not affect the acceptability of the new risk, to the public.

A recent paper (Starr, 1977) describes four different evaluations of future risk as follows:

1. Real risk, as eventually will be determined by future circumstances when they fully develop

2. Statistical risk, as determined by currently available data, typically as measured actuarially for insurance-premium purposes

3. Predicted risk, as analytically predicted from system models structured from historical studies

4. Perceived risk, as intuitively seen by individuals

It is Item 3, predicted risk, that is determined in risk-assessment studies. It has been shown (Slovic, 1975, 1977) that Item 4, perceived risk, rarely agrees with real risk in a range of instances where the real risks are known. Slovic's experiments have shown that even for risks where an individual has had much experience, the magnitude of the risk is intuitively underestimated or overestimated. If the reference risk -- the risk that society is currently exposed to -- is thus misperceived, the magnitude of the new risk cannot be assessed reliably.

The USCG's role and objectives differ from those of the terminal owner or Federal Power Commission, who must be sensitive to public concerns. One can argue, therefore, that the USCG need not consider risk perception in reaching decisions on the acceptability of a risk. One may also argue that the USCG need only consider (1) whether the risks for LNG transportation are no greater than the risks associated with the water transportation of other hazardous materials and (2) whether the USCG in fact can adequately control LNG shipping and dockside operations. These arguments for ignoring the concept of risk perception are quite weak, however. Considering only the concept of risk comparability has its pitfalls, too. Very little work done on the risks of water transportation of hazardous materials lends itself to comparison with LNG. (This situation, of course, could be corrected). Also, in case of an accident, the public and Congress will view the USCG no differently than the terminal owners or FPC and other government bodies. Thus, the USCG should be concerned with the public's perception of risk.

It has been suggested (Slovic, 1977) that to answer the question, "how safe is safe enough?" or "is this technology acceptably safe?", "we need to develop a model of risk acceptance that would be useful to systems designers and policy makers. Such a model would not dictate what risks society should accept but, instead, should reflect the public's considered values and preference".

H. CONCLUSIONS

The assessment of the risk of water tranportation of LNG is worthwhile, but care must be exercised in interpreting the results of risk studies. Numerical estimates should not be taken literally. However, they can be useful in identifying possible system weaknesses and likely failure modes; as a guide for decision makers; and as a tool that can be used to scrutinize and criticize the decision maker. Although numerical estimates of risk should not be taken literally, the risks of water transportation of LNG appear to be low.

The reliability of any risk analysis depends on the adequacy of the experimental (or experience) data base, the validity of synthesized probability data (i.e., probabilities of events are modelled from similar systems, but not measured), the validity of subjective probability estimates (conjecture), and the accuracy of the physical models used in the analysis.

The risk assessments that were reviewed ranged from those based almost entirely on conjecture to those that provided considerable justification of input data.

A major limitation of all the risk assessments evaluated was that even the most detailed studies overlooked credible accident scenarios.

Analyses that are called risk assessments differ significantly. Some studies focus on determining the probability of an undesired event (e.g., a large LNG spill); others focus on determining the consequences of the spill; and some studies concentrate on even narrower aspects of the problem. However, the broader definition of risk assessment encompasses both probability and consequences.

Almost every LNG risk study emphasizes the low-probability, catastrophic event. Low-probability events are inherently difficult to assess to the degree of accuracy and confidence level that is desired.

I. RECOMMENDATIONS

Risk assessments should be periodically updated, because new knowledge or changing conditions during the lifetime of a project can affect the conclusions of the original assessment.

Additional accident scenarios, for the high-consequence, low-probability events, should be evaluated for their risks.

Risk should be assessed not only for the high-consequence, low-probability events, as is currently the practice, but also for the low-consequence, high-probability events. (The public's acceptance of LNG can be affected by less-than-catastrophic events).

The risks associated with water transportation of LNG and with other hazardous materials should be compared. Comparative estimates are generally more accurate, and more readily understandable, particularly if the basis for comparison is common practice, e.g., comparison of LNG fires with gasoline fires. The Coast Guard in consultation with an advisory group should establish the basis for risk comparisons (e.g., cargoes and ports to be studied).

The applicability of risk-benefit analysis should also be evaluated. Better input data should be developed to increase the reliabiliity of risk analyses. A worldwide incident-reporting system, including coverage of minor incidents and near misses, would help to provide relevant data.

Data from "man-in-the-loop" trials at a ship-simulator facility should be collected. Such data will increase the reliability of synthesized probabilities for ship collisions at specific sites.

When probability data are used, confidence levels and discussions of uncertainties should be provided.

Risk-assessment studies should include evaluation of secondary effects--e.g., effects of accidents at nearby hazardous facilities and at the LNG storage facility on the ship at its berth.

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APPENDIX A

BACKGROUND ON LIQUEFIED NATURAL GAS SAFETY RESEARCH*

TABLE OF CONTENTS

*Opinions in this appendix are those of the cited authors and do not necessarily reflect the views and recommendations of the panel. For critical appraisals of some of the subjects the reader should consult the appropriate chapters of this report.

I. SHORE-SIDE RESEARCH

A. LAND STORAGE TANK STUDIES

The LNG land storage tank is very important from the point of view of safety. The only fatal accidental release of LNG in the United States in Cleveland, Ohio, in 1944, was probably due to faulty tank materials of construction (136 people were killed). Safety studies of LNG tanks cover more than design, because operations such as purging can have a major impact on the safety of LNG tanks. Much of the work on materials of construction applies to ship's tanks as well as land tanks.

The factor usually cited as responsible for the disaster in Cleveland in 1944 was brittle facture of the tank metal caused by insufficient nickel in the steel alloy; other design factors contributed to the tragedy after the cryogen release. Nine percent nickel steel has been shown to be suitable for use with LNG, and a large body of work has been done in this area. In one of the more important studies (Zick et al, 1962), full-scale tanks were tested to destruction at -196°C. The goal of the test series was to prove the suitability of 9 percent nickel steel in the quenched and tempered condition and to show that stress-relieving was not necessary for steels heat treated by quenching and tempering or by double normalizing and tempering. The quenched and tempered material proved superior, and the burst strengths recorded were four to six times the ASME code design stress. The ASME later approved 9 percent nickel steel of either heat treatment.

Spaeder and Berger, 1970, examined the factors that make 9 percent nickel steel strong and tough. They concluded that tempering significantly affects the volume fraction of the various phases in the metal.

Benter and Murphy, 1967, U.S. Steel Corp., in part of a program entitled "Operation Cryogenics," studied the toughness of 9 percent nickel steel. They focused on the fracture characteristics of quenched and tempered steel at -196°C using the drop-weight test and the crack starter explosion-bulge test. The Nil Ductility Transition (NDT) temperature for the thin plate was below -263°C. Explosion-bulge tests also showed that the NDT temperature was below -196°C. The test series proved that 9 percent nickel steel remains ductile at temperatures much lower than LNG temperatures.

Maruoka, 1975, Sumitomo Metal Industries, Ltd., reported on the development of a submerged-arc welding technique for 9 percent nickel steel in large-diameter pipes for LNG. Two problems had to be overcome--weld cracks, and substandard weld-joint properties. An extensive experimental program showed, for example, that molybdenum was effective in decreasing cracks. The author found that Hastelloy C wire, which contained both molybdenum and tungsten, and a ZnO_2-SiO_2 base flux produced satisfactory weld properties even at -196°C. Coefficients of thermal expansion of the welded metals were almost equal to that of the virgin metal. Welded, 9 percent nickel-steel pipe was produced successfully on a pilot scale.

The International Nickel Co. Inc., in 1975, published a compendium of research on the low-temperature behavior of 9 percent nickel steel over a wide range of temperatures, but with emphasis at low temperatures. Some of the topics covered include chemical composition, heat treatment, impact properties, fracture toughness, hardness, fatigue, and weldability.

Cordea et al., 1972, of Armco Steel investigated the properties of 5 percent nickel steel. Cost was a major consideration, with 5 percent nickel steel being about 20 percent cheaper than the 9 percent nickel material. Yet, with a three-step heat treatment, the author's CRYONIC 5 alloy displayed toughness equivalent to that of 9 percent alloys. The data indicated that the 5 percent alloy was acceptable for LNG service.

The Aluminum Company of American, 1974, prepared a compendium of the properties of aluminum for cryogenic service. Aluminum, the major competitor of 9 percent nickel steel for LNG service, was used extensively in the space program and is used widely in land and ship LNG tanks. Data were given for low-temperature toughness and tensile strength. Tensile strength actually increased as the temperature decreased, both for virgin metal and, to a lesser extent, welded metal for at least one aluminum alloy and weld-filler alloy. Also discussed are impact tests, tear resistance, fracture toughness, and fatigue strength.

Concrete, too, is suitable for LNG service. Wozniak, of Chicago Bridge and Iron (CB&I), and Salmon and Huang of Sergent and Lundy, 1975, studied the feasibility of concrete as a secondary containment barrier. There had been interest in tall concrete dikes close to the tank in addition to low earthen dikes farther from the tank. A prestressed concrete wall, reduced in scale, was designed and built for a series of cryogenic tests. In case of tank failure, the wall may suddenly be thermally stressed to LNG temperatures, exposed to thermal radiation if the LNG is ignited, ana subjected to the full liquid head. Vertical and horizontal cracks were cast into the wall to serve as crack starters.

Two tests were run with the test wall, one with full prestressing and one with partial prestressing. Some LNG leakage did occur, but it was small and related to wall defects. The test wall, the authors said, performed generally as predicted in the design stage.

Hashemi and Wesson, 1971, of University Engineers examined systems for minimizing variations in tank pressure so as to reduce boiloff losses. As normal boiloff occurs, because of heat leakage through the insulation, the pressure in the vapor space increases until venting occurs or a boiloff compressor is activated. Sudden changes in atmospheric pressure can also cause rapid vaporization. Unless these vapor-generation rates are understood, pressure-control systems can be oversized, leading to inefficient design.

How the components of LNG individually vaporize is important, for the problems of rollover and flameless explosion depend on the concentrations in the tank. Vaporization can also be important in designing send-out systems and in custody transfer. Aging or weathering of LNG was investigated by Shell Pipeline Co. (Engar and Hartman, 1972), as discussed in the flameless explosion section of this appendix. Shah and Aarts, 1973, of CB&I investigated aging by preparing a mathematical model that calculated the heat-leak rate into land storage tanks and the component-vaporization rate for each time interval.

Tank operation is relatively straightforward. The difficulties come about when a tank is taken into or out of service, since if either is done incorrectly, a flammable mixture can result inside the tank, leading to disaster. Hanke et al., 1974, of CB&I reported on several related research projects. Perlite, and expanded inorganic insulator, when mixed with methane and air, burned at the perlite surface but would not burn below the surface; the glass-fiber resilient blanket burned weakly, with the binder material being eventually consumed. Nitrogen was used successfully to purge methane in perlite with and without a resilient blanket. Hanke also developed a mathematical model for the quantity of purge gas required. The author's purging models showed reasonable agreement with the actual field data. They concluded that the purging of LNG tanks safely into and out of service was feasible.

B. ROLLOVER

One of the unexpected occurrences in the liquefied natural gas industry occurred August 21, 1971, at the SNAM terminal at La Spezia, Italy. About 18 h after the completion of cargo transfer from the LNG carrier Esso Brega, the tank pressure suddenly rose and the safety valves opened; about 318 m^3 of LNG vaporized and was released. Fortunately, there were no injuries nor was any damage done (Sarsten, 1972). This incident and several others like it have prompted extensive research. Since few are willing to risk overpressurizing LNG tanks, research has concentrated on computer simulations and small-scale experiments with noncryogenic analogs.

The conventional explanation of this rapid vaporization is embodied in its name, rollover. If the composition of the tank's contents and of the LNG being added are different, stratification will result if mixing does not occur on loading. The different compositions can arise either from different sources of the liquid or from aging of the tank's contents. The denser, methane-poor layers on the bottom are warmer, and the vaporization is suppressed by the lower-density, cooler, methane-rich layers on top. Mixing between layers is slow, and only the top layer is in thermal equilibrium with the vapor space. As lower layers warm, the density differences become smaller until the densities are about equal; then the layers mix rapidly--hence the term rollover. As the warmer layer or layers reach the topmost layer, the suppressed vaporization is released and rapid flashing occurs. The danger lies in overpressurizing the tank or in emission of a large vapor cloud from the safety valves (Smith et al., 1973).

Chattergee and Geist, 1972, developed a computer simulation for establishing guidelines for reducing the chances of layering. (They modeled a multilayer system by creating heat and mass balances. Heat and mass flux rates measured in salt-water layered systems were adapted to LNG systems.) This model well simulated the historical record in three very different rollover incidents and led to recommendations on ways to avoid rollover. The recommendations included the now-standard top loading of LNG that is heavier than the tank heel, and bottom loading of LNG that is lighter than the heel.

Single-component substances cannot stratify spontaneously, but some LNG compositions can do so. Nitrogen is often present in small proportions. It has higher density but a lower boiling point than methane, so it is possible to have autostratification followed by rollover. As energy leaks into the well-mixed liquid, nitrogen preferentially boils, leaving a surface layer cooler but less dense than the bulk, which leads to stratification. There has been at least one incident of this type. Chattergee feels that the phenomenon cannot occur when the nitrogen concentration is below 0.5 percent, but it can occur when the concentration is above 4 percent; the behavior between 0.5 percent and 4 percent is uncertain. Prevention by eliminating nitrogen is the only solution, as recirculation will only add energy to the system, making the top layer even cooler (Chattergee and Geist,1976).

The tank heel can age because of the long time between deliveries, so the ship's cargo and the shore facility's tank content could differ significantly in concentration.

The Germeles, 1975, model uses a multilayer system with two components, methane, and a single pseudo fluid representing all other liquids. The model is significantly different from the model of Chattergee and Geist, 1972, but shows good agreement with the La Spezia incident.

C. DISPERSION FROM SPILLS ON LAND

One of the lessons learned from the Cleveland disaster in 1944, and from storage tanks in general, is that sufficient diking to deal with catastrophic tank failure is necessary. Furthermore, a desirable design feature for LNG storage facilities, and one that might become required at the national level, is that a flammable vapor cloud not cross a facility's boundary line. This possibility provides the motivation for studying boiling rates on land and cloud travel over land.

Curiously, the characteristics of spills on land are approximately the opposite of those of spills on water. The area of the land spill is determined by the dike walls while the area of the water spill continuously expands. Also, the ground under an LNG spill soon freezes, leading to a low, steady-state, vaporization rate, whereas water does not seem to freeze under a spill. On land, therefore, vapor-generation rate is at a peak toward the beginning of the spill and drops off to a much lower, steady-state rate; on water the vapor-generation rate increase throughout the spill as long as the LNG pool expands, because the rate of energy input from the underlying water remins constant. Also, the water spill is always modeled as unconfined and on a flat surface, but land spills always have dikes that present obstacles to the dispersion of vapor. Unlike the smooth surface of water, the dike floor can be rough or smooth, and can be composed of different materials. Because of these distinctions between spills on land and on water, the two require separate evaluations.

In 1960 and 1961, Conch Methane Services, Ltd., conducted a series of small-scale tests on land at Lake Charles, La., in preparation for large-volume international trade in LNG. A diked area, 1.52 m x 1.52 m, was used with sensors along the downwind axis at the dike wall and 3 m from the dike. The sensors were placed at heights up to 0.69 m above ground level. The peak vaporization rate lasted only a short period, leveling off to a low steady-state value. The flammable downwind zone followed the same pattern, being flammable for longer distances initially and declining to shorter distances as the dike floor froze. At steady state the vapor concentration was distributed normally as a function of height (Conch, 1962; Arthur D. Little, 1971).

Gaz de France conducted tests at Nantes with a series of four diked areas, 3 m x 3 m, 6 m x 7 m, 7 m x 7 m, and 14 m x 14 m. The investigators also measured the vaporization rate of LNG on various types of soils to account for the initial flash from a land spill. A Gaussian model was modified for use in correcting the data from the spill tests. Deviations from the time-average vapor concentration appeared significant when the average concentration fell below 3 percent. The investigators concluded that only massive spills could lead to significant vapor travel because the largest diked area, about 200 m², gave rise to a flammable-vapor-cloud travel of only 100 m, this being initial flash (Humbert-Basset and Montet, 1972; Gideon et al., 1974a).

One of the larger LNG research and development efforts was carried out for the American Gas Association (AGA) during the late 1960s and early 1970s. A major part of the effort was the early TRW spill series. In these tests, a diked area 1.5 m in diameter with walls 0.15 m high was used in 0.19-m³ spills. Boiloff rates were varied by changing the water content of the clay-soil dike floor. The vapor concentrations were measured using sensors 15 m and 30 m downwind from the dikes. Measurements were taken in the vertical and in the crosswind direction at the two stations (Arthur D. Little,Inc., 1971).

Wilcox prepared an empirical dispersion law for the AGA. He used the TRW data just described. First, he "guessed" the functional dependence of concentration on the distances, downwind, crosswind, and vertical; on the dike diameter; and on the wind velocity. Then the various constants were derived using the experimental data. The results differed from the more common dispersion equations. Wilcox's form is Gaussian, but the exponents are not of the usual form. For example, the velocity of the wind usually appears as inversely proportional to vapor concentration; Wilcox correlates it as inversely proportional to the square of concentration. Also, the weather cannot be factored into the equation (Wilcox, 1971).

The next effort, involving a large series of spills, was carried out for the AGA by Battelle Columbus Laboratories (BLC) at the TRW Capistrano Test Site (CTS) in California. Dispersion tests were run from diked areas 1.8 m, 6.1 m, and 24 m in diameter. Spill sizes were 0.38 m³, 4.6 m³, and 51.3 m³ of LNG, respectively. The LNG was 0.10 to 0.15 m deep and assayed 71 percent and 96.6 percent methane, with most tests performed with at least 90 percent methane concentration. A three-dimensional array of up to 36 Mine Safety Appliances sensors was used in these tests, with a thermocouple at each sensor. Also, thermocouples were placed in the bottom of the dike. The LNG level was measured and the local weather conditions were monitored. Some 28 land-spill dispersion tests were run, and the data analyzed for each. BCL noted significant cracking in the dike floor; this cracking was associated with short-term increases in the vaporization rate. These increases were superimposed on the usual initial peak vaporization rate followed by a dropoff to steady state (Duffy et al., 1974).

Arthur D. Little, Inc. (ADL), as part of this AGA project, developed a multiphase model for vapor dispersion from a diked area based on the TRW data and other work. The model began with an analysis of the time required to fill the dike volume with vapor, assuming the cryogen spill time to be essentially zero. The second step was to calculate the flow rate of the vapor over the lee edge of the dike by calculating the total mass-flow rate followed by a positioning of the vapor on the dike edge. The dispersion is Gaussian using a line source as the dike edge. The model agreed well with the experiments except within one dike diameter from the dike. Small modifications were made to the classical Gaussian expression to account for complicating factors. Further work was recommended with weather conditions more stable than the unstable-to-neutral that TRW found at the CTS. A computer program was prepared for the model (Drake et al., 1974).

Welker of University Engineers analyzed the CTS tests. The boiloff rate on land was developed for short times considering only the energy input from the soil, while for long times a role was played by convection from air, radiation from the sun, and sensible heat from the LNG itself. Using a classical Gaussian plume model and the data from the 24-m test from the TRW series, Welker compared the experimentally measured concentration data with his calculated concentrations using Brookhaven weather condition "C," neutral. These comparisons were performed for each of the 36 sensor locations used in the test. Generally there was good agreement between them, with reasonable scatter from the sensors. There was some difficulty in situations where the calculated concentration was less than 0.01 percent - there were peaks of short duration close to or exceeding 5 percent (Welker, 1974a).

For the AGA, Parker compared his 1970 model to the data correlated by BCL from the tests at the CTS. Parker's model was based on the classic Gaussian plume model with modifications for vapor negative buoyancy and the presence of the dike wall. This model showed general agreement with the data from 0.45-m-high dike walls used by BCL in its tests. Parker's calculations predicted that increasing the dike height from 0.45 m to 2.4 m would reduce the distance the flammble vapor cloud would travel by a factor of two. Similarly, increasing the height from 0.45 m to 4.9 m would reduce the downwind-travel distance by a factor of three (Parker, 1974).

The BCL tests at the CTS were limited in that they were not conducted in stable weather conditions, but only in unstable and in netural conditions. This was a serious limitation, because an inversion could make a significant difference in the downwind hazard. BCL performed two additional tests for the AGA at the West Jefferson test facility. These tests were run in a dike 1.8 m in diameter and with a low wall to measure dispersion during an inversion. The tests had three other objectives--better LNG depth instrumentation, an improved dike floor, and a major emphasis on safety; otherwise the tests were similar to those at the CTS. The dike floor at the CTS had cracked, which increased the effective area, while the new dike floor was uniform and resistant to cracking. The gas sensors used were the same as those at the CTS, but, unfortunately, when the new tests were run, the sensors either had failed or did not perform accurately. The results of the tests showed that the sensors were not performing properly, hence, there were no acceptable quantitative data on concentration. The improved dike floor, Mylar over brick, caused the low, steady-state evaporation rate to be reached much more rapidly than with the CTS soil floor. BCL personnel felt they had demonstrated the feasibility of tests performed under inversion conditions (Gideon et al., 1974).

The Japan Gas Association was commissioned by the Natural Resources and Energy Agency of the Japanese Government to conduct a series of LNG vapor-dispersion and fire tests. These tests were conducted in 1974 and 1975 at the Sodegaura terminal of the Tokyo Gas Company, Ltd. The 1974 tests involved two diked areas, 2 m by 2 m, and the 1975 test a diked area, 10 m by 10 m, plus ignition tests. The tests were well instrumented; for the dispersion tests, 72 gas sensors were employed. The tests included three spills in the 10 m by 10 m dike, one on water in a diked area (to simulate water spills), and two burns on land. A classical Gaussian dispersion model was used to correlate the dispersion data, but, with neutral weather conditions, the dispersion coefficients did not reflect the strong layering found by many others (for example, Burgess et al., 1970, 1972). Also, concentration profiles were developed (Japan Gas Association, 1976).

Meroney of Colorado State University has been involved with wind-tunnel simulations of LNG spills with the support of the U.S. Department of Energy (DOE). A test of this technique involved the simulation of one of the American Gas Association land spills at the CTS. The entire spill sequence was simulated; carbon dioxide or cooled helium-nitrogen mixtures were used to simulate LNG densities. While many of the test parameters could be scaled down for the wind tunnel, not all could be scaled down at the same time. A wind tunnel test section, 1.8 m by 1.8 m by 29 m, was used, with temperature-controlled air stream and boundary walls. Test results included a qualitative, visual study of the flow field around the dike and tank structures and a quantitative measurement of gas concentrations produced by a tracer released from the diked area. Meroney found good agreement with the AGA test. Future plans include pretest simulation of each test planned in DOE's LNG spill-test program to help in such matters as instrument placement (Meroney et al., 1978).

Spills of LNG on both land and water have been run. These tests are few in number because large LNG spills are difficult and fairly expensive to run. If the results from land spills could be used for water spills, and vice versa, a significant increase in the spill data base would result. Gideon of BCL critically examined most of the spill tests to that time for the AGA. He found different correlations for concentrations close to the spill and far from the spill; also, instantaneous spills led to different correlations than continuous spills. For water spills, the variables used were X (Distance), C (concentration), M (mass spilled), $\dot{M}$ (mass spill rate), and U (wind velocity). For land spills, A (area) was substituted for the mass variables. For short distances the correlations used were $XC/M^{3/4}$, and XC/A, while for long distances, the correlations were $X^2C/\dot{M}$, $X^2C/M^{3/4}$, and X^2C/A. The experimental data correlated equally well with or without the wind velocity, so another set of correlations was prepared, the above correlations being multiplied by the velocity, U. Gideon concluded that data for instantaneous spills could not be used with continuous spills. Differences between instantaneous land and water spills could be accounted for by varying the vaporization rate. Water spills, he concluded, were difficult to instrument, expecially in determining the pool area on water as a function of time. Correlations between instantaneous spills on land and on water differed by a factor of seven (Gideon et al., 1974a).

D. LAND-SPILL FIRE STUDIES

A major hazard from land storage of LNG is the release of cryogen followed by ignition and a land-pool fire. Since the peak vapor-generation rate occurs when the LNG first contacts the unfrozen dike floor, a fire then is larger than when the ground is frozen and vaporization has fallen to a lower steady-state rate. Various governmental and industrial safety codes specify the maximum thermal-energy flux at the plant boundary, based on a given flux for a specified time leading to a certain level of injury. The flux is usually given as 3.2 kW/m^2 to 32 kW/m^2. The wide discrepancy is based on differing judgments on the acceptable level of damage to innocent bystanders. Predicting the thermal flux at a distance from a given fire is a significant problem for the LNG industry. Much has been done experimentally in this area to determine radiation fluxes and to model fires.

Conch performed a series of large fire tests at Lake Charles, La., as part of the 1960 and 1961 research effort of the U.S. Bureau of Mines. Dikes of 1.5 m by 1.5 m and 6.1 m by 6.1 m were used in these tests. For comparison, gasoline was burned. The flames from gasoline and LNG were similar in size; the gasoline flame was very sooty, while the LNG flame was clean. The investigators found that the average radiation for LNG was 750 kW/m^2 and for gasoline 540 kW/m^2. They pointed out that the 50 percent higher heat of combustion for gasoline approximately compensated for LNG's higher boiling rate and made the following qualitative observations: flame heights were roughly three times the diameter; wind reduced the flame height; and no frothing or boilover occurred (Conch, 1962; Burgess and Zabetakis, 1962).

Burgess and Zabetakis of the U.S. Bureau of Mines, with partial support from the Continental Oil Co., conducted an experimental program of LNG spills and burns; this work and the Lake Charles tests discussed above were parts of the same test effort. The percentage of thermal energy radiated was as much as 34 percent, suggesting that all hydrocarbons burning in large-diameter pools will radiate about the same fraction, perhaps as high as 38 percent. Burning rates of shallow LNG pools proved difficult to measure accurately, but values as high as 1.16 cm/min were measured. On a volume basis, LNG burned faster than gasoline. The thermal radiation per unit area of fuel was between 750 kW/m^2 and 860 kW/m^2 for LNG in 3.0-m diameter pools, and it declined as the pool diameter increased. Similar values for gasoline were observed for smaller pool diameters, and the radiation flux declined for larger pools. Ignition of vapors above LNG pools within the period of peak vaporization rate produced a large momentary flash, but no overpressure or liquid splashing. The ignition of LNG in the steady-state vapor-ignition period led to a steady-state flame. The authors concluded that LNG can be stored safely in aboveground diked tanks (Burgess and Zabetakis, 1962).

The American Gas Association (AGA) work on dispersion included fire tests. The goal was to run experimental pool fires and develop predictive models. Duffy of Battelle Columbus Laboratories (BCL), ran the dispersion and fire tests. Fire tests were run at the TRW Capistrano Test Site (CTS). Radiation measurements were made with wide-and narrow-angle radiometers, total heat-flux meters, wood samples, skin simulators, grating spectrometers, and pyrometers. Thermocouples were placed with the wood samples, placed downwind to measure air temperatures, and placed above the dike floor to measure vapor temperatures. There were 14 fire tests: seven 1.8-m diameter fires, six 6.1-m diameter fires, and one 24-m diameter fire. The largest test was not completed as some equipment failed before the fire covered the entire surface. The highest vaporization rate was 1.6 cm/min, and the highest radiation flux (average values for the same test) was about 62 kW/m², which was recorded from the 24-m diameter test. The authors developed a general method for calculating the radiation flux to a target surface based on the test results. The method considered the source intensity; flame-base size; vaporization rate; flame shape, including "holes" in the flame, flame height, and flame tilt angle; and the geometric view factor. They concluded that the source intensity was about 178 kW/m² (Duffy et al., 1974).

Welker of University Engineers (UE) analyzed the data from the BCL tests. He included some data from tests at the Ansul test facility at Marinette, Wis. The radiant fluxes from the radiometers, skin simulators, and wood blocks led to an estimate that an optically thick flame would have a flux of about 143 kW/m². Welker provided a simplified method for calculating radiation fluxes using the view factor, fire-base size, and flame-tilt angle. He also developed a more complex, more exact model (Welker, 1974).

Attalah and Raj of Arthur D. Little (ADL), as part of the analysis of the BCL tests, were charged with selecting, if necessary, modifying a model that would correlate the experimental data. After considering the existing LNG burn experiments, they estimated the total emissive power of the flame to be 100 kW/m². The model selected was similar to Welker's, but some of the terms differed in value. A computer model was prepared for determining the radiant flux; this was a comprehensive, all inclusive model, including such factors as the "wet soil thermal conductivity." A listing of the computer program was included in the report (Attalah and Raj, 1974).

Carpenter and Shackleford of TRW examined the spectral data from the BCL tests at the CTS. Several infrared spectra were reproduced and analyzed. The authors concluded that, for LNGs containing higher hydrocarbons, the highest thermal flux occurs toward the end of the fire when the higher hydrocarbons are present in greater concentrations. The carbon-soot emission then predominates as well. At least for the 1.8-m diameter fire, the lower the wind speed, the higher the thermal radiation. Also for the 1.8-m fire, there were intensity fluctuations (with an instrument time constant of 0.3 s) of a factor of more than 100 for narrow-field measurements and about three for wide-field measurements, with flame temperatures as high as 1400°K (Carpenter and Shackleford, 1974).

May and McQueen of Esso Research & Engineering Co. had the opportunity to measure the thermal radiation from a very large, irregularly shaped LNG fire. The LNG input rate to the burning trench was well defined, at 2150 m^3/day to 6360 m^3/day, but the pool area was poorly defined. Radiometers were located at various distances along three directions, at ground levels and at elevated locations. The authors used a point-source model for the land fire, similar to Burgess' model for an LNG-spill fire on water (see Burgess et al., 1972). A very important parameter for such models is how much of the combustion energy is radiated outward. Time-averaged values of the radiated energy as a fraction of the total energy showed that only about 16.4 percent of the energy was radiated. This value was measured with elevated radiometers; a lower value, 12.4 percent, was measured with ground-level radiometers, because the dikes tended to shield some of the fire from the radiometers at ground level (May and McQueen, 1973).

The Japan Gas Association carried out a series of spill tests involving dispersion and fire at the Sodegaura terminal of the Tokyo Gas Company, Ltd. in 1974-75. These safety tests were commissioned by the Natural Resources and Energy Agency of the Japanese Government. Combustion tests were performed in 2 m-by-2 m square dikes with LNG being added continuously. Three combustion tests were run; unlike previous tests elsewhere, the LNG was more than 99 percent methane, coming from Kenia, Alaska. Ignition was difficult and would not occur unless the igniter was placed some distance into the visible cloud. Only about 13 percent of the total energy was radiated outward, and the total radiant flux from the flame surface was low, about 58 kW/m^2, probably because of the sootless methane flame (Japan Gas Association, 1976).

Along with the fire tests, several theoretical models have been developed for burning pools. Wilcox prepared a very theoretical model for a class of fire that included LNG. The model was an involved development including an entrainment law that described the air input, followed by a thermochemical analysis. Wilcox solved the radiation-heat-loss term, nondimensionalized the equations, and provided the initial conditions. A computer program was written to solve these very involved equations for an LNG fire. Comparison of calculated and experimental flame-height data indicated good agreement only for small fires, as large fires have "swirl," which was not included in the model (Wilcox, 1975).

Raj of Arthur D. Little presented a state-of-the-art review of LNG fires in 1977. He noted that there were two ways to calculate the thermal-radiation flux as a function of distance from a fire. The first way was the point-source model where complete combustion occurs at the center; the fraction of combustion energy radiated outward is an important parameter. The radiation flux at the receptor was determined by dividing the radiated energy by the area of the hemisphere whose radius is the distance from the receptor to the fire center. The second model was the plume-flame model, in which the entire visible flame was assumed to radiate energy and the invisible portion was not. The flux to the receptor is the product of the flame's emissive power, the flame's emmisivity, the view factor, and the atmospheric transmissivity. Raj evaluated each of these four factors, recommending the best values or methods of calculation. In particular, he recommended 100 kW/m^2 as the flame's emissive power. Finally, he addressed flame-height prediction and wind tilting of diffusion flames (Raj, 1977).

E. LAND-SPILL FIRE PROTECTION

The need to learn to combat fires has stimulated a large amount of research. With an LNG-spill fire, the goal usually is not to extinguish the fire completely, but to control it--to reduce the rate of burning and to avoid an unignited LNG vapor cloud's drifting downwind and causing even more damage than the original pool fire. Reducing the thermal flux, in some situations, could permit the stoppage of LNG flow. Other actions could be taken to ameliorate the effects of such fires on structures.

Perhaps the first major experimental program was the Conch tests at Lake Charles, La. Fire extinguishment tests were run in a diked area, 6.1 m by 6.1 m. The extinguishing agent was dry, finely powdered sodium bicarbonate. In two tests, flow rates of 91 kg/s and 25 kg/s, delivered by a turret nozzle, extinguished the fire; lower flow rates, delivered by hand lines, either failed to extinguish the fire or allowed the fuel to reignite rapidly. (No extinguishing tests were carried out at the Bureau of Mines facility). Sodium bicarbonate could extinguish LNG fires if about 0.68 kg of powder per second were applied to each square meter of surface; the surface had to be covered completely. LNG fires were easier to extinguish than gasoline fires (Burgess and Zabetakis, 1962).

The American Gas Association's (AGA) research effort into LNG hazards included two series of fire tests in 1971 at the Philadelphia Gas Works and in 1972 at the Ansul fire facility at Marinette, Wis. The goal was to gather data on the effectiveness of high-expansion foam and dry chemical agent. Wesson, 1974, of Wesson and Associates analyzed the test results. Typical foam expansions ranged from 100:1 to 1000:1; the foams work by diluting the oxygen, preventing free movement of air in a fire, cooling the fire by converting water to steam, and reducing the thermal radiaton back to the liquid surface. The spills at Philadelphia were made into 1.5-m and 3.0-m diameter pits, and those at the Ansul site were in dikes, 6.1 m by 6.1 m and 9.1 m by 12.2 m. The fire data were taken after precooling--that is, the fires were at steady state when the data were taken. The Ansul tests were conducted with two types of foam generators and two foam concentrates, one in each generator. Wesson provided data on fire-control time as a function of foam-application rate, pool size, and foam expansion ratio, as well as data on reduction of thermal radiation as a function of foam-expansion ratio. The foams appeared to reduce thermal radiation more effectively than water spray, which also was tested. High-expansion foams significantly reduced vapor concentration in unignited spill tests. Dry chemicals tested included potassium bicarbonate, monoammonium phosphate, and urea-potassium bicarbonate. Data were collected on LNG-fire extinghishing time as a function of application rate, pool size, and type of chemical. Wesson concluded that certain high-expansion foams can control LNG fires, consequently reducing thermal flux. Minimum application rates for dry chemicals were established. The required quantity of foam and dry chemical per unit area of fire was independent of the fire area.

As a continuation of the AGA work, University Engineers (UE) conducted a series of spill tests at Norman, Okla., in which the vaporization rate was varied by using a fire test pan with water pipes installed. High burning rates, up to 3.8 cm/min, simulated the early period in an LNG spill before the impoundment area freezes; tests were run on fires 1.5 m and 3.0 m in diameter. The usual methane detectors and radiometers were provided. High-expansion foams reduced the vapor concentration by as much as 80 percent within one pool diameter; the effectiveness of the foam depended on the degree of expansion. The thermal radiation was reduced by as much as 95 percent by high-expansion foams. Finally, the extinguishing time and minimum quantity for extinguishment for dry chemicals was related to the LNG burning rate (University Engineers, 1974).

The Ansul Co. a producer of fire-fighting systems and agents, has been test-extinguishing large natural-gas fires (three series, 246 tests) and LNG-pool fires (two series, 143 tests) since 1951. Ansul has reported useful data for commercial extinguishing applications, recommended suitable safety factors, and briefly discussed application techniques (Ansul, undated). The LNG-fire tests were reported in more detail in Wesson, 1974, and University Engineers, 1974.

University Engineers (UE) performed a series of small-scale fire tests for the U.S. Coast Guard to test several control methods. One major goal was to establish a basis for designing fire tests so large that they would be on the margin of extinguishable LNG fires. UE showed the importance of trained fire fighters in attacking LNG fires--the minimum chemical-application rates and times were not valid for untrained personnel. Obstructions on land and on ship could alter the extinguishment requirements, but UE found that as long as the chemical agent covered the liquid surface, the required application rate was not altered. Water spray, to reduce thermal radiation, proved largely ineffectual. While some beneficial effect was noted, water sprayed directly on the object to be protected would have been much more effective. Spraying water into LNG vapor clouds showed some benefit, with the water spray facilitating turbulent mixing. Finally, extinguishing LNG fires on water was no different from extinguishing fires on land if correction were made for the higher burning rate on water. All tests were carried out in pool fires of 9.3 m^2 (Brown et al., 1976).

Failure of adjacent tanks would compound the hazard from an LNG tank failure, so, to the extent possible, tanks should be protected from each other (Bureau of Mines, 1946). Direct control and/or extinguishment of LNG fires are active methods of doing so. In some ways, passive protection--as with insulating coatings--may be superior. Wesson and Lott of Wesson and Associates investigated this issue. They listed as acceptable the following types of coatings: cement compounds, ablative coatings, subliming compounds, and intumescent mastic compositions. In their opinion the following were unacceptable: standard thermal-insulation systems, refractory protection systems, intumescent-paint compounds, and water-of-hydration plasters. The authors surveyed the literature in this field. No data were available for LNG-fire tests of these coatings, but they felt that the existing data could be applied to LNG tanks and fires. One problem not covered completely in the literature was the effect of cryogenic thermal shock. Wesson and Lott performed small-scale experiments on the phenomenon using liquid nitrogen. Samples exposed to the cryogen showed effects varying with the primer used. Two coated samples were exposed to a liquefied-petroleum-gas (LPG) torching impingement fire; one had been exposed to cryogenic thermal shock, and one had not been. The authors concluded that coatings gave superior protection, but that some coatings failed when exposed to liquid nitrogen (Wesson and Lott, 1977).

II. WATER-SIDE RESEARCH

A. SHIP STUDIES

Clearly one of the most important elements in the LNG industry is the LNG carrier, which can carry huge quantities, up to 125,000 m^3, of the cryogen. To develop technically and commercially acceptable ships, the various designers, builders, and suppliers necessarily have undertaken extensive research and development. Such programs are required by the many regulatory agencies worldwide as well. Unfortunately, most of this work remains proprietary, so only a few research programs can be discussed here.

Most of these programs involve the LNG tank. Of particular interest is the spherical type of tank and the Moss-Rosenberg design for the spherical LNG tank has been discussed extensively in the open literature. The sphere, being essentially a simple shape, lends itself to accurate mathematical analysis, which may not be feasible for more complex designs. Howard of Moss-Rosenberg reported analyses of the Moss-Rosenberg sphere. Three related studies were performed. First, in a complete mathematical analysis, the deflections of the tank under the various types of service loads were calculated. Then the fracture-mechanics properties, such as critical crack lengths and rates of growth of fatigue cracks, were developed experimentally. Finally, nondestructive tests were devised to set limits on the maximum-size defects that could go undetected in the tank at the time of delivery. The crack growth rates that were calculated demonstrated that before a crack grew to the critical length and the tank failed, the crack would be detected by the cargo leak-detection equipment. Furthermore, the crack would propagate slowly enough to allow ample time to complete the voyage and offload the tank. Such tanks are of the leak-before-failure type and may be judged to be failsafe. Extra attention was paid to the equatorial ring, where the tank is connected to the supporting cylinder or skirt (the tank bottom does not contact the inner hull). During the hydropneumatic test of a tank from the first of the Moss-Rosenberg, 125,000-m^3 LNG carriers, the stresses and strains were measured as a function of fill volume and of time. The results supported the concept of leak-before-failure. The calculated stresses agreed reasonable well with the measured stresses.

A long-term, in-service test program was begun on one ship; monitoring equipment was installed on the tanks and tank-support structures. The intent was to monitor the tank long enough to gather data over a wide spectrum of sea conditions (Howard and Kvamsdal, 1977). In another report, Howard described the methods developed to establish the degree of sphericity of the tank. About 100 reference markers were precisely located by theodolites on the inner surface, and about 1200 more were approximately located. Accurate location of the 1200 markers was accomplished by stereoscopic photography, and of the 100 precisely-located markers by photogrammetry. This method worked well. Also, Howard reported reasonable agreement between the calculated and measured stresses during hydropneumatic tank testing (Howard et al., 1977).

LNG carriers were the subject of three projects of the Ship Structure Committee (SSC), which is sponsored by the U.S. Coast Guard, the U.S. Naval Sea Systems Command, the Maritime Administration, the Military Sealift Command, the American Bureau of Shipping, and the U.S. Geological Survey with the participation of several other organizations. The SSC emphasizes the improvement of the hull structure of ships. In the first SSC study, the effects on a ship's hull of the catastrophic failure of an entire cargo tank were calculated. Sanders Associates, Inc., prepared the study, which is of great importance in evaluating the survivability of an LNG carrier after such a catastrophe. A simple methodology was developed for calculating the temperatures and stresses in the hull metal after tank failure. Small-scale model tests were run, and the findings generally agreed with the calculated predictions. Also considered were the dangers from tank overpressurization caused by rapid vaporization of the spilled LNG in the inner hull space. The investigators felt the ship probably would not survive (Becker and Calao, 1973).

The two further SSC projects involved research on damage to ships' cargo tanks from the acceleration forces produced by the tanks' cargo. Some types of tanks, if partially filled with LNG, could be damaged on encountering a heavy seaway; this has happened at least twice. In one SSC project, Southwest Research Institute compared the forces from LNG tank loadings to the then-current (1974) rules established by eight agencies such as the Coast Guard, the American Bureau of Shipping, and Det Norske Veritas. Four types of tanks and 17 types of tank loadings and ship accelerations were considered in evaluating the eight sets of requirements. Finally, the authors prepared a set of model and full-scale tests to verify the ship motions used in these evaluations (Bass et al., 1976). The second effort, also by Southwest Research Institute, is still in progress. It is a continuation of the previous effort, motivated by the sloshing damage occurring in slack loaded, membrane-type LNG carriers. The first of many parts is a review of existing mathematical models of tank-sloshing, with model tests scheduled to provide additional sloshing data. Model tests will also delineate the response to membrane-type tanks to sloshing forces. From the results the investigators will prepare new methods for calculating sloshing forces and tank-wall response. The final task is the preparation of methods for taking account of LNG sloshing in designing LNG tanks and their supporting structures.

Great progress has been made over the years in preventing and combating LNG fires. Faced with this new cargo and with novel containment systems, the Coast Guard contracted with University Engineers, Inc. (UE), to study fire safety aboard LNG ships. UE examined the range of possible LNG-spill volumes and selected the maximum extinguishable spill size; larger spills cannot be extinguished by present equipment and methods. The investigators evaluated how to extinguish the maximum extinguishable fire and what equipment was necessary. This evaluation was compared with the regulations imposed by the Coast Guard and by the Inter-Governmental Maritime Consultative Organization (IMCO). UE considered the effectiveness of additonal ways to reduce the damage from fire, such as spill containment, water spray, and inert gases. The relative risk of fatality was estimated through fault-tree analysis for both the LNG carrier and transfer operations. The total risk was expressed as a chance greater than 1 in 10^{10} of a fatality for each man-hour of exposure. A figure of 10^{10} is typical of natural disasters. Interestingly, the risk from transfer operations was greater than that from the LNG carrier alone (Welker et al., 1976). A second part of the UE work involved a series of small-scale tests, simulating LNG spills and LNG-spill fires, conducted in a 3 m-by-3 m pit. The major effort was in providing data for scaling LNG tests to be run in the future. However, one group of tests simulated fire fighting aboard ship, where questions had been raised as to whether obstacles such as pipes within the fire might increase extinguishing time and the amount of dry-chemical extinguishing agent required. Tests with obstacles showed that as long as the dry chemical can cover the entire surface of the fire, its effectiveness is not reduced. A test series using water spray and water fog to reduce the thermal radiation flux striking a surface showed that these techniques were marginal at best and that a better use of the water is direct impingement to cool the surface to be protected (Brown et al., 1976).

Survivability of an LNG carrier when its hull is exposed to fire was examined by Authen and Skramstad of Det Norske Veritas. Their thermal analysis considered a fire along one side of the carrier's hull; many simplifying assumptions characterizing the fire were necessary to solve the problem. A method for calculating the temperature of the inner and outer hulls was presented. Both the membrane and the independent spherical tanks were considered. Scenarios were presented for each type, both for cases where the tank fails and for cases where it survives. The authors suggested several means of increasing the chances of ship survival, such as water ballast in optimum locations and water spray on the deck and outer hull. While no answers were given as to the actual chances of an LNG carrier's surviving such a fire, the study did point the way toward future work (Authen and Skramstad, 1976).

Liquefied-gas ships, especially LNG carriers, must meet rigorous design requirements, including the ability to withstand low temperatures. Hulls are subject to brittle fracture, and conventional oil tankers have suffered damage from low ambient temperatures. This problem looms large with LNG service from Alaska. Hicks and Henn of the Coast Guard analyzed the ambient-air and water temperatures by month for 12 U.S. ports. They sampled the historical weather record and gave low temperatures for each port for each month. For service to U.S. ports, they recommended designing ships to the following design ambient temperatures: Alaska--five knots air at -29°C and still water at -2°C; lower 48 states--five knots air at -18°C and still water at 0°C (Hicks and Henn, 1976).

Jettisoning equipment was installed on seven 75,000-m^3 vessels, and full-scale tests were run on the Gadila, as described by Kneebone of Shell. Five tests, ranging from 27 m^3 to 198 m^3, were run. Variables included vessel speed, wind speed, and jettisoning rate. No large electrostatic fields were generated, and the vapor cloud did not threaten the vessel; vapor-plume dimensions were measured. Finally, a series of recommendations was developed for safe jettisoning (Kneebone and Prew,1974; Prew, 1976).

New cargo-containment systems of interest include those that do not contain a metal primary barrier. One group of these systems, the wet-wall type, has LNG directly in contact with insulation. None is yet in LNG service, and there are questions as to the consequences if the system failed locally and LNG contacted the inner hull. One study in the open literature (Metz et al., 1975) considered this problem. The authors first developed a casualty scenario and then identified the critical structures in the ship's inner hull. The sudden contact of ambient metal with cold LNG produces stresses which may accentuate the existing stresses in ships. Flaws present in the inner hull prior to the failure of the wet-wall system could be magnified and conveivably lead to failure. Small-scale trials were run to test whether critical portions of the inner hull would fail. The results from the thermal-stress analysis and the small-scale tests showed that carbon-steel stiffeners and webs might require improvement. The cold surface of the inner hull would not fail, with or without preexisting cracks.

Even if an LNG carrier could be designed and built so that no failure was possible, human error could lead to problems. In this vein, Operations Research, Inc., and Engineering Computer Optecnomics, Inc., studied the tasks performed by shipboard and terminal LNG personnel for the U.S. Coast Guard and prepared guidelines for crew training and crew licensing for both ships and unmanned barges. Because of the limited operating experience with LNG shipping when the study began, the task-analysis technique called Functional Job Analysis was modified for this purpose. Here the job is reduced to individual tasks, and each task is studied for its proper level of required training and licensing. For example, one of these tasks is to "monitor the exiting gases in order to assure that the oxygen level is less than 2 percent by volume prior to starting tank cooldown spray operations," which is far removed from the usual job description for a chief mate. A sequence was developed for training crewmen--from shore-based instruction, to provisional licensing, to the final full licensing; in particular, on-the-job training was deemed insufficient. License renewal would not be automatic; a recent LNG voyage or recent shore-based training would be required. The authors concluded that all crew members, even those who would not likely come in contact with LNG, should be taught the properties and hazards of LNG (Porricelli et al., 1976).

De Frondeville, 1977, has prepared a record of the experience of LNG vessels plus a description of the various tank designs, vessels, and trades as of the date of publication, 1976. He considered the shore terminals, liquefaction trains, storage tanks, and peak-shaving facilities. De Frondeville proposed the formation of a "reliability information bank" and, by implication at least, a data bank for safety as well.

B. FLAMELESS EXPLOSION

One of the more spectacular events of the LNG-safety research effort occurred when workers at the Bureau of Mines poured LNG onto a small aquarium partially filled with water. Many such spills had been performed before, uneventfully. This time, suddenly, there was an explosion, destroying the aquarium; there was no fire. Larger spills on a large pond were scheduled next, as part of the investigation of LNG-vapor dispersion. Again, the work went forward without incident until, after several spills, there was a large explosion just as the LNG struck the water. As before, there was no fire. While no instrumentation was in place to measure the strength of the explosion, it was estimated to be equivalent to a "stick of dynamite." Small popping sounds noticed before had been attributed to cryogen boiling inside an encapsulating ice layer. There was, however, no immediate explanation for the more violent phenomenon (Burgess et al., 1970). Apparently, this was not the earliest incident of an LNG flameless explosion (FE). During the 1956 tests for the Constock project, LNG was poured continously onto the Bayou Long waterway in Louisiana for several days. A few FEs were observed. Many other cases of LNG FEs have been recorded (Enger and Hartman, 1972).

Currently, the flameless-explosion phenomenon is explained as follows. Consider a cold liquid on a warm solid. There are four boiling regimes in such a situation. At small temperature differences between the liquid and the solid, natural convection and conduction occur. As the temperature difference increases, nucleate boiling begins, with heterogeneous nucleation being provided by all but the cleanest, smoothest surfaces. As the nucleation rate increases with the temperature difference, an unstable transition regime ensues until, when the temperature difference becomes large enough, film boiling begins. Since the vapor film acts somewhat as an insulator, the heat flux is actually greater for nucleate boiling until the system reaches the transition boiling-temperature regime in which the flux declines to film boiling. With a liquid boiling on a clean liquid surface, nucleation must be homogeneous. What appears to be happening with LNG after it is spilled on water is that it begins in the film-boiling regime. As the methane component is preferentially vaporized, the temperature difference declines and the transition regime is entered. The vapor film collapses, and the two liquids come in intimate contact. Some hydrocarbon mixtures, including some aged commercial LNG, are already in the transition regime when spilled on water. The cryogen, because of a lack of nuclei, begins to superheat. The limit of superheat, or the greatest amount of heating that the cryogen can withstand before vaporizing, eventually is reached. For those warm liquids that freeze in contact with the cryogen, no FE is possible because of heterogeneous nuclei on the solid. Similarly, an FE cannot occur when cryogen contacts warm solids initially. Once the limit of superheat is reached, an FE occurs. Some of the superheat energy released goes into the latent heat of vaporization and some into sensible heat. The volume increase so rapidly that an "explosion" occurs. This is a nonchemical reaction; substances such as liquefied nitrogen could undergo FEs as well as hydrocarbons.

There are basically two theories of the limit of superheat, the thermodynamic theory and the kinetic theory. The thermodynamic theory rests on the relationship $(\partial V/\partial P)_T$. When this relationship equals zero, the limit of superheat is reached; for real spills on water, the pressure is necessarily ambient. Note that $(\partial V/\partial P)_T$ should be less than zero, but it cannot realistically be positive. Since the region about the superheat limit is metastable, the physical-property data are poorly understood. The term $(\partial V/\partial P)_T$ therefore, cannot be calculated accurately. The calculation for mixtures such as LNG is even more complex. The temperature corresponding to the limit of superheat at one atmosphere is either 0.84 or 0.89 of the critical temperature, depending on the equation of state used. The kinetic theory rests on the concept that the rate of homogeneous nucleation varies as a function of temperature. For pure liquids near the limit of superheat temperature, the rate of nucleation increases by orders of magnitude for each degree of temperature increase. Calculations cannot give the actual limit of superheat, but can give a temperature range over which the nucleation rate is sufficient for vaporization. Apparently, FEs have occurred many times in other systems, such as pulp-mill smelt and water, nuclear-reactor molten metals and water, molten aluminum and water, and molten steel and water. Water, of course, need not be the warm fluid. An excellent exposition on this topic may be found in Reid, 1976.

Garland and Atkinson of the University of Maryland experimentally investigated the FE phenomenon for the U.S. Coast Guard. Their LNG was liquefied from laboratory gas which was about 95 percent methane. Small quantities were spilled on water and on 12 pure liquids or liquid mixtures without producing an FE. Pouring LNG onto water with a 1-mm surface film of hexane or toluene produced an FE each time. The rise in pressure caused by the FE ranged from 2 to 8 atm. Removing some of the high-boiling constituents from the LNG reduced the likelihood of FEs. Further tests, in which FEs were produced using 10 to 100 ml of LNG, showed no correlation of overpressure with cryogen volume. However, the pressure rise seemed to increase with the volume of the hydrocarbon on which the cryogen was spilled. Finally, repeated spilling of the same volume of LNG onto the same sample of hexane produced increasing overpressures. The authors concluded that the FE was a serious LNG hazard (Garland and Atkinson, 1971).

Burgess et al., 1970, considered three possible FE mechanisms; ice encapsulation, clathrate formation, and superheating followed by rapid vaporization. LNG proved difficult to encapsulate, and the time required to form methane-water clathrates in the laboratory proved too long for that mechanism to be the cause of the phenomenon. A later effort by Burgess et al., 1972, was no more effective in rapidly generating methane-water clathrates. Test pourings of LNG onto a layer of pentane and hexane on water produced explosions, as did mixtures of LNG on pentane and hexane. Several mixing tests of LNG with propane produced only one weak FE. Propane and hot (68°C) water were very effective in generating FEs. It was felt, though, that the methane concentration was very high when the two FEs occurred in the first study (Burgess et al., 1972).

Shell Pipe Line Corp. conducted an extensive program of spills of hydrocarbons on water. In some 235 spills into a confined container,three types of responses were noted: with LNG spills sufficiently large, a coherent ice layer formed, but no FEs occurred; with smaller spills, a partial ice layer prevented all but "popping" noises; with even smaller spills, no ice formed, and sometimes FEs occurred. Other liquefied-gas mixtures were spilled onto water or other warm liquids; the temperature of the warm liquid was varied. Results indicated that, of various mixtures of methane, ethane, propane, and n-butane, none would exhibit FEs except where the methane concentration was below 40 percent. The point is important, because most commercial LNG contains between about 90 percent and 99 percent methane, except for Libyan LNG, which contains less than 70 percent methane. Aging of LNG in storage tanks was measured. Calculations based on the assumption that methane was the sole component of the boiloff gave conservative, but approximately correct values of the methane concentration versus liquid-fraction boiloff. The tank contents had to be aged to 10 percent or less of the initial volume before the methane concentration could fall below 40 percent. Aging during vaporization was also possible--that is, most of the LNG could boil away, leaving a methane-deficient cryogen on water. Calculations suggested that only spills of greater than 114 m^3 could possibly undergo FE. Of course, even after the cryogen had reached the proper concentration it would be spread over a wide area and its potential for doing shock damage would be limited, particularly since it would be improbable that all of the remaining liquid would reach the limit of superheat simultaneously (Enger and Hartman, 1972).

Nakanishi and Reid experimented with various cryogens (liquefied methane, nitrogen, ethane, pipeline gas, and synthetic LNG, a mixture of propane and methane). They spilled these cryogens on water, spilled water on cryogens, spilled cryogens on ice, and tried several other variations. One variation was the use of a hydrocarbon film between the spilled cryogen and the water. It was hypothesized that two conditions were necessary but not sufficient for an FE; that the interfacial liquid must wet the cryogen, and that the warm liquid must have a low freezing point. In one series of tests, Reid observed from below the release of liquefied pipeline gas on water coated by *n*-hexane. Initially the cryogen was separated from the *n*-hexane by a film of vapor. Suddenly the cryogen spread out and contacted the *n*-hexane surface. An FE followed. In a similar test, the water temperature was monitored 3 mm below the *n*-hexane-water interface. The temperature decreased immediately after spillage, but recovered rapidly; then it fell slowly until, over a period of less than 0.4 s, it fell 25°C and an FE occurred. This observation suggested a cryogen superheat of roughly 35° to 40°C (Nakanishi and Reid, 1971).

In a recent report, Reid discussed some 150 tests in which pressurized nitrogen provided the force for injecting the cryogen into the warm liquid. The higher the initial impact velocity, the greater the measured overpressure when FEs occurred. Overpressures were as high as 13.6 atm. Also, injecting the cryogen into the warm liquid allowed some pairs of cryogen and warm liquid (e.g., ethane-water) to undergo FE, whereas spilling the cryogen did not. Methane, however, did not undergo an FE when injected into water (American Gas Association, 1977).

Reid, 1977, reported on the phenomenon of superheated liquids and how they relate to FEs. Examining homogeneous nucleation theory, he arbitrarily defined the homogeneous nucleation temperature, T_{Sl}, as corresponding to the temperature at which 10^6 vapor embryos form every millisecond for each cubic millimeter. This temperature is usually within a few degrees of the limit of superheat, a good agreement, he felt, when the many approximations were considered. He surveyed past FE events and the various explanations advanced to explain them. For an FE to occur when cryogens are spilled on water, the warm liquid temperature, T_W, must be close to or greater than T_{Sl}. When T_W is only 4 percent to 6 percent greater than T_{Sl}, the probability of an FE is the highest. For all warm fluids, T_W must be close to or greater than T_{Sl}; for the greatest probability of FE, the ratio T_W/T_{Sl} is somewhat above 1.0, depending on the warm fluid. Now for pure liquefied methane spilled on water, T_W/T_{Sl} is 1.77, much too high for an FE. Reid suggested that if the cryogen were injected at sufficient velocity, the vapor layer from the stable-film boiling might be stripped from the interface, resulting in intimate contact between layers, followed by an FE. Ethane poured on water has never undergone FEs, but with the impact technique, it did. After reviewing the many theories, Reid concluded that there is not enough evidence to prove one mechanism for all FEs.

Porteus and Reid, 1976, provided a very useful compilation of spills of pure cryogens on water, along with binary mixtures of cryogens on water.

A detailed examination of the thermodynamic model of the FE is provided by Rausch and Levine. Their model predicts behavior only at atmospheric pressure. When the interfacial temperature is about 84 percent of the critical temperature, a shock wave will occur. For water-cryogen systems, the water temperature must be about 110 percent of the cryogen's critical temperature; water temperatures much higher than that were predicted not to lead to shock waves. The authors performed a series of experiments using Freon 12 on water, Freon 22 on water, propane on water, and Freon 114 on ethylene glycol. Both the 84 percent and 110 percent values were closely followed; as predicted, both liquefied methane and liquefied ethane spilled on water failed to produce FEs (Rausch and Levine, 1973). In a later paper, Rausch and Levine calculated the pressure of the shock wave based on theoretical considerations. Near the critical region, the viscosity looms large in importance. Put colloquially, the energy transfer was increased due to the squeeze provided by the bulk viscosity. An involved procedure led to an estimate of 34 atm as the strength of a methane-FE shock wave. Mixtures, of course, were not covered by this model, but the authors felt the model might still apply (Rausch and Levine, 1974).

Anderson and Armstrong, 1972, at Argonne National Laboratory investigated the FE phenomenon theoretically and experimentally. Experimentally, water was injected into molten sodium chloride. The energy for the resulting FE was either stored in the superheated liquid or was transferred across a very large interfacial area between the two liquids; that is, the cold liquid can fragment into small pieces with a much greater total surface area. The experimental results, they felt, supported the idea of the fragmentation of the cold layer, but the exact mechanism was still unknown. The observed explosive energy was as much as 25 percent of the maximum theoretical energy available for the FE. Whether this fraction can be used with large LNG spills was not known. Finally, the authors suggested that submerged injection of LNG could be more hazardous than simple spills.

Nelson, 1973, demonstrated that the LNG-water interaction is much less violent than the interaction of the pulp-mill smelt with water. For the former, the immediate film-boiling decays into superheating in the transition region, followed by the FE. For smelt dropping into water, the process of film boiling, superheating, and FE breaks the smelt into small parts, moving at high velocity relative to the water. The process favors intimate contact between the smelt fragments and water, followed by superheating and additional FEs. This chain reaction resulted in much greater damage.

Witte and Cox, 1971, of the University of Houston investigated FEs on a theoretical basis. While they accepted the concept of superheating, they added the idea of fragmentation in a manner similar to Nelson's. Basing the fragmentation mechanism on the molten metal-water and molten salt-water events, they proposed that LNG droplets were encapsulated in ice layers, pressurizing the LNG vapors. This was their explanation for the observed poppings. Three candidate mechanisms for fragmentation were rejected as a result of tests of molten metal in water. The rejected mechanisms were violent boiling; cold liquid trapped inside a shell of the warm liquid; and Weber Number instability, a measure of the inertial forces on the warm liquid falling through the cold liquid overcoming the warm liquid's surface tension. Fragmentation, then, was triggered by other droplets' fragmenting.

Opschoon, 1974, of the Central Technical Institute TNO (the Netherlands) performed a theoretical study of the LNG-water interaction followed by a review of the experimental tests. He accepted the thermodynamic model of superheat and through superheat energy-transfer calculations estimated the mechanical energy of the LNG-water FE at about 1.2 J/cm². Opschoon added that the Rausch-Levine estimate of overpressure was too large. He felt that only minor damage to nearby structures is possible when LNG spills on water.

In the early 1970s, the Coast Guard requested that the National Academy of Sciences' Committee on Hazardous Materials examine the issue. Katz, 1973, of the Committee, prepared a state-of-the-art review in 1972. He concluded that liquefied methane will not undergo an FE when spilled on water and that LNG will have to be aged drastically, either by vaporizing in the storage tank or boiling on water, before it will undergo an FE.

C. DISPERSION FROM SPILLS ON WATER

The behavior of LNG when spilled on water has been of great interest to all concerned with importation of the cryogen by ship. Of particular interest is the maximum distance an unignited cloud might travel downwind and still remain flammable. Also of major importance is the problem of pool and cloud fires. The downwind dispersion problem involves several steps, some of which apply to the fire problem. These steps include the pool spread-rate, the vaporization rate per unit area as a function of time (including the question of the formation of ice), the buildup of an inventory of vapor above the pool, the gravity-induced spreading of this inventory, the rate of dispersion, and the significance of pockets of vapor whose concentration is higher than average. Not all of these steps are necessarily significant or even exist in actual releases.

Burgess of the U.S. Bureau of Mines studied the dispersion problem for the U.S. Coast Guard beginning in 1968. Small quantities of LNG were poured onto a water-filled aquarium mounted on a load cell to determine the vaporization rate. Next, larger quantities-- up to 0.5 m^3-- were spilled onto a pond. These spills were essentially instantaneous. An overhead camera provided data on pool spread-rates and showed that no coherent ice layer was formed. A coherent ice layer could reduce significatly the vaporization rate and, therefore, the downwind travel distance. Hydrocarbon sensors provided data on the dilution of the vapor cloud. Burgess concluded that the vapor cloud, in effect, provided its own thermal inversion, which led to predictions of rather long travel distance for the flammable vapor cloud. Also important was his finding of significant peak-to-average ratios of vapor concentration. The thermal inversion or layering was said to occur because the vapor cloud was warmed not by contact with the water below or by the sun, but only by mixing with ambient air. Since the diluting air was thereby cooled, the vapor-air mixture remained heavier than ambient air. Burgess' predictions came from a model based on the Gaussian plume dispersion. Surprisingly, the data suggested the existence of significant pockets of vapor whose concentration was heavier than average. Thus the distance downwind for which the cloud remained flammable should not be calculated to the lower flammable limit, but to a much lower concentration. The pool-spread data suggested that the rate of spread was constant (Burgess et al., 1970). In follow-up work, Burgess generally confirmed his earlier results. Spills of a continuous type were used this time; the quantity of LNG released was about 10 m^3. Again, the model based on the test results showed that the cloud would travel long distances downwind (Burgess et al., 1972).

Feldbauer et al., 1972, of Esso Research and Engineering Co. conducted a series of 17 LNG spills at Matagorda Bay, Texas. The spills ranged from 0.73 m^3 to 10.2 m^3. This work was part of the American Petroleum Institute's LNG spill study. The larger tests were classified as intermediate in spill time, rather than instantaneous or continuous. Esso found the same type of vapor layering and lack of ice formation as in the Burgess tests, but with a lower peak-to-average ratio of vapor concentration. The spills led to a new model in which the boiloff vapor did not immediately take on the wind velocity, but rather built an inventory above the pool. The inventory passed through a gravity spread phase and then a vapor-dispersion phase. A series of point sources arrayed in a line accounted for the rather large-diameter cloud, and from each point dispersion was modeled as Gaussian. The downwind distances predicted were generally less than those given by the Burgess model.

Boyle and Kneebone, 1973, of Shell Research, Ltd., conducted a series of laboratory tests on LNG spillage on water. This was also a part of the American Petroleum Institute's research on LNG-water spills. The authors measured the evaporation rate on water at 0.024 kg/m²s; if ice formed the rate rose to 0.20 kg/m²s. They also studied the factors influencing the formation of ice, which caused a shift from film boiling to nucleate boiling with an increase in boiling rate. The spreading rate of LNG was measured at about 0.76 m/s initially, but fell rapidly with time. The LNG pool on water broke up when the amount of LNG fell below 0.78 kg/m². Water was picked up into the vapor cloud during the LNG vaporization process and amounted to as much as 8 percent by weight of the LNG. Vapor-cloud travel experiments were conducted in a wind tunnel; the cloud was a wide, flat plume with a depth-to-width ratio of 1:25.

Kneebone and Prew, 1974, of Shell Research, Ltd., described the jettisoning tests from the 75,000-m³ LNG carrier Gadila. In five tests, from 27 m³ to 198 m³ of LNG were released. These remain the largest spill tests on water to date. Since the emphasis was on evaluating the safety of the jettisoning apparatus, the data were not as detailed as in other test series. Each test lasted about 10 min and so was a continuous spill. The layering in this series was greater than that observed by Burgess. The ratio of the vertical to the horizontal dispersion rate was 1:25 instead of Burgess' 1:5; the latter is also the ratio found during thermal inversions. Complicating the issue was the fact that some of the LNG vaporized before reaching the water. Kneebone said that the data for his larger spills correlated well with the model by Esso.

The Japan Gas Association, 1976, performed a series of spill tests for the Japanese Government at the Sodegaura terminal of the Tokyo Gas Company, Ltd. One test included pouring LNG (more than 99 percent methane) onto water in a diked area. This technique was novel, for the problem of determining the pool area as a function of time was circumvented by using the dike. The water did not freeze during the experiments, and no FE occurred. The dispersion coefficients and concentration profiles did not differ markedly from those measured in land spills.

Lind of the Naval Weapons Center, China Lake, Calif., is performing dispersion tests as well as cloud and pool burns of LNG spills on water. All expriments are not yet complete, and the results obtained have not been evaluated completely. However, it has been observed qualitatively that an icelike white solid was formed with a spill of less than 5.7 m³ on a pond 50 m by 50 m and about 1 m deep.

Further study of this icelike material is scheduled. No reports are available as yet.

The U.S. Department of Energy, 1978, has published an assessment indicating a need for further LNG research. While the complete program has not been adopted as yet, if implemented it will include spills. The cornerstone of the plan and the bulk of the budget lie in three series of spill tests: small, about 5.7 m^3 (under way at China Lake); medium, about 40 m^3; and large, perhaps 1000 m^3. The 1000-m^3 tests would have a release time of several minutes and probably would be classified as intermediate rather than instantaneous spills. The proposal includes a comprehensive program of instrumentation development and test-facility construction.

Questions remain about the length of the downwind hazard zone. The main question usually is phrased as: given a maximum credible spill involving an LNG carrier, how far can the cloud travel and still be flammable? The maximum credible accident probably was first defined by the U.S. Coast Guard as an instantaneous release of the entire contents of a single tank in the largest LNG carrier. This volume is given as 25,000 m^3, the volume of each of the five tanks on the 125,000-m^3 ships (U.S. Coast Guard, 1976). An instantaneous release, though probably not very realistic, was chosen for want of a more realistic release rate. Since large spill tests are so expensive and difficult, many have attempted to model the phenomenon directly without new spill tests. Havens, 1977, has analyzed some seven models for the U.S. Coast Guard, including the Burgess and ESSO models discussed above.

The following discussion is based on Havens' analysis. The seven models differ significantly. For example, the Burgess model employs a simple Gaussian dispersion from a point source without a gravity-spread phase or correction for the pool area. The Esso model uses a series of phases: vapor buildup over the LNG pool; gravity spread with air entrainment; and a series of point sources arranged in a line to simulate the large vapor cloud. The Germeles model is a Gaussian dispersion from a point source corrected for the pool diameter; an earlier step involves a gravity-spread phase incorporating air entrainment. The Coast Guard model, developed by Arthur D. Little as a part of the emergency response tool, the Chemical Hazards Response Information System (CHRIS). The model is a Gaussian dispersion from a point source, corrected for the pool diameter but without a gravity-spread phase. The Fay model uses a relationship based on the Gaussian dispersion from a point source with no correction for an area source; it includes a gravity-spread phase with no air entrainment. The Federal Power Commission (FPC) model is somewhat different. The vapor forms a cylinder above the pool, with the diameter of the cloud being equal to the maximum pool diameter. The cloud undergoes a gravity-spread phase without air entrainment. Movement of the vapor from above the spill site is governed by heat transfer from the air. The vapor then undergoes a Gaussian dispersion from a point source with a correction for an area source. The Science Applications, Inc. (SAI), model is unique. It is a computerized model that uses a finite-difference solution of the combined equations for conservation of energy, mass, and momentum. Gravity spread with air entrainment is involved. This model requires large amounts of computer time and is expensive to use. Havens categorizes the models as follows: The Fay, Germeles, and Coast Guard models are of the instantaneous vapor-release or puff type; the Burgess, Feldbauer, and FPC models are of the continuous vapor release or plume type; and the SAI model solves the combined equations for conservation of energy, mass, and momentum.

Table 8 gives the downwind travel for a 25,000-m^3 spill of LNG, given the specific conditions, such as weather, recommended by the model developers. The SAI distance is for 37,500 m^3. Havens noted that the distances change dramatically if other specific conditions are used. The problem with such predictions is that there are data for the small spills for which the models are calibrated, but not for the larger spills. Thus the models generally agree for small spills, but not for large spills; furthermore, a plot of cloud concentration versus distance for a 25,000-m^3 spill shows that a small change in concentration at the 5 percent or lower-flammable-limit part of the curve gives a large change in distance.

D. UNDERWATER RELEASE

The entire experimental record for underwater release of LNG consists of a single set of tests. An underwater release could result from collision with an underwater obstacle, or a bulbous, projecting bow might puncture an LNG carrier below the waterline. Underwater release of LNG is important because immediate ignition of the spill is less likely than if the release were at or above the waterline. The unknowns include the vaporization rate and the effects on the LNG carrier. Thus the conventional models of vapor dispersion and the survivability of the damaged carrier itself are in question.

Table 8 Comparison of Predictions for a 25,000-m^3 Spill (Havens, 1977)

Model	Downwind Travel Distance, km
Puff	
Fay	20.8
Germeles	18.5
Coast Guard	26.2
Plume	
Burgess	40.6-81.0
Esso	8.37
FPC	1.21
Combined equations	
SAI (prediction for 37,500 m^3)	1.93

The aforementioned single test set was performed by Burgess el al., 1972, for the Coast Guard. Five-gallon (0.02-m^3) containers were submerged in about 3 m of water and explosively ruptured. Two tests were made. In both cases only vapor reached the surface, and there was no visible fog, as occurs when LNG is spilled on land or on water. These observations were interpreted as demonstrating that the LNG vaporized totally underwater and that the vapor may have been warmed as well. The more rapid vaporization from an underwater release could lead to much longer downwind travel for the hazardous vapor cloud. However, if the vapors were warmed too close to the temperature of the water, the downwind travel would be much less because the cloud would be lighter than air at ambient temperature.

Raj and Reid, 1978, have theoretically analyzed the release of LNG below the waterline from an LNG carrier. Of the possible scenarios, they examined a jet of LNG into water. Unfortunately, there were few experimental data on which to base a model, but the authors prepared a model relating the size of the liquid slug to the rise-time and percent liquid vaporized. The quantity of LNG vaporized increased with the fragmentation of the liquid jet. The authors added that the calculated velocities of the jet and of the rise of the liquid slug were below the 20 m/s at which it is known that FEs do not occur.

E. WATER-SPILL FIRE STUDIES

A collision leading to a cargo release from an LNG carrier most probably would result in a large pool fire rather than an unignited boiling pool giving rise to a vapor cloud. The argument usually advanced is that collisions sufficiently energetic to breach an LNG vessel's cargo tank will cause enough frictional heating and sparks to ignite the LNG vapors. Alternative sources of ignition are present on the LNG vessel or on nearby ships. Experiments at China Lake and at the Bureau of Mines (Burgess et al., 1972) showed that vapor clouds burn back to their source.

Usually, the critical pool-fire problem is stated in terms of the thermal-radiation flux as a function of time for a given instantaneous release of LNG. This dynamic problem is more difficult than, say, a steady-state release, but is a realistic statement of a worst-case accident. Evaluation of this problem will help in deciding such issues as siting requirements. The instantaneous spill requires the determination of the pool spread-rate, which is not well understood. The LNG burning rate on water per unit area is known, assuming no ice forms, but the pool area and, therefore, the total energy release rate are not well known. Furthermore, the peak thermal flux received by an individual or structure will be of short duration, so more information is required on the human response to thermal radiation, which response varies rapidly with time. Much work has been done with LNG fires on land with their fixed area, but the LNG fire on water has received less attention.

The Naval Weapons Center, China Lake, Calif., is performing tests of pool fires on water for the Coast Guard, with financial assistance from the U.S. Department of Energy and the American Gas Association. No reports of this work are yet available. Quantities of up to 5.7 m^3 of LNG were released rapidly onto a pond of water 50 m by 50 m and about 1 m deep. The spills were ignited either at the start of the spill or after some delay incurred in an attempt to achieve a large pool diameter and hence a large fire. Theoretically, once an optically thick flame is achieved, no larger fire is necessary. Radiometer measurements were taken, but the data are not yet available. Interestingly, an icelike material was observed in the films of some of these tests, and the phenomenon is being investigated. Qualitatively, the height-to-diameter ratio of the fire appeared to be significantly greater than the 3.0 or so observed in LNG fires on land. In addition to this work, the Department of Energy has proposed a series of large fire tests on water.

Theoretical analyses are useful, especially until the China Lake results are reported. Perhaps the first analysis was provided by Burgess et al., 1972. The burning rate per unit area of LNG on a frozen substrate (as would be the case in a land fire at steady state) was added to the vaporization rate of LNG on water as found experimentally. The sum was the estimated burning rate of LNG on water per unit area. The authors assumed that, as an upper limit, 40 percent of an LNG fire's energy would be radiated outward. They modeled the fire as a point-source fire and calculated the radiation flux received at a certain distance from the center of the pool fire. The flux recieved was the total energy rate divided by the area of a hemisphere whose radius was the distance from the receptor to the center of the pool. The diameter of the pool and the burning rate gave the total energy release, and the diameter could be calculated from the experimental data for the size of an unignited LNG pool as a function of time and initial spill volume.

Raj and Kalelkar, 1973, used a modified force-balance oil-spread model to predict the pool diameter as a function of time. They allowed for vaporization of the LNG resulting from energy input to the pool from both the water and the fire. The time to burnout was calculated from the rates of spread and liquid regression. The next step, the calculation of flame height, was difficult. In land (diked) fires, a ratio of height to diameter of 2.7 was observed, so a ratio of 3.0 was picked to provide for large-diameter spills, where the authors said, most such ratios break down for other fuels. The flame was modeled as a tilted cylinder. The calculation of the radiation received involved evaluation of the view factor from this tilted cylinder. Other terms, such as atmospheric transmissivity and flame emissivity, were treated conservatively. The authors present a set of useful plots of maximum thermal flux as a function of distance and spill size.

Stannard, 1977, has developed a third model. He began with Burgess' spill-spread model, adding a term representing Burgess' factor for the LNG burning rate on a frozen substrate. Stannard gave equations for the view factor for tilted and untilted cylinders and calculated the receptor's subtended solid angle. From these equations he calculated the critical distances for damage to human skin. He pointed out that thermal flux builds slowly to the maximum, so people would have time to escape from the fire.

III. RESEARCH COMMON TO BOTH SHORE AND WATER

A. VAPOR-CLOUD DEFLAGRATION

Vapor-cloud fires are a serious matter; one simple rule states that everyone within a deflagrating vapor cloud but outside a building or other shelter will die. Strehlow, 1972, reviewed some 107 non-LNG vapor-cloud incidents from 1930 to 1972, plus the LNG disaster in Cleveland in 1944 (Bureau of Mines, 1946). The overwhelming majority of these clouds did not detonate, but deflagrated. In the 107 incidents, about 386 people died, 136 of them in the Cleveland episode. Cloud fire clearly is a significant hazard, for under certain circumstances an LNG-vapor cloud could drift a short distance into a built-up area and endanger life. Unresolved are two important issues: the level of the thermal flux from the fire; and whether the flame front will travel through the entire vapor cloud against the wind and, if so, how fast. Note that ignition is likely to occur near the leading or downwind edge of the cloud.

Lind et al., 1977, of the Naval Weapons Center, China Lake, Calif. are doing work sponsored by the Coast Guard, with financial assistance from the American Gas Association. Here, up to 5.7 m^3 of LNG is released as rapidly as possible onto a pond of water 50 m by 50 m and about 1 m deep. The LNG is allowed to vaporize, and the vapors drift downwind. Flares ignite the cloud some distance from the pond. As yet there are no reports of this work, but preliminary qualitative results of these 1977 and 1978 tests indicate that the flame front can propagate upwind. After correcting for the wind velocity, the flame speed appears to be of the same order as found in the author's hemisphere tests (Lind et al., 1977). Radiometer data are not yet available. The flame propagation is quite similar to that found qualitatively by Burgess et al., 1972, during a test in which a continuous LNG release on water was ignited downwind. The flame front advanced slowly upwind to the source. No radiometer data were taken.

Hardee et al., 1978, of Sandia Laboratories considered the hazards from LNG fireballs. They postulated three types of fireballs: a premixed cloud that burned as a fireball; a pure fuel cloud that burned as a turbulent diffusion flame; and a fire that caused overpressure in an LNG storage tank, with rupture and formation of a fuel/air cloud. The authors developed models for the first two cases. Optically thin fireballs of methane, both pure and premixed, were produced. They included pure methane fireballs of 0.10, 0.15, 1.50, and 10.0 kg and premixed stoichiometric fireballs of 1.5, 3.5, and 10 kg. The thermal-radiation fluxes measured at the surface led to an estimated surface flux of 469 kW/m^2 for an optically thick, premixed fireball. This estimate agreed reasonable well with data from the Cleveland disaster of 1944 (Bureau of Mines, 1946). The authors concluded that large LNG fireballs could cause third-degree burns at several miles from the center of the fireball.

By analogy with cryogenic fuel releases and the resulting fires in the space program, Fay and Lewis, 1971, suggested that burning LNG-vapor clouds would have the appearance of fireballs. They constructed a theoretical model in which certain scaling laws were established. The rise height of the fireball varied as the 1/3 power of the vapor cloud's initial volume, the maximum flame diameter as the 1/3 power, and the combustion time as the 1/6 power. Very small-scale tests were conducted with spherical soap bubbles filled with pure methane, ethane, or propane. Hot wires ignited the spheres, which ranged in volume from 20 to 190 cm^3. The results confirmed the postulated scaling rules.

Raj and Emmons, 1975, modeled a vapor-cloud fire as a wall fire, a two-dimensional fire that moves through the cloud perpendicular to the wind. They postulated one or more point-source ignitions that coalesce into a wall of fire. The model assumes a wedge-shaped burning region normal to the wind; the length of the wedge is the width of the cloud. The wedge is widest at the top of the vapor cloud and comes to a point at the bottom of the cloud. Once steady-state burning begins,the dimensions of the wedge should remain constant. The model was used to calculate the width of the wedge at the top of the cloud, giving the thickness of the flame. The height of the flame is related to this width, so the thermal radiation can then be easily calculated.

B. VAPOR-CLOUD DETONATION

As serious as an unconfined vapor-cloud fire may be, an unconfined detonation of an LNG-vapor cloud could be much more serious. Unconfined detonations of hydrocarbons in air have an explosive effect equivalent to 5 to 15 times the weight of the hydrocarbon in TNT. Fortunately, assuming a Gaussian plume, only a small part of an LNG-vapor cloud is within the flammability limits, and even less is near stoichiometric. Burgess calculated that only 10 percent of the cloud at most is flammable at any one instant (Burgess et al., 1974). Nevertheless, there is reason to ask whether LNG-vapor clouds can detonate in the manner of Liquefied Petroleum Gas clouds. Defining the problem is difficult in some ways; because of the varying concentrations of the components of LNG, one must ask not only whether methane detonates, but also whether vaporized LNG detonates. The presence of hydrocarbons heavier than methane appears to be significant in producing vapor detonations. It has been established that pure methane can detonate in a confined space.

In order to study the behavior of detonating methane-air mixtures one must first achieve a propagating detonation. There are no recorded cases of such a detonation in accident situations. In tests, methane-air detonations usually have been initiated directly with high explosives, rather than by other mechanisms that might cause a deflagration-to-detonation transition (DDT).

Kogarko et al., 1966, published work on direct initiation of methane-air detonations. While they reported having achieved a methane detonation, the work has been criticized as being on too small a scale to allow the effects of the initiator to be separated from those of the methane. Others have pointed out their inability to duplicate the results.

TRW, 1969, conducted a series of unconfined-detonation tests in spherical balloons for the American Gas Association at the TRW Capistrano Test Site. Seven tests were run with a stoichiometric mixture of natural gas and air. The natural gas was about 88 percent methane. Five tests were run in balloons 1.5 m in diameter, two in 6.1-m balloons, and one with an initiator but no fuel. The high-energy initiator was Composition 4, at weights ranging from 384 g to 680 g. The 6.1-m tests were large enough to show that the detonation decayed as it passed through the cloud. This result suggested that the 1.5-m diameter tests, which showed apparent propagation of detonation, should be considered too small relative to the weight of the initiator. TRW concluded that the question of detonability of unconfined natural gas had not been answered, and that further work was needed.

Vanta, 1973, at Eglin Air Force Base, simulated an unconfined vapor cloud using a rectangular framework covered by a thin polyethylene sheet. Natural gas was detonated twice by about 1.0 kg of high explosive, but the detonations were said to be erratic. The detonation propagated the length of the bag, 4 ft. In several other tests, with less initiator and more distance for propagation, the natural gas failed to detonate.

Bull, 1976, of Shell Research, Ltd., experimented with the methane-oxygen-nitrogen system in stoichiometric proportions, in which the nitrogen was deficient relative to its concentration in air. Bull used polyethylene bags with a charge of tetryl, a high explosive, placed either centrally or at one wall. He correlated the amount of tetryl required to initiate direct detonation with the ratio of the concentration of nitrogen to that of methane. The data gave a reasonably straight, semilogarithmic plot of the minimum weight of tetryl required to initiate detonation versus the nitrogen-to-methane ratio. Extrapolation of the line to the stoichiometric concentration of methane in air suggested that 22 kg of tetryl should lead to direct initiation. One requirement for such a test is a bag large enough to allow the effects of the tetryl to be separated from those of the methane. Bull estimated this minimum propagation length as 11 m.

Boni et al., 1977, of Science Applications, Inc., performed small-scale tests with a methane-oxygen-nitrogen system like Bull's and got similar results. They developed an involved computer simulation of this system to calculate minimum energies required for detonation. The computer simulation was validated over the range of the experiments performed by Bull and Boni. Calculations indicated that direct initiation of detonation of methane-air would require 1000 kg to 10,000 kg of tetryl, as compared to the 22 kg estimated by Bull. Experiments with propane and acetylene have shown this type of behavior, in which a plot of the weight of explosive required for direct initiation versus the nitrogen-fuel ratio shows that the weight rises sharply as the ratio approaches that of the fuel stoichiometric in air. Also, Boni's calculations show that an initiator too weak to cause a steady-state propagation can nevertheless, generate an erratic, pseudodetonation that after a short time will decay to a deflagration.

Benedict of Sandia used a column made of a thin plastic sheet over a metal framework to contain the fuel-air mixture. The column was 2.4 m square and 6 m long. He found that 3.6 kg of Detasheet, a sheet explosive, was sufficient to initiate directly a detonation wave over the length of the column. A 4.1-kg charge proved sufficient for a column 12 m long. In several other tests, the wave failed to propagate the full length of the experimental chamber because of lower explosive charge and/or smaller chamber cross-section. High-speed photography was used to determine whether the vapor-air mixture detonated (Benedict, to be published).

Nicholls of the University of Michigan used a pie-shaped detonation chamber to simulate a segment of a spherical detonation. He, too, measured the initiator energy necessary for direct initiation of the methane-oxygen-nitrogen system and plotted the weight of explosive versus the nitrogen-methane ratio semilogarithmically. Extrapolation to methane-air gave a requirement of 535 g of Detasheet. However, Nicholls found in his plot a region where the experimental results did not clearly indicate whether a propagating detonation occurred (Gabrijel et al., unpublished).

C. GELATION

Recent work has demonstrated that LNG can be converted into a thixotropic gel. In theory, such a gel would spread slower than liquid LNG on both land and water; to the extent that the gel's yield strength exceeds the static pressure of the gel inside a ruptured tank, the cargo might not leave the tank at all. Also, the vapor film between the gel and its warm substrate should be more stable than with liquid LNG; that is, the gel favors film boiling over nucleate boiling, so the rate of vaporization per unit area is reduced significantly. In theory, then, LNG could be altered to present less risk in case of spill.

Shanes, 1977, of the Massachusetts Institute of Technology prepared gelled liquefied methane using colloidal particles (1 to 1000 nm) of methanol and of water as gelants. Hydrocarbon mixtures were liquefied to simulate LNG. Gelation reduced the vaporization rate by a factor of two or three by preventing the shift from film boiling to nucleate boiling. Generally, the gels are non-Newtonian fluids with time-dependent rheological properties. At high shear rates, gels behave as Bingham plastics. Dynamic-yield stresses, measured using an oscillating force, ranged from about 10 $dynes/cm^2$ to about 900 $dynes/cm^2$. Static-yield stresses, measured by the height of the gel that can support itself, again ranged from 10 $dynes/cm^2$ to 900 $dynes/cm^2$. The greater the concentration of gelant, the greater the yield stress. Gelant concentrations ranged up to about 6 percent by weight.

Aerojet Energy Conversion Co. has been involved in the gelation of cryogens since 1962 and is undertaking a project in this area for the U.S. Department of Energy (DOE). There is a degree of continuity between Shanes' work and Aerojet's, since Shanes used Aerojet's method to form gels. The method consists of injecting a stream of gelant vapor, diluted with a carrier gas, through a heated tube below the cryogen. Aerojet has gelled methane with particles of water, methanol, trimethylaminoborane, and trimethylamino-boron trifluoride in concentrations as low as 1 percent by weight. The company says the gelling agent should be highly volatile at ambient temperatures; should form no ash during combustion; should be sufficiently stable to resist pyrolysis below 450°C; should be noncorrosive; should possess fuel value, and should be inexpensive. Aerojet intends to experiment with water and methanol. The project for DOE will have five parts: gel preparation; gel characterization; safety tests; preliminary design of an industrial-scale gelation system; and a preliminary economic assessment (Aerojet, 1977).

The Energy & Minerals Research Co., 1977, has been involved in the gelation of liquids and liquefied gases. The company has gelled methane, propane, butane, nitrogen, hydrogen, and ammonia. It has observed that the vaporization rate for gelled liquefied nitrogen is considerably lower than for nongelled liquefied nitrogen.

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APPENDIX B

A CRITICAL REVIEW OF THE LITERATURE DEALING WITH LNG VAPORIZATION AND DISPERSION AFTER SPILLS ON LAND AND WATER

TABLE OF CONTENTS

I. INTRODUCTION

This appendix summarizes the literature, up to August, 1978, relating to the technical aspects of spills of LNG on land and water. The length of the review reflects the large number of papers and reports that have been written on the subject. Many of the papers cited have not appeared in journals, but were prepared for special meetings and industrial/government reports or were simply memoranda from individuals describing specific findings. Critical comparisons and comments have been provided to help the reader evaluate the literature sources.

The review is divided into three principal parts: Section II, land spills; Section III, water spills; Section IV, the available information relating to variations in concentration within a dispersing LNG cloud.

II. LNG SPILLS IN DIKED ENCLOSURES

A. MODEL SCENARIOS

Experimental test programs and mathematical models dealing with the consequences of an accidental release of LNG on land have been limited, with rare exceptions, to spills in confined areas. Interest generally has been focused on the fate of LNG vaporized within a diked area surrounding an LNG tank. This general scenario has led to an emphasis on vapor-dispersion models based on a transient, continuous source. Instantaneous or puff sources are not believed to represent realistic cases.

In predicting the consequences of a large LNG release within a diked area, there must be some agreement on the type or magnitude of the spill. Usually a piping failure is assumed; to be conservative, the largest pipe that penetrates the tank is the one chosen to fail. The leak is then assumed to occur at the maximum possible rate consistent with a full tank or with the maximum possible flow in the line. There may or may not be a time limitation on the leak, depending on the type of accident or on the automatic/manual shutoff sequences that could stop the leak.

A second, and far more drastic, accident that may be chosen is catastrophic collapse of the tank. In this case, the diked enclosure is assumed to be filled instantaneously with LNG--that is, the tank empties in a very short time.

The first type of event described above is called a design accident, and the National Fire Protection Association (NFPA) 59A Code normally has selected it for dike and facility-hazard studies. The second type of event may be called the tank-collapse accident. It is chosen occasionally where the effects of severe seismic disturbances or sabotage are of interest.

In either case the spilled LNG contacts the dike floor and, possibly, the dike and storage-tank walls. Because of the mildly superheated state of the escaping LNG, which is stored at superatmospheric pressure in the tanks, some of it flashes into vapor.

The escaping LNG boils when it contacts the warmer dike floor and walls. Liquid may or may not accumulate, depending on the relative rates of spill and boiling. Except in the tank-collapse accident, the dike usually fills with dense, cold vapor. When overflow does occur, LNG begins to disperse downwind.

In almost all cases, the vapor is considered to be pure methane at its normal atmospheric boiling point (111°K). Ethane, propane, and higher hydrocarbons are assumed to be nonvolatile. This assumption is reasonable until the methane concentration becomes quite low; then the boiling rate would drop almost to zero for a time as the dike floor warms to the boiling point of ethane. Essentially pure ethane would then be vaporized. Later, a propane-vaporization period would be expected if the original LNG contained a significant amount of that hydrocarbon. Normally, only the methane-vaporization period is of interest in hazard evaluations because in this period the vaporization rates are highest.

To model the hazards of an LNG spill into a diked area, therefore, one must be able to estimate boiling rates of LNG on various substrates used as dike floors and walls; to take into account specific dike configurations (e.g., sloped dikes, vapor fences); and to model the downwind dispersion characteristics of the vapor overflowing the dike walls. The desired result, in most instances, is the prediction of hazardous zones downwind in terms of both extent and time.

B. BOILING RATES

1. Experimental Data and Analytical Results

Various types of construction materials are used or have been proposed for use as dike floors and walls. The most common is compacted soil. However, interest is being shown in specialized materials--such as lightweight insulating concrete--for facilities where it is imperative to minimize the rate of boiling. Most experimental boiloff data on boiling rates have been obtained at the LNG Research

Center at Massachusetts Institute of Technology. Insulated boxes were prepared with various substrates, and LNG or liquid methane was spilled on the substrate. The mass vaporized was followed as a function of time using a load cell coupled to a data-acquisition computer.

For all but a few substrates, a simple one-dimensional heat-conduction model correlated the experimental data quite well. The substrate was modeled as a semi-infinite slab, and the spill of LNG corresponded to a step-change in temperature at the boundary. Heat-transfer rates were then assumed to be limited by conduction in the substrate. Boiling resistances at the interface were shown to be insignificant for the substrates studied. However, liquid nitrogen could not be used as, in this instance, a high surface resistance prevented the use of a simple conduction model.

Assuming homogeneous substrates with temperature-independent properties, the rate of boiling is expressed as,

$$\dot{M}/A = (k\rho C/\pi)^{1/2}\ \Delta T/\Delta H_v\ t^{1/2} \tag{1}$$

where

$\dot{M}/A$ = rate of boiling, kg/m^2s

k = average substrate thermal conductivity, $kW/m^{\circ}K$

ρ = substrate density, kg/m^3

C = substrate heat capacity, $kJ/kg^{\circ}K$

ΔT = initial temperature difference between LNG and the substrate, °K

ΔH_v = enthalpy of vaporization of LNG, kJ/kg

t = time, s

The physical properties of the substrate can be grouped conveniently with the terms ΔT and ΔH_V (which usually are considered to be constant at about 180°-190°K and 511 kJ/kg, respectively) to give

$$\dot{M}/A = F\ t^{-1/2} \tag{2}$$

where $F = (k\rho C/\pi)^{1/2}\ \Delta T/\Delta H_v$

As noted earlier the measured variable was not the rate of boiling but the total mass vaporized as a function of time. Thus, integrating Eq. (2),

$$M/A = 2F\ t^{1/2} \quad (3)$$

with M/A equal to the total mass of LNG evaporated per unit area, kg/m^2. The slope of the M/A vs $t^{1/2}$ graph is then 2F. A typical example of a test with an insulated concrete, Dycon K-23, is shown in Figure 6. The value of the boiling parameter, F, for this concrete is about $4.7 \times 10^{-2}\ kg/m^2s^{1/2}$.

The MIT LNG Research Center has measured F for a number of substrates (Table 9). The results have been corrected for minor heat losses through the Styrofoam (polystyrene) insulating walls of the test box.

2. Insulating Concretes

Two types of commercially available, insulating concretes have been tested. Dycon concrete, manufactured by the Koppers Co., consists of cement, sand (?), and Styrofoam spheres as aggregate. A binder is added to enhance the bond between the Styrofoam and the cement, and the concrete is prepared with a blowing agent. The two Dycon concretes tested differed in the size of the polystyrene spheres and thus in density. Tests were made with and without a waterproof paint on the surface; no effect of the surface coating on boiloff rates could be detected.

The other concretes studied were prepared by W.R. Grace. Zonolite-3300 is made from cement and vermiculite with reinforcing glass fibers. The material is rather strong considering its relatively low density. G-34 is a denser but less strong vermiculite concrete without glass fibers. Zonolite - 3300 is blown rather than cast and so may be useful for insulating vertical dike walls should that be desirable.

The best concrete tested, considering both strength and insulating properties, was the Zonolite-3300. All insulating concretes must be well sealed against moisture on top and bottom to insure their insulating qualities.

The Firefighting School at Texas A&M University has conducted a few LNG-vaporization tests in a basin constructed of Dycon insulating concrete (Wesson, 1977). The basin is 6.1 m by 6.1 m by 0.91 m. The liquid's depth was measured as a function of time with a probe at one corner of the basin (Table 10, columns 1 and 2). The data shown in Figure 7 are well correlated by Eq. (2) with an F value of $6.5 \times 10^{-2}\ kg/m^2s^{1/2}$ for this concrete.

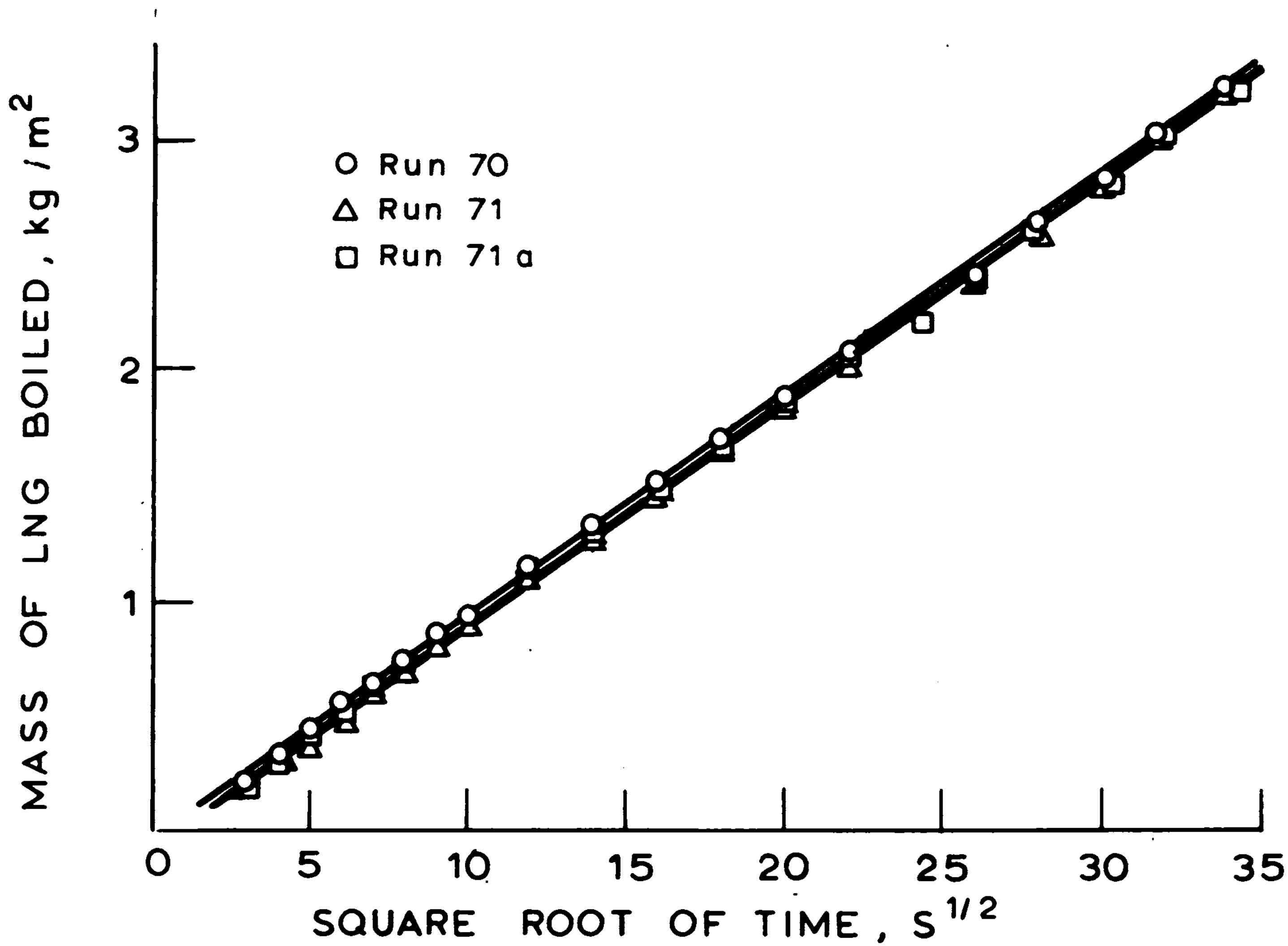

Figure 6 Experimental Boiloff Data for LNG on Dycon K-23 Insulated Concrete

Table 9 Boiling Parameters for LNG Spills on Various Substrates*

Material	Density kg/m^3	Boiling Parameter, °F $kg/m^2\ s^{1/2}$
Insulated Concrete		
Dycon K-23	290-370	4.7×10^{-2}
Dycon K-35	510	6.5×10^{-2}
Grace Zonolite - 3300	410	4.5×10^{-2}
Grace G-34	545	8.8×10^{-2}
Dry sand	-	5.3×10^{-1}
Sand, 1-3% moisture	-	$\sim 5.8 \times 10^{-1}$
Soil, 0-8% moisture	-	$\sim 5.0 \times 10^{-1}$
Soil**	-	$\sim 7.0 \times 10^{-1}$
Wet soil (T = 50°C)***	-	1.5
Dry soil (T = 15°C)***	-	1.0
Wet sand***	-	4.6×10^{-1}

*Except where indicated, the results were obtained from the LNG Research Center, Massachusetts Institute of Technology, Cambridge, MA 02139.

**AGA tests at San Clemente, CA, AGA Project IS-3-1, Report on Phase II work, July 1, 1974; Drake and Reid, 1975.

***Humbert-Basset and Montet, 1972.

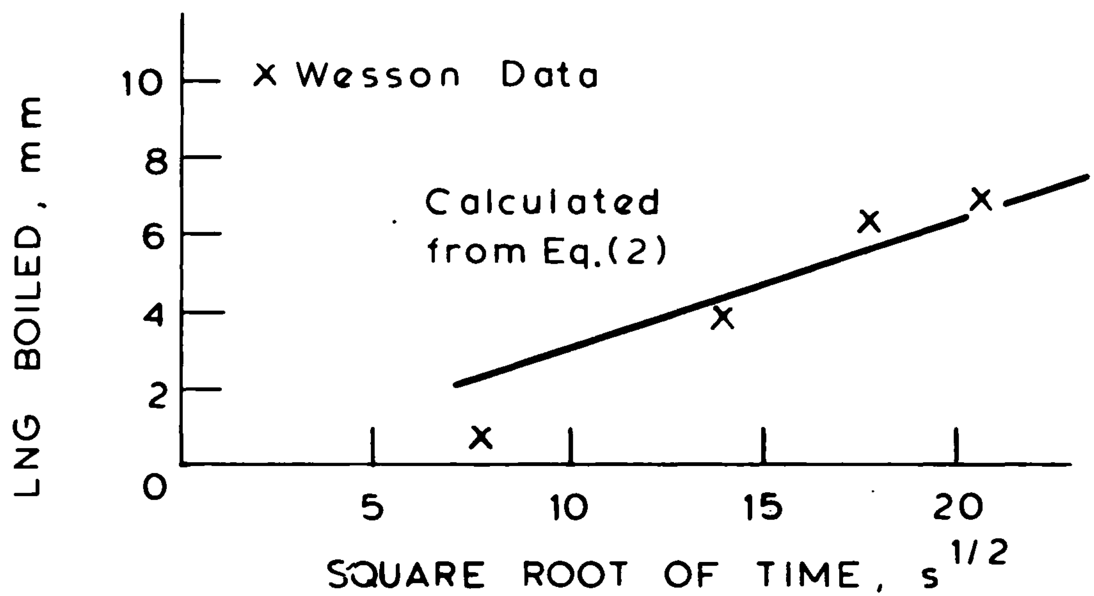

Figure 7 Results of Tests at Texas A&M Firefighting School

Table 10 Results of Texas A&M Firefighting School Tests of LNG on Dycon Concrete

time (min)	depth (in)	$t^{1/2}$ $(s^{1/2})$	Δh (mm)
0	4.65	0	-
1	4.61	7.8	1.0
3.15	4.50	13.8	3.8
5.23	4.40	17.7	6.4
7.05	4.38	20.6	6.9

Koppers Co., 1976, in cooperation with Parker, 1976, carried out a few boiloff tests with LNG on an insulated concrete believed to be very similar to Dycon K-35. The boiloff tray was 25.4 cm in diameter, and both walls and base were made from the Dycon concrete. The densities of the wall and floor concretes were 580 kg/m^3 and 505 kg/m^3, respectively. About 660 cm^3 of LNG was spilled. The tray rested on a load cell, and readings were taken at intervals of 30 s. To reduce convection, a Mylar shield was placed on the periphery. The LNG was condensed from the laboratory supply line and was reported to contain a significant amount of air. If the air resulted from leakage in sampling, as suggested by Parker, then the LNG was approximately 97.5 percent methane with some 2 percent ethane and traces of higher hydrocarbons. The estimated density of the liquid was about 430 kg/m^3.

Data for three tests were analyzed. The test conditions and results are shown in Table 11 and Figure 8. Data for KO-1 and KO-2 were supplied by Koppers Co. and for KO-3 by Parker.

Table 11 Test Conditions and Results From Koppers Co. Spills of LNG on Dycon K-35

Test	Boiling Parameter, F $kg/m^2s^{1/2}$
KO-1	8.8×10^{-2}
KO-2	1.2×10^{-1}
KO-3	6.3×10^{-2}

In Figure 8, the data are plotted as in Figure 6. The absolute value of the ordinate is not important; the slope of the linear portion of the curve is the significant parameter in determining the thermal properties of the concrete when heat transfer is controlled by conduction.

Tests KO-1 and KO-2 produced boiling parameters (F) higher than shown in Table 9 for Dycon K-35. Also, at long times, the data fall above the linear line when extrapolated. This result may reflect convection effects, which would become more important at long times. In test KO-3, a linear relationship was found to give a good fit with the data for the duration of the test, and the boiling parameter, F, agrees well with that shown in Table 9.

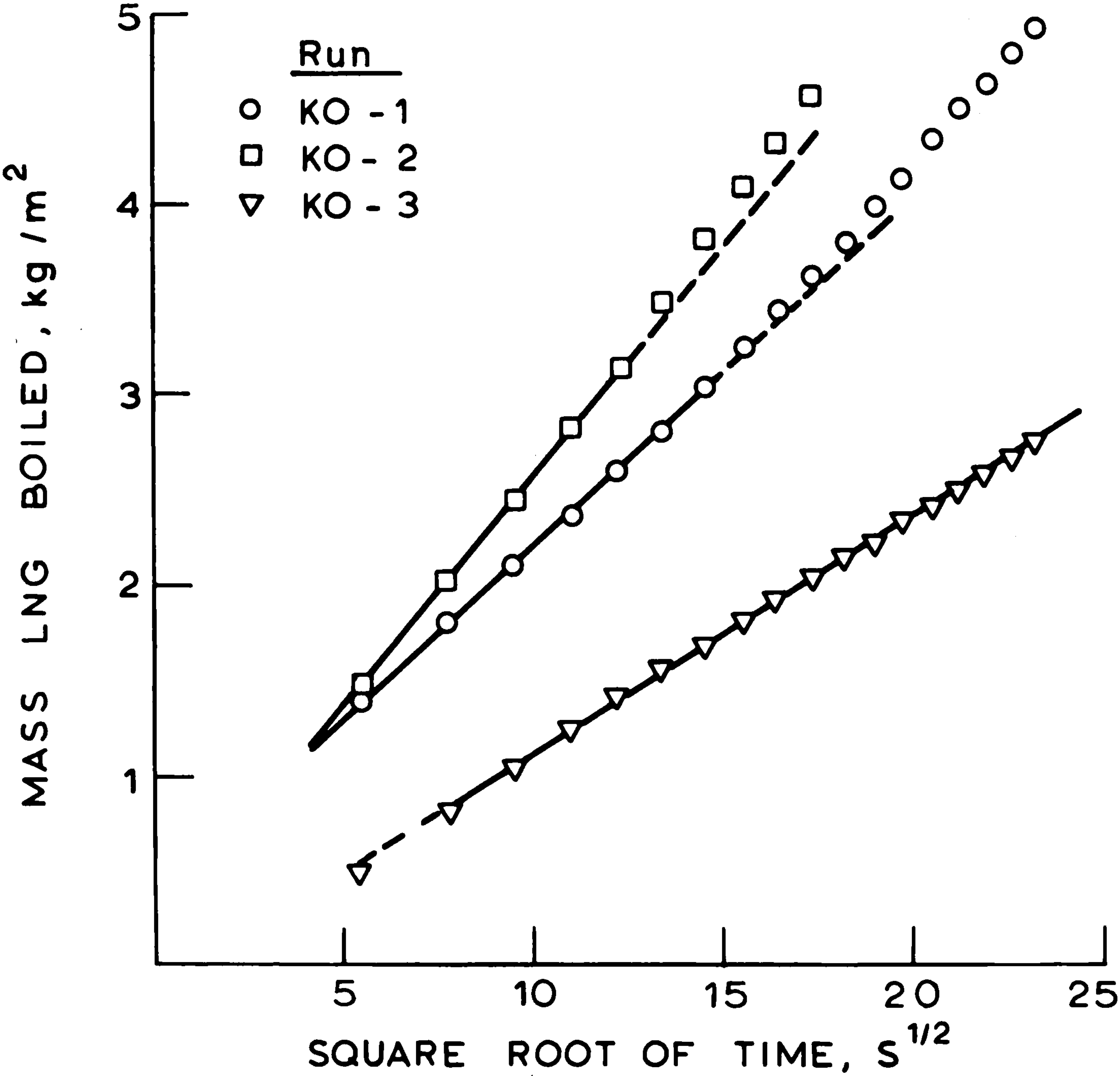

Figure 8 Koppers Co. Tests on Dycon Insulated Concrete

3. Soil

The F values for soil in Table 9 vary widely, but all are significantly higher than for insulating concrete. Percolation and soil cracking often occurred and led to rapid vaporization. Because of this effect, standard literature values for thermal properties of soils should not be used to calculate F.

4. Crushed Stone

Values of F for crushed stone are not shown in Table 9. Spills on such a material lead to very high boiling rates, and Eq. (3) is not applicable.

5. Polyurethane

No F values are given for polyurethane in Table 9. In a few tests with dry polyurethane slabs, very low values of F ($\sim 2-3 \times 10^{-2}$) were noted. Water-soaked slabs yielded much higher values (~ 0.3). Polyurethane-foam coatings for dike floors are certainly feasible, but they require regular maintenance to prevent absorption of moisture and deterioration from sunlight.

6. Corrugated Aluminum

A novel insulating material for dike floors, suggested by the Boston Gas Co., is corrugated aluminum sheets laid on packed soil and sealed to prevent leakage. Preliminary tests of this simple concept indicated that boiling rates would be lower than with insulating concretes. Four tests were then run. These results are shown in Figure 9, where the mass boiled off is plotted against time (not $t^{1/2}$). After about 100 s, the rate of boiling decreases significantly and then changes little during the remainder of the test. The experimental scatter probably results from different soil-aluminum contact areas in the various tests. The data are correlated, approximately, with composite-slab theory in Section II-C-7.

The boiling rate of LNG on the corrugated aluminum is significantly less than on any other substrate tested, with the exception of dry polyurethane. Aluminum shows real promise as, a simple, economical, dike-floor insulation.

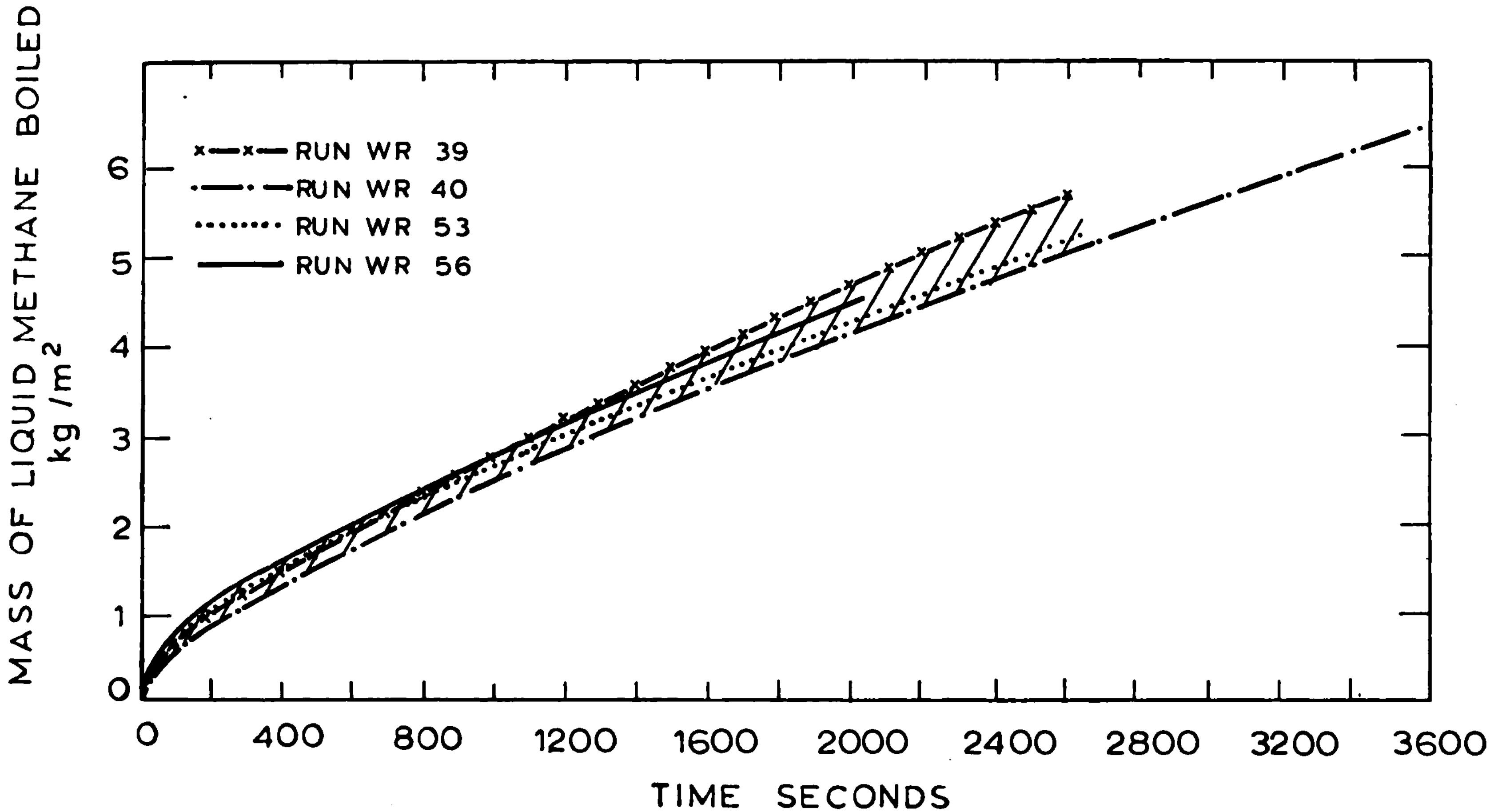

Figure 9 Boiling Rates of LNG on Corrugated Aluminum Over Soil

C. EFFECT OF DIKE CONSTRUCTION METHODS

1. Maximum Overflow Rates

Dikes surrounding an LNG tank may be constructed in many ways, with corresponding effects on overflow rates. In each facility, however, the enclosed volume must be somewhat larger than needed to hold a full tank of liquid. Some dikes have relatively low walls, but enclose a large area; other dikes are high and near the tank. Changes in dike design are often suggested to modify the rate of boiling should an LNG spill occur. These changes may include sloping floors, compartmentalization, vapor fences, etc.

In addition to dike design, there are the two previously noted spill scenarios: a continuous, but finite-rate spill, and a tank-collapse spill. In the finite-rate spill, the effect of spill rate on vapor production must be considered. The likelihood that a tank-collapse spill will occur is extremely remote, but often it is used to place an outer boundary on potentially hazardous zones.

In all the discussion to follow, we assume that Eq. (1) describes the boiling rate of LNG on a solid substrate. With certain materials (e.g., corrugated aluminum), boiling rates are not correlated by this equation, so the analyses would require modification.

One conclusion reached readily is that a low value for the boiling parameter, F, in Eq. (1) is very important in controlling the maximum rate of vapor overflow from a dike. Consider a simple case where the dike has a flat floor and is covered rapidly by spilled LNG. The total vapor evolved is given by M/A, from Eq. (3), multiplied by the dike area. The maximum rate of vapor overflow occurs just when the dike fills with vapor since, at any later time, the boiling rate is lower. If the distance from the liquid's surface to the top of the dike wall is H, then at the time, t_{ov}, when the dike is filled with vapor of density ρ_V, there has been $H\rho_V$ kg/m² of vapor evolved. Thus, from Eq. (3),

$$H\rho_V = 2Ft_{ov}^{1/2}$$

Solving for t_{ov} and substituting into Eq. (1)

$$(\dot{M}/A)_{t_{ov}} = 2F^2/H\rho_V \qquad (4)$$

The value of dike-floor materials with a low value of F is apparent, since, for many hazard analyses, the maximum downwind hazard distance of a vapor cloud is based conservatively on $(M/A)_{t_{ov}}$.

2. Continuous Spills into a Flat Dike

For very small leak rates, the dike floor will not be entirely wetted by liquid for a long time. For more rapid spills, the LNG vaporizes initially as fast as it enters the dike, but later, as the floor cools, liquid begins to accumulate.

To analyze a continuous spill in a flat dike, consider a simple case where liquid contacts the dike floor at a point near the center and spreads radially while boiling. Eq. (1) is assumed to describe the rate of vaporization at any point covered by liquid. The spill rate is $\dot{M}_\ell$ (kg/s), and the total boiling rate over all wetted areas if $\dot{M}_e$. Then, it can be shown (Arthur D. Little, Inc., 1974; Drake and Wesson, 1976),

$$\dot{M}_e = \dot{M}_\ell \quad 0 < t < t(R) \tag{5}$$

$$\dot{M}_e = (2/\pi)\ \dot{M}_\ell \sin^{-1} (R^2/a^2 t^{1/2}) \quad t > t(R) \tag{6}$$

At long times, Eq. (6) simplifies to

$$\dot{M}_e = (2/\pi)\ \dot{M}_\ell\ (R^2/a^2)\ t^{-1/2} \tag{7}$$

R is the equivalent radius of the dike. (For a square dike of sides L, $R = L/\pi^{1/2}$). t(R) is the time when the entire dike floor is wetted. It is calculated from Eq. (8)

$$t(R) = R^4/a^4 \tag{8}$$

The parameter a is given by

$$a^2 = 2\dot{M}_\ell/\pi^2 F \tag{9}$$

As an example, suppose a 45,000-m^3 storage tank is surrounded by a square dike 80 m on a side with dike walls 8 m high. The dike floor is packed soil with an F of 0.7 $kg/m^2s^{1/2}$. An accident is hypothesized to occur with a leak of 1 m^3/s. From Eqs. (8) and (9), with the liquid's density assumed to be 420 kg/m^3,

$$a^2 = (2)(420)/(\pi^2)(0.7) = 122\ m^2/s^{1/2}$$

$$t(R) = (80/\sqrt{\pi})^4/(122)^2 = 280\ s$$

The floor is completely wetted after about 280 s. Until then, the evaporation rate equals the spill rate; after 280 s, the evaporation rate diminishes as given by Eq. (6). The vapor dike can hold (80 x 80 x 8) m^3 of saturated vapor or about 8.7 x 10^4 kg. With a leak rate of 420 kg/s, the dike is full of vapor after about 207 s; thus overflow occurs at a vapor-flow rate equal to the spill rate, i.e., at 420 kg/s distributed along an 80-m wall or at a rate of 5.2 kg/m s.

3. Dike Sumps

To reduce the area of contact between spilled LNG and the dike floor, particularly in accidents involving piping, sumps may be used to collect the LNG in a limited region. In such cases, the sump may be treated as a miniature dike. An analysis of boiling rates of LNG in a sump can be quite complex because one must consider heat transfer from the walls and bottom. This problem is treated in some detail in an AGA report (Arthur D. Little, Inc., 1974).

4. Sloping Dike Floors

Essentially all dike floors at LNG facilities are sloped to some degree to allow rain or melted snow to run off. It is also desirable to slope dikes so that spilled LNG flows away from the tank to avoid thermal shocks to the base of the outer tank in the event of an accident. Sloped dikes also may reduce LNG vaporization rates, especially in accidents with a high, continuous spill rate, because the LNG flows preferentially to lower regions and covers less area than it would in flat dikes.

The problem of estimating vaporization rates from LNG spills into sloping dikes is treated in detail elsewhere (Arthur D. Little, Inc., 1974). This analysis considered three configurations: a rectangular dike sloped in one direction; a rectangular dike sloped in two directions; and a circular dike sloped away from a central tank.

In the analysis it was assumed that trenches were provided to direct spilled LNG to the lower parts of the dike and that no significant vaporization occurred until the liquid reached the pool at the low region. As the pool grew, it covered additional warm dike floor, but at the same time the rate of boling in the covered areas was decreasing as given by Eq. (2).

To illustrate the results, consider a sloped dike as shown in Figure 10. In this case, the total boiling rate, $\dot{M}_e$, is related to the spill rate, $\dot{M}_\ell$, by

$$\dot{M}_e = \pi F(\dot{M}_\ell \; W/2\rho_L \; \tan\theta)^{1/2} \qquad (10)$$

$\dot{M}_e$ and $\dot{M}_\ell$ are in kg/s. W is the dike width in meters at the low end. ρ_L is the liquid density in kg/m^3, θ is the slope angle, and F is the heat-transfer factor (Table 9) in $kg/m^2 \; s^{1/2}$. Eq. (10) is only valid when the right-hand side of Eq. (10) is significantly less than $2\dot{M}_\ell$ (Arthur D. Little, Inc., 1974). This criterion is normally satisfied at large spill rates. Note that Eq. (10) predicts a constant rate of evaporation with time, assuming that $\dot{M}_\ell$ does not vary.

To illustrate the striking effect of sloping a dike floor, consider the previous example: a 1 m^3/s spill into a square dike, 80 m by 80 m with 8-m walls. With a flat dike, vapor overflowed after ∿200 s at a rate of 420 kg/s. If the dike had been sloped by, say, 3°, then with Eq. (10)

$$\dot{M}_e = (\pi)(0.7)[(1)(80)/(2)(\tan 3)]^{1/2} = 61 \text{ kg/s}$$

To fill the dike with ∿8.7 x 10^4 kg of vapor, more than 1400 s would be required, and the rate at overflow would be only 61 kg/s or 0.76 kg/m s.

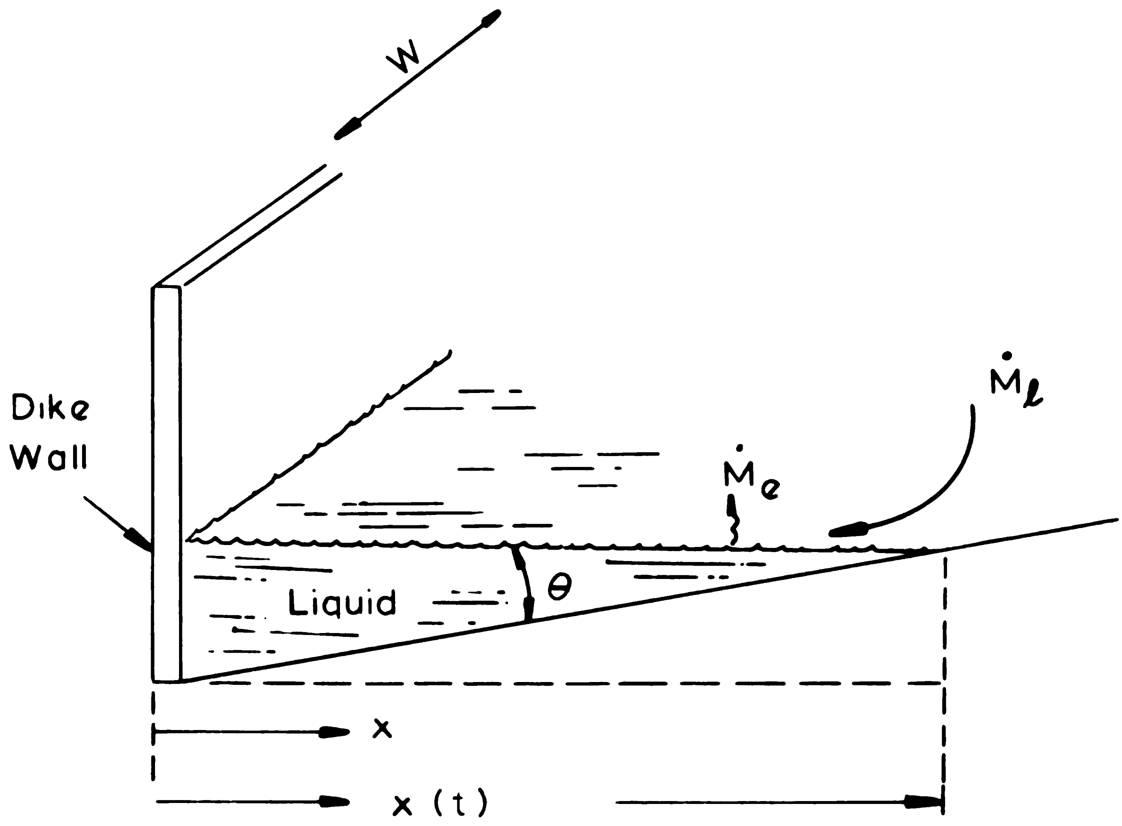

Figure 10 Illustration to Demonstrate Eq. (10)

A rectangular dike sloped in one direction reduces net evaporation rates somewhat more effectively than either a rectangular dike sloped in two directions or a circular sloped dike.

5. Compartmentalized Dikes

The floor of a compartmentalized dike is constructed with low walls laid out in some prescribed grid pattern. These walls are staggered in height, but are always lower than the main walls of the dike. Should a leak occur anywhere in the dike, only one compartment would be flooded initially, so the heat-transfer area of the floor would be reduced significantly. The grid would be so designed that if the leak continued long enough to fill the first compartment, LNG would overflow into the next compartment and so on until all compartments were flooded.

The compartment walls could be of reasonably light construction; earth or cement blocks might be employed. Access to the tank would be somewhat restricted unless radial walls were employed.

For spills of short duration, compartmentalization would perform quite well. In most aspects, the results are similar to those for a dike sump, i.e., the boiling rate is kept low and the full dike is used to accumulate vapor, thus delaying overflow until the rate has subsided to a low value. If one is planning only for a spill of short duration, however, a simple dike sump would be preferable to compartmentalization.

For sustained spills at large flow rates, compartmentalized dikes are not desirable. Flow into the first compartment produces a rapid evolution of vapor which, however, decreases with time. Because of its large volume, the dike can act as an accumulator for this burst of vapor, delaying overflow until the net boiling rate declines. Should the leak continue until the dike fills with vapor, overflow of liquid from the first compartment into an adjacent one would lead to a new,large burst of vapor. Because the dike itself is already full of vapor, a significant overflow pulse would be expected. This pulse would result in a large downwind concentration of methane for a brief period. Such pulses would be noted everytime a fresh compartment was flooded.

It is not necessarily true that the downwind concentration from each pulse is less than the maximum expected if no compartments were present. In a simple, flat dike, the vapor-generation rate from the floor is large initially, but it is dampened because of the large volume of the dike, which is assumed to fill with cold, dense methane before overflow occurs. For a compartmented dike, analysis predicts an increase in downwind concentration with each successive pulse, and concentrations from the later pulses have been calculated to be larger than if no compartments were present (Arthur D. Little, Inc., 1974).

6. Vapor Holdup Concepts

With dikes where LNG vaporization rates decrease with time, the time to vapor overflow can be lengthened and the peak overflow rate reduced by adding vapor-holding capacity to the system. Vapor-holding capacity can be added most easily by increasing the height of the dike, but adding dike capacity to hold vapor is not usually an acceptable investment. However, vapor dikes never need to hold liquid and so need not be constructed like the dike wall proper. From a design standpoint they need only be rigid enough to withstand expected wind loadings.

An alternative is to place a leaky vapor fence on top of the dike wall proper. Vapor can bleed between slats at a controlled rate while still accumulating behind the fence. This concept is illustrated in Figure 11. A method for computing the rate of leakage for a fence with pickets of a given width and centerline spacing is available (Arthur D. Little, Inc., 1974).

7. Use of Thin Insulations on Dike Floors

The analysis of vaporization rates in Section II-B assumed that the substrate was infinitely thick. However, a layer of insulating material on a dike floor would have finite thickness. The estimation of the boiling rate of LNG on a thin insulation over soil is discussed in detail elsewhere (MIT, 1978). The results in one case are shown in Figure 12, where the rate of energy extraction is plotted against time for a system composed of Dycon K-35 insulating concrete (See Table 9) over packed clay soil. The parameter δ is the thickness of the concrete. The soil was assumed to be infinitely thick. It can be seen that little is gained by using concrete thicker than about 0.05 m (5 cm). A slab that thick also would be strong enough to walk on.

The two-slab theory also was used to correlate the data for corrugated aluminum over soil. In this case the system was modeled as an air layer over soil. As shown in Figure 13, the experimental boiloff data fell in a band between air-layers 1 and 2 mm thick, but the correlation is not particularly good.

D. VAPOR DISPERSION

This section is divided into three parts. In the first, the major experimental test programs are described. In the second, a brief review of the theory of vapor

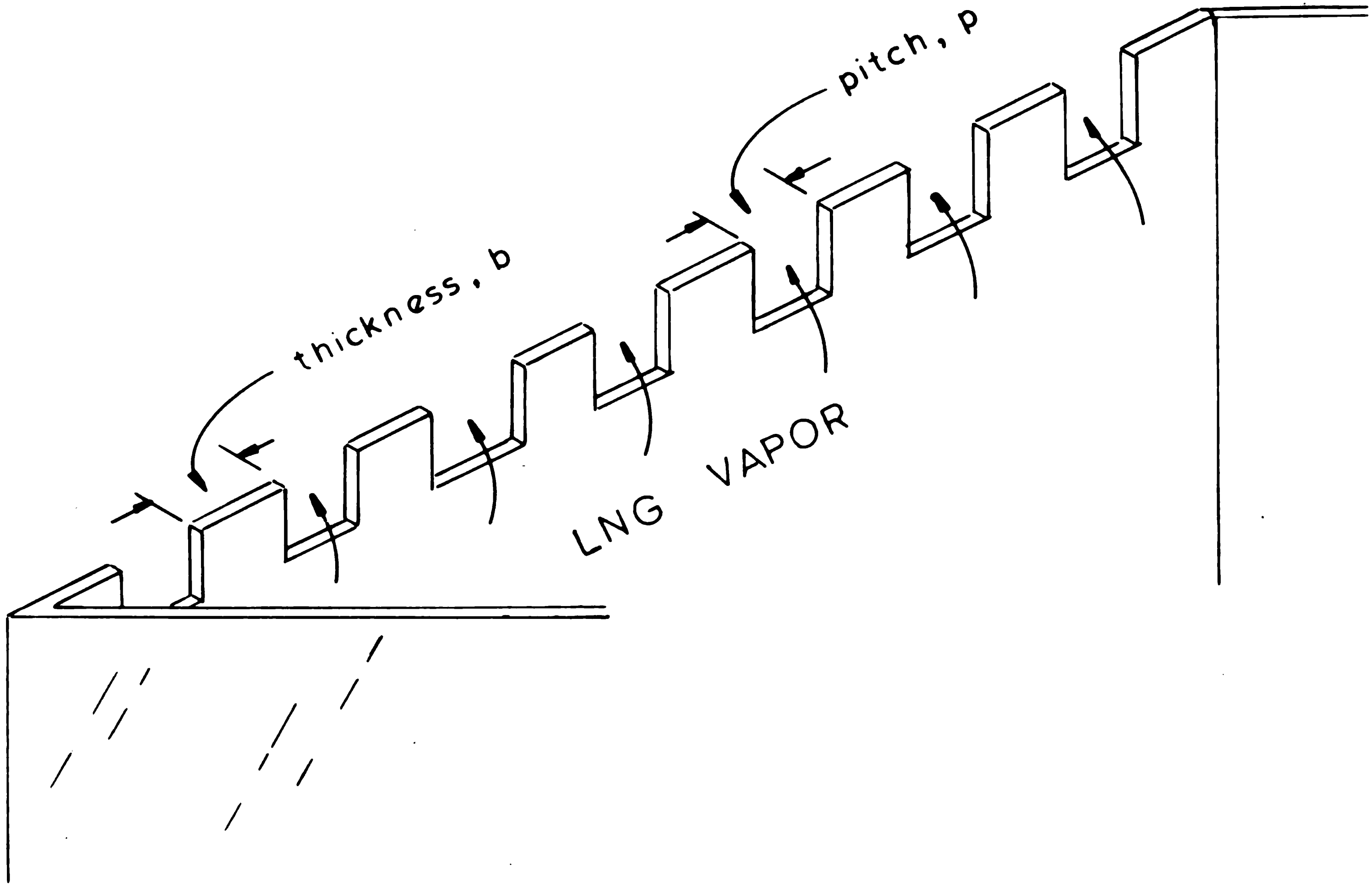

Figure 11 Schematic Illustration of a Vapor Fence on a Dike Wall

dispersion is covered; elements from this subsection will also be of value later when vapor dispersion from water spills is discussed. In the final part, the theory and experimental results are compared and conclusions drawn.

1. Experimental Test Programs

a. Gaz de France. Dispersion of LNG vapor was studied in a program carried out by Gaz de France in the area of the FOS-SUR-MER Terminal (Humbert-Basset and Montet, 1972).

Evaporation Tests. The rates of boiling of LNG spilled on typical soils in the test area were determined experimentally. A container 1.07 m on a side and 1.2 m high was used. It was insulated on the outside with perlite or polyurethane foam. An unstretched balloon was hung over the top of the container. Spills of 50 l of LNG were made, whereupon the boil-up vapor inflated the balloon. The silhouette was photographed every two seconds, and the quantity of vapor generated was estimated from the photographs.

The soil samples could be heated with a steam coil to as high as 50°C. Relatively warm soils were of interest because LNG export terminals were expected to be in hot climates. Also, the initial water content of the soil could be varied. The LNG ranged from 70 to 94 mole percent methane.

As noted earlier, the results of the evaporation tests could be correlated by a simple, one-dimensional heat-transfer model resulting in Eq. (1). The boiling parameter, F, for the soils and sand tested is given in Table 9.

Large Spill Tests. The test site consisted of 20 cm of Loire sand surrounded by clay dikes 50 cm high. The height could be raised to 1 or 1.5 m by adding side plates. The pool-surface area was 14 m on a side, but compartmentation could be used to form pools down to 3 m square.

At the pool site, the ambient temperature, pressure, humidity, and wind speed were recorded. Marking stakes 5 m high were set downwind to allow cloud height to be determined from photographs. Thermocouples and methane-gas detectors were attached to these stakes. In addition, explosion meters and vacuum sample jars were placed downwind.

Forty-three spills were made, and useable data were obtained from 20 of them. The data consisted primarily of methane concentrations at various locations. Wind speeds ranged from near zero to 7 m/s. Up to 3 m³ of LNG was spilled in a typical test. However, a continuous flow of 10 m³/hr was used in one test.

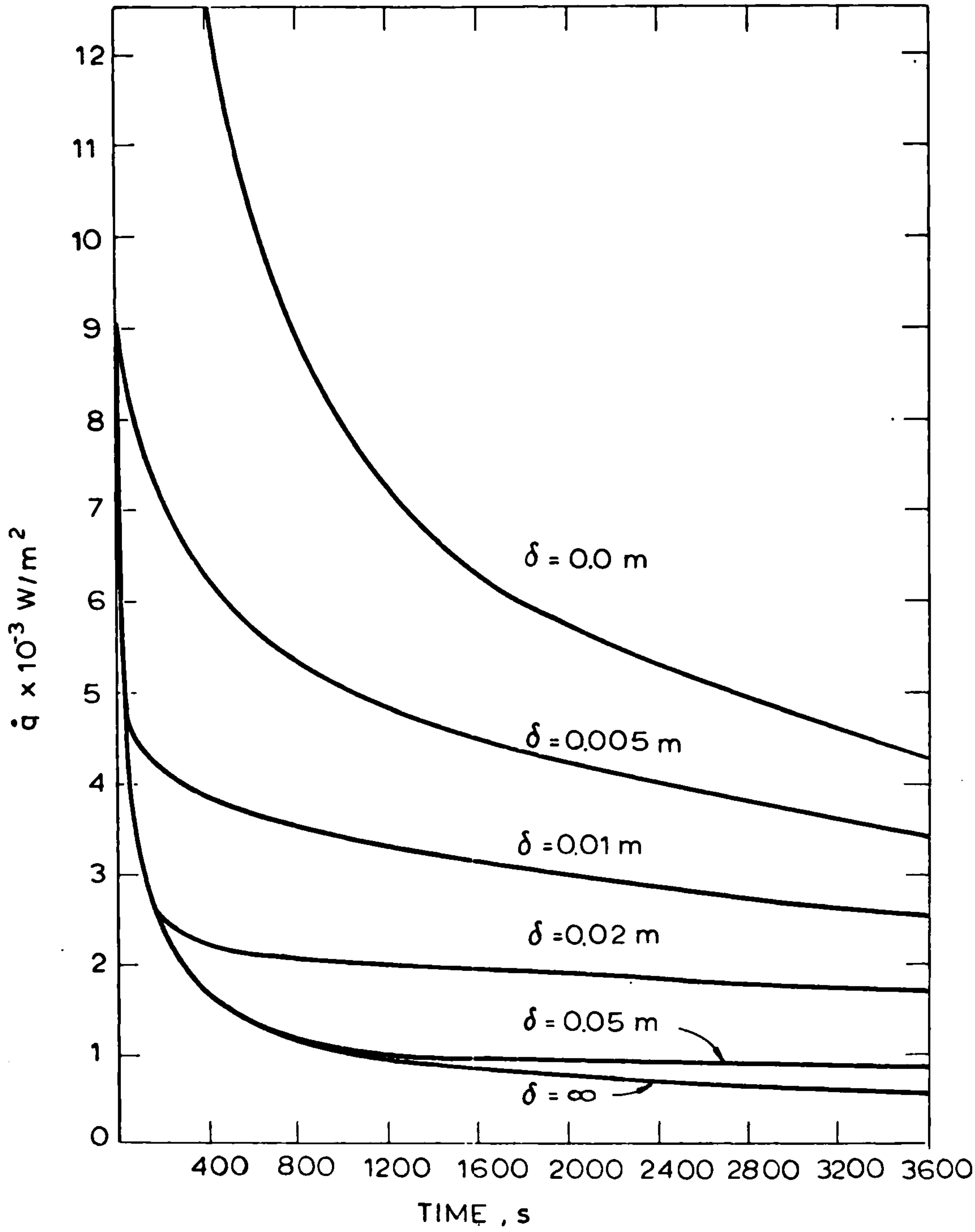

Figure 12 Heat Flux vs. Time for Composite of Dycon K-35 Insulating Concrete Over Packed Clay Soil

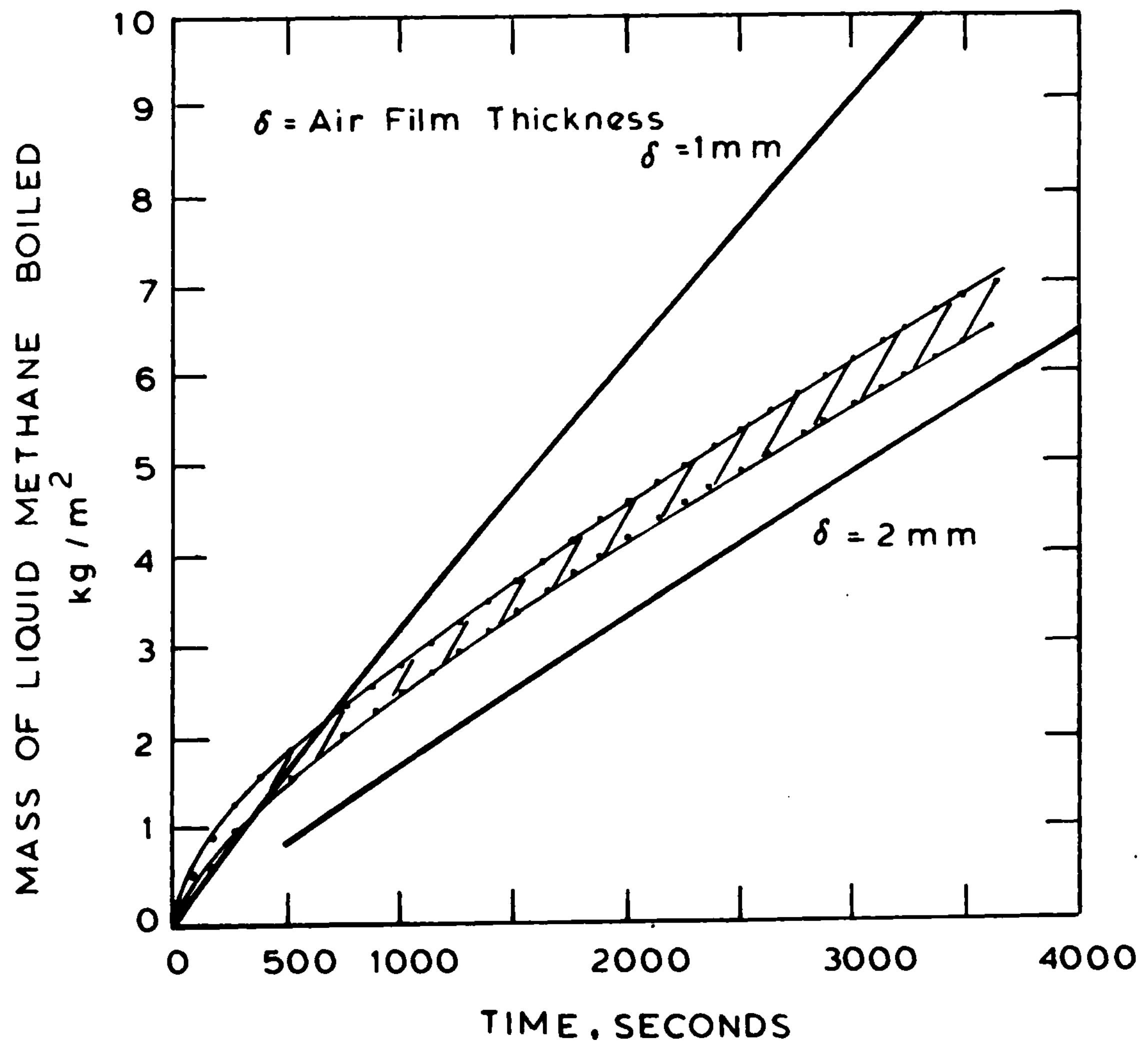

Figure 13 Comparison of Boiling Curves Between Calculated Air-Soil Composites and Corrugated Aluminum Over Soil

One of the most interesting observations was the fact that, at low wind speeds and high atmospheric humidity, the LNG vapor-plume rose with an average vertical component of about 0.15 m/s while moving downwind. The models developed to correlate the dispersion data are discussed later.

b. Buxton-Bund. A series of LNG spill tests was sponsored by the British Gas Council to demonstrate the integrity of dike (bund) walls containing burning LNG (Carne et al., 1971). Some gas concentrations and plume observations were also obtained.

The test dikes were 3.66 m square at the top and 3.6 m deep. Wall slopes ranged from 1.5 to 2.1. Three tests were run with LNG fed through an insulated line 3.8 cm in diameter. In two of these tests the dike floor was precooled with liquid nitrogen. After the dike was cold, the LNG vaporization rate was quite low; even with no wind, flammable concentrations were not found more than a meter or so from the dike. No dispersion modeling was attempted.

c. TRW. Wilcox, 1971, reported on a series of LNG spill tests in a dike 1.5 m in diameter with 0.15-m walls. 0.19 m^3 of LNG was spilled onto clay soil in this enclosed area. Boiloff rates were similar to those obtained by Gaz de France, except with wet soil, when the LNG boiled more rapidly. Some LNG was reported spilled outside the diked area, which makes evaluation of the test results somewhat uncertain. Also, measured downstream temperatures were unusual and did not appear to change when the sensors were enveloped by the plume. In addition, the vertical dispersion was found not to depend on distance downwind, and concentrations were inversely proportional to the square root of the wind speed. The results obtained differ significantly from those of other studies and have not been duplicated. The modeling is considered suspect and is not treated further here.

d. Lake Charles. The U.S. Bureau of Mines (Burgess and Zabetakis, 1962; Conch Methane Services, Ltd., 1962) investigated ignition hazards and thermal-radiation intensities of LNG fires from a diked area 1.5 m in diameter. Downwind-dispersion measurements were few and were limited to the centerline axis 3 m downwind from grade to 0.7 m high. Concentrations were quite scattered, and no correlation of the data was given.

e. University Engineers. Wesson et al., 1974, studied fire-suppression techniques for burning LNG pools and also did a few vapor-dispersion tests. Over a limited range of variables, they suggested that the downwind concentration was proportional to the boiling rate and inversely proportional to wind speed and decreased as the downwind distance increased. These results are not unusual, but they do not yield a general correlation. In a few tests, foam was sprayed on the evaporating pool; the boiling rate increased, but the downwind (grade-level) concentration of methane decreased. The reasons for the decrease probably relate to addition of heat to the vapor by the foam and dilution of vapor by the gas in the foam. However, the use of foam to disperse LNG vapor and so reduce hazard is feasible only with very small spills. Foam is valuable in fire control, and if its use is justified for that reason, it may also help slightly to disperse unignited vapors.

f. Liquid-Oxygen Spill Tests. Liquid oxygen was pumped into an earthen dike, 0.9 m in diameter, with walls about 0.3 m high (Lapin and Roster, 1967). Water was sprayed into the pool to prevent a change in rate of evaporation as the ground cooled. Oxygen concentrations were then measured downwind with various atmospheric conditions. There were two interesting qualitative observations: oxygen-enriched air was found only within the water-fog cloud that moved downwind. For this reason the dispersion process could be analyzed visually (In LNG spills, flammable mixtures sometimes occur outside the visible cloud at low relative humidities.) The observation also supports the assumption made in most LNG-spill models that little vapor overflows any dike wall except the one in the downwind direction. Vaporization rates of 0.75, 1.25, and 2.5 kg/s were used. These rates are equivalent to regression rates of 0.3 to 3 mm/s.

Analyses of the data indicated that dispersion was very rapid at wind speeds higher than 4 m/s; no significant oxygen enrichment was noted beyond 1.5 to 3 m. At lower wind velocities, the few data given seem to indicate reasonable rapid dispersion in the first 7 to 15 m but little dispersion beyond this distance. This finding does not agree with most theoretical dispersion models. Considerable layering was observed, especially in tests at low wind speeds--i.e., the vapor cloud clung to the ground and spread laterally. This is not surprising, because oxygen vapor is nearly 2.5 times denser than LNG vapor with each at its saturation temperature.

g. Ammonia-Spill Tests Ball, 1969, reported on a spill of liquid anhydrous ammonia into a pool 1.5 m by 6.7 m. Concentrations of about 1 percent were noted 500 m downwind. Wind speeds were not given.

During 1968-69, ammonia spill tests were conducted by the Museum National d'Histoire Naturelle under the auspices of a consortium of public and private groups involved in the handling or safety of liquid ammonia (Resplandy, 1969). Two test dikes, each 4 m in diameter and 20 cm deep, were constructed. One was lined with earth, the other with cement.

Ammonia concentrations downwind of liquid spills were measured, but observers also reported formation of an aerosol, especially during the first seconds after the spill. The downwind concentrations did rise suddenly to a peak and then decayed fairly rapidly. Such results were consistent with the observed behavior of the source, but source strengths were not measured in the tests, so dispersal was not analyzed quantitatively. A detailed analysis would have required additional information about the aerosol phase.

The most comprehensive ammonia-spill test program carried out to date was sponsored by the U.S. Coast Guard and conducted by Arthur D. Little, Inc., in 1973 (Raj et al., 1974).* The spills were of several sizes--from a few liters to 0.19 m^3 of liquid ammonia--and all were on or under water. Changes in the temperature of the water in the vicinity of the spill, as well as downwind ammonia concentrations, usually were measured.

Liquid ammonia differs from LNG in that an appreciable fraction of it will dissolve in water and form aqueous ammonium hydroxide; in fact, depending on the type and quantity of spill, from 50 percent to over 90 percent of the ammonia did not enter the vapor phase. The portion that did vaporize formed a cloud of Gaussian profile, but the cloud rose as it moved downwind being, apparently, less dense than air. LNG clouds are denser than air and should be negatively buoyant. However, in the Gaz de France tests, it was found that even vaporized LNG may become slightly buoyant in humid air.

h. Refrigerant-12 Gas Dispersion. Van Ulden, 1974, discusses the spreading of cold Refrigerant-12 (Freon-12) vapor near the ground. Refrigerant-12 is 4.2 times denser than air. A 1000-kg spill was made.**

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* Additional large-scale ammonia-spill tests are planned for 1978-79 at China Lake.

** Using a vapor density of ~6 kg/m^3 for Refrigerant-12 the vapor-spill volume was 165 m^3. To achieve this same volume of gas with LNG, a spill of ~0.7 m^3 of liquid would have to be used.

The saturation temperature of Refrigerant-12 is 243°K, so water vapor was condensed and the cloud's profile could be followed photographically as the cloud moved downwind in a wind speed of 3 m/s at 10 m. A dispersion model was developed and is described later.

i. AGA LNG-Spill Program. The most comprehensive LNG-spill tests on land were coordinated by the American Gas Association, 1974. The tests were made with dikes of three diameters: 1.8 m, 6.1 m, and 24.4 m. Useful data were obtained from 17 spills into the smallest dike, nine spills into the intermediate size dike, and two spills into the large dike. Weather conditions ranged from neutral to slightly unstable. The dike floors were compacted clay soil which ranged from 3 percent to 18 percent moisture. Boiloff rates were well correlated by Eq. (1), and the boiling parameter F is given in Table 9. The dike was about 0.5 m high. A few tests were made with higher dikes, but the data from them are questionable.

Instrumentation and photographic coverage were extensive. Weather conditions (wind speeds, humidity, temperature, lapse rate) were recorded. Methane concentrations and cloud temperatures were monitored at 36 sites whose location varied. In addition to dispersion measurements, many fire/radiation tests were carried out.

Even with careful planning, the final data, after reduction, were often disappointing. The concentration measurements showed wide scatter; the transient response was fairly slow ($\sim$20 s); the accuracy at high methane concentrations was poor; the calibration of the sensors was difficult to maintain; the boiloff rates were hard to monitor; and the wind often changed direction and speed abruptly during a test. Thus, it was difficult to develop sound models to fit all the data. Nevertheless, these AGA tests are the basis of most existing models for the estimation of LNG-vapor dispersion following a spill on land.

j. Japanese Tests. The Japanese Ministry of International Trade conducted LNG-spill tests in pools 2 m x 2 m and 10 m x 10 m in July 1974 and July 1975, respectively. A summary of the procedures and results is available (Wesson, 1975). Some temperature and downwind vapor-concentration data are available, but not thoroughly analyzed. Wesson concludes that the data generally agree with the results of the small-scale tests in the AGA LNG program.

k. Summary of Land Spills. Only two spills of LNG on land (Gaz de France and AGA) have produced enough data to test theoretical dispersion models. The largest test was in a circular area of some 470 m² (AGA), and the largest spill was about 50 m³ of LNG (AGA). Essentially no test data are available for spills in stable weather nor for high dike walls. The AGA test program did include some high-dike tests, but the results were not useful because a significant quantity of LNG was spilled outside the dike. The Gaz de France tests took place at high humidity, whereas the absolute humidity for the AGA tests was relatively low. As will be emphasized later, there is clearly a major qualitative difference between the behavior of plumes from these land spills and those from large-scale tests over water. In the land spills to date, dispersion has been rapid, especially vertically, and the results could be modeled with correlations not dissimilar to those used in dispersion of air pollutants. In the tests over water, the cloud is more stable, disperses slowly vertically, and spreads laterally.

2. Mathematical Modeling

a. Background The study of the dispersion of vapors in the atmosphere touches many disciplines, and even a crude understanding of the phenomenon explains many unusual natural phenomena. For example, the rare female luna moth seeks its mate by emitting chemicals which disperse in the atmosphere and are detected up to 30 km downwind by the male. Similar, but less astounding, odor-tracking is practiced by many hunting and hunted animals. The scientific community became interested in the quantitative aspects of atmospheric dispersion for perfecting the use of poison-gas generators and for utilizing smoke screens (Sherwood, 1949). Today, the shipment of large quantities of volatile chemicals by land or water creates a potential hazard should an accident result in a large release.

There is no unified, quantitative atmospheric dispersion theory at present, even if we limit ourselves to the lower levels of the atmosphere (where the term micrometeorology is applicable). Anyone who has watched the movement of smoke issuing from a stack can well realize the difficulty of tracing this smoke downwind. We do recognize, in general, that dispersion is intimately related to wind speed, atmospheric turbulence, temperature lapse rate, and air density. Superimposed on these variables are those specific to the case of interest, e.g., stack gases are often buoyant and enter the atmosphere with a vertical-momentum component, while some vapors are cold and denser than air and may even condense water in the atmosphere. Other gases may react with oxygen. The whole spectrum of turbulence in the lower atmosphere is so complex that few studies in depth have been done. The ground itself modifies the wind-velocity gradient appreciably, and only at a height called the "gradient wind level," does the frictional drag of the ground become insignificant. This gradient wind height varies with the roughness of the terrain as well as with the temperature lapse rate.

Methane vapor, at ambient temperature, is less dense than air and so would tend to disperse upward. However, methane vapor generated from a boiling pool of LNG is denser than air because of its low temperature (around 112°K). Buoyancy effects, whether positive or negative, are most pronounced near the source. The dispersing vapors approach neutral buoyancy as they mix with air and are warmed by the ground, water condensation, vegetation, etc.

To facilitate the analysis of vapor dispersion, the geometry and duration of the source must be defined. Mathematical models are usually based on point sources, line sources, or area sources. A rapid release and vaporization may be treated as instantaneous, whereas a release of longer duration would be analyzed using a continuous-source model.

Once the source model is selected, the dispersion analysis is carried out using some atmospheric mixing model. These models are approximate. They incorporate empirical parameters to describe atmospheric turbulence as a function of various categories of atmospheric stability. Other complex wind-plume interactions include momentum transfer as the vapors are entrained; wind-velocity gradients near the ground; additional turbulence generated in the wake of objects such as tanks, dikes, or piping; and the effects of irregular terrain. For continuous sources, the most common analytical approach simply assumes that the plume moves at a constant speed equal to the average wind speed.

In the following sections, general types of atmospheric-dispersion models are presented; the techniques for estimating atmospheric dispersion coefficients are then described.

b. General Types of Atmospheric Dispersion. Mathematical models that can be used to calculate downwind concentrations of vapor can be formulated by two general approaches: the statistical and the gradient approach. The statistical approach was proposed by Taylor, 1921, and developed in some detail by Pasquill, 1962. The turbulent-energy spectrum is employed to obtain mean-square distances of travel of identified particles at specified times. Though the statistical method is more realistic than the gradient approach, it is only now receiving serious attention in solving real air-pollution problems (see, for example, Fahien et al., 1974, and Berlyand, 1972).

The gradient method is almost crude in comparison. But it has proved immensely useful as a framework on which to develop models that make predictive equations agree with data. The basic tenet of this approach is that the rate of dispersion depends on the gradient of the concentration. When applied to molecular-transport processes, this approach becomes Fick's law. For eddy diffusion, the comparable basic differential equation for a point source becomes:

$$\frac{dC}{dt} = \frac{\partial}{\partial x} (K_x \frac{\partial C}{\partial x}) + \frac{\partial}{\partial y} (K_y \frac{\partial C}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial C}{\partial z}) \tag{11}$$

Here, C is the concentration at time t, at a distance specified by rectangular coordinates x, y, and z measured from the point source. Eq (11) is not very useful. It cannot be solved analytically, and when it is used, the eddy dispersion parameters (K_x, K_y, K_z) are normally assumed to be independent of the coordinates. In addition, a wind velocity is normally introduced and superimposed on any eddy diffusion caused by atmospheric turbulence.

In addition to the use of theoretical models, interest is growing in simulating the dispersion of vapors in small wind tunnels. A document from the Department of Energy, 1978, describes preliminary tests wherein dispersion of vaporized LNG was modeled. While the wind-tunnel approach is attractive in terms of time and cost, the inability to simulate the Reynolds number has led to a number of questions. The very low wind speeds--less than 0.15 m/s--used for the scale models may or may not be adequate to provide estimates for large-scale spills. As far as is now known, work is continuing in the wind tunnel at Colorado State University.

c. Continuous Point-Source Model. Sutton, 1953, used the gradient approach with a continuous-source model to show that, at steady state,

$$C = \frac{\dot{Q}}{2\pi\sigma_y\sigma_z U} \exp \left\{ -\left[\frac{y^2}{2\sigma_y^2} + \frac{z^2}{2\sigma_z^2} \right] \right\} \tag{12}$$

Here, $\dot{Q}$ (in kg/s) is a constant point-source strength of vapor, y and z represent the crosswind and vertical distances between the emitting source and the point of measurement. U is the wind velocity. The dispersion parameters σ_y and σ_z have dimensions of length and depend on weather conditions as well as on the distance between the source and point of measurement.

In Eq. (12), no diffusion was assumed in the downwind (x) direction.

The relation between the eddy dispersion parameters in Eq. (11) and the dispersion parameters in Eq. (12) is:

$$K_y = (1/2)(U/x)\ \sigma_y^{\ 2} \tag{13}$$

$$K_z = (1/2)(U/x)\ \sigma_z^{\ 2} \tag{14}$$

An alternate formulation of Eq. (12) involves a different type of dispersion parameter, i.e., if we write.

$$K_y = (U_x^{\ (1-n)}/4)\ C_y^{\ 2} \tag{15}$$

$$K_z = (U_x^{\ (1-n)}/4)\ C_z^{\ 2} \tag{16}$$

then

$$C = \frac{\dot{Q}}{\pi U\ C_y\ C_z\ x^{2-n}}\ \exp\left\{-\left[\left(\frac{1}{x^{2-n}}\right)\left(\frac{y^2}{C_y^{\ 2}} + \frac{z^2}{C_z^{\ 2}}\right)\right]\right\} \tag{17}$$

This is the equation used by Welker et al., 1969. The dispersion coefficients were obtained from Haugen et al., 1961. The employment of Eqs. (15) and (16) originates from Sutton's treatment of a mean sequare displacement of a vapor packet during downwind dispersion. After diffusing for time t, the mean-square displacement $\overline{y^2}$ was found to be

$$\overline{y^2} = (1/2)\ C_y^{\ 2}\ (Ut)^{2-n} \tag{18}$$

The exponent n comes from assuming a power-law expression for the wind profile (Beals, 1971), i.e.,

$$U(z)/U(z_o) = (z/z_o)^p \tag{19}$$

$$n = 2p/(1 + p) \tag{20}$$

Usually $p \sim 1/7$ so $n \simeq 0.25$. If p = 1, then n = 1, and this extreme value is sometimes used.

Eq. (12) is now more widely used than Eq. (17).*

*The dispersion parameters C and σ are related through Eq. (13) through (16). For example,

$$C_y = \sqrt{2}\ x^{0.5n-1}\sigma_y$$

As will be shown later, $\sigma_x \sim x^q$, where q is somewhat less than 1, depending on the atmospheric stability class. If n were 0.25 (as noted above) and q were 0.875, C_y would be independent of x.

Eq. (12) has appealing simplicity and, within the limitations imposed by the assumptions that went into the model, provides a convenient starting point for correlating experimental data. For applying it to real situations, however, many modifications have been suggested. A summary of the final equations for a number of cases is available in a workbook (Turner, 1969). The following sections discuss how Eq. (12) may be modified to apply more closely to LNG spills.

d. Atmospheric Boundary Layer. It is well known that wind speeds vary with height. For LNG spills and the dispersion of cold methane vapor, the wind-speed profile near the ground may be significant, and measured speeds at 3 to 4 m may not correlate well with wind speeds at the surface. At what height should one measure the wind velocity to determine an appropriate U in Eq. (12)? There is no definitive answer, and Eq. (12) was derived on the premise that there was no gradient in wind speed. In practical calculations, one uses out of necessity a speed (when available) measured at the height of the source. Few analyses have been made to verify the reasonableness of this approach, although Peters and Klinzing, 1971, have recently solved, approximately, the case of a ground-level source emitting into a wind where $U = f(z)$. For a power-law velocity gradient (see Eq. (19)) and a normal lapse rate ($p \sim 1/7$), these authors showed that one could err considerably in predicting downwind concentrations if an average wind velocity were employed. The lower the point of measurement, the larger the errors. Furthermore, if p is larger than 1/7, the error increases. This important problem obviously needs more study.

e. Ground Reflection. The parameter z in Eq. (12) is the vertical distance between the emitting source and the point of measurement. To allow for reflection from the ground, the term $\exp(-z^2/2\sigma_z^2)$ is normally broken down to:

$$\exp(-z^2/2\sigma_z^2) \rightarrow \exp[-(z-H)^2/2\sigma_z^2] + \exp[-(z+H)^2/2\sigma_z^2]$$

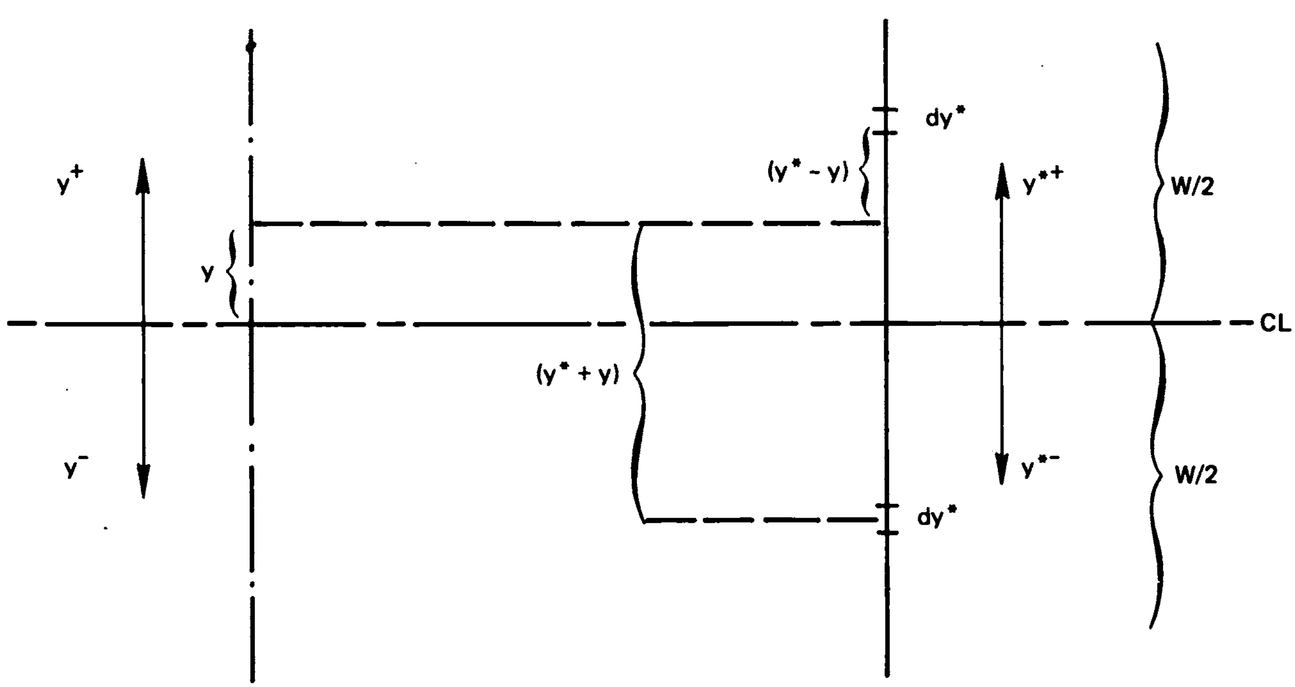
where z on the right-hand side denotes the height of the measurement point above grade and H is the height of the source, again relative to grade. If H = 0, the right-hand side collapses to twice the left-hand side. This correction arises from the theory of images and is open to some suspicion, especially since it ignores boundary-layer effects in the reflecting plane.

Using the ground-reflection correction, Eq. (12) becomes:

$$C = \frac{\dot{Q}}{2\pi\sigma_y\sigma U}\left\{\exp\left[-\frac{y^2}{2\sigma_y^{\,2}}\right]\right\}\left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^{\,2}}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^{\,2}}\right]\right\} \quad (21)$$

f. <u>Continuous Line Source.</u> Equation (21) is applicable only to a point source. For a line source, it may be integrated, assuming that the line consists of an infinite array of points of length dy*.

Consider the diagram below.



The line source is finite with a half-length W/2. The point of measurement is at y (±) from the plume centerline. For an element dy* (+), the crosswind dispersion distance is |y*| - |y|; for an element dy* (-), the distance is |y*| + |y|. Thus, the (+) and (-) sides of the line source must be considered separately. To convert Eq. (21) into a continuous line-source equation, define:

$$Z^* = \frac{1}{\sqrt{2\pi}\,\sigma_z}\left\{e^{-(z-H)^2/2\sigma_z^2} + e^{-(z+H)^2/2\sigma_z^2}\right\} \tag{22}$$

then

$$C = \frac{\dot{Q}_L Z^*}{U}\left(\frac{1}{\sqrt{2\pi}\,\sigma_y}\right)\left[\int_0^{W/2} e^{-(y^* - y)^2/2\sigma_y^2}\,dy^* + \int_0^{W/2} e^{-(y^* + y)^2/2\sigma_y^2}\,dy^*\right] \tag{23}$$

Let

$$\left.\begin{aligned} r^2 &\equiv (y^* - y)^2/2\sigma_y^2 \\ &\text{and} \\ s^2 &\equiv (y^* + y)^2/2\sigma_y^2 \end{aligned}\right\} \tag{24}$$

then

$$r = (y^* - y)/\sqrt{2}\sigma_y \quad : \quad dr = dy^*/\sqrt{2}\sigma_y \tag{25}$$

$$s = (y^* + y)/\sqrt{2}\sigma_y \quad : \quad ds = dy^*/\sqrt{2}\sigma_y$$

so

$$C = \frac{\dot{Q}_L Z^*}{U} \cdot \frac{1}{\sqrt{\pi}} \left[\int_0^{r^*} e^{-r^2}\, dr + \int_0^{s^*} e^{-s^2}\, ds \right]$$

$$r^* = \left(\frac{W}{2} - y\right) / \sqrt{2}\sigma_y, \quad s^* = \left(\frac{W}{2} + y\right) / \sqrt{2}\sigma_y$$

but since $\mathrm{erf}\,(W) = \frac{2}{\sqrt{\pi}} \int_0^W e^{-q^2}\, dq$, then

$$C = \dot{Q}_L Z^* Y^* / U \tag{26}$$

where

$$Y^* = \frac{1}{2} \left\{ \mathrm{erf} \left[\frac{(W/2) - y}{\sqrt{2}\sigma_y} \right] + \mathrm{erf} \left[\frac{(W/2) + y}{\sqrt{2}\sigma_y} \right] \right\} \tag{27}$$

and Z^* is given in Eq. (22).

As $W/2$ becomes large, $Y^* \rightarrow 1$; for any W, if $y = 0$, $Y^* = \mathrm{erf}\,(W/2\sqrt{2}\sigma_y)$. Equation (26) is applicable for a continuous, uniform, line source.

g. Continuous Area Source. A closed analytical solution cannot be obtained for an area source. Two approximate approaches are used. In one, the area is subdivided into a grid, and the emission from each square is treated separately as a point source of a strength proportional to the area of the square (Ragland, 1973). Then, the downwind contributions from all squares are added to obtain a cumulative total. This approach neglects all interactions.

The second approach is not greatly different. The area is subdivided into strips perpendicular to the wind direction. Each strip is treated as a continuous line source with the same strength as the finite strip. As before, the contributions are added to obtain a downwind concentration.

In both methods, if the spacing of the grid or strip is small, hand calculation is tedious and computer methods are preferable.

h. Virtual Point Sources. The point-source model may also be modified to analyze area sources. One such method assumes that the area source is generated from a virtual point source of the same strength located some distance upwind. The distance to the upwind point is normally approximated by assuming that the standard deviation of the Gaussian plume at the area source is equal to the characteristic radius of the source. Then, since the plume's standard deviation is the horizontal dispersion coefficient, it is possible to calculate the distance to the virtual source using the relationship between σ_y and x. One can make other assumptions, such as finding the distance from a virtual point source at which the concentration at the centerline of the plume reaches 100 percent. (The concentration at a point source is infinite.) Because of the inaccuracies of fitting the virtual point-source model at the area source, it should only be used for estimating concentrations more than several source diameters downwind.

i. Dispersion Parameters. The most widely used correlations for σ_y and σ_z in Eq. (21) were presented by Gifford and discussed by Cramer, 1957. As shown in Figures 14 and 15, σ_y and σ_z are related to weather conditions and downwind distance. Analytical expressions to fit these curves have been suggested by McMullen, 1975:

$$\sigma = \exp[I + J(\ln x) + K(\ln x)^2] \qquad (28)$$

where σ is in meters and the downwind distance, x, in kilometers. The constants, I, J, and K for σ_y and σ_z are given in Tables 12 and 13.

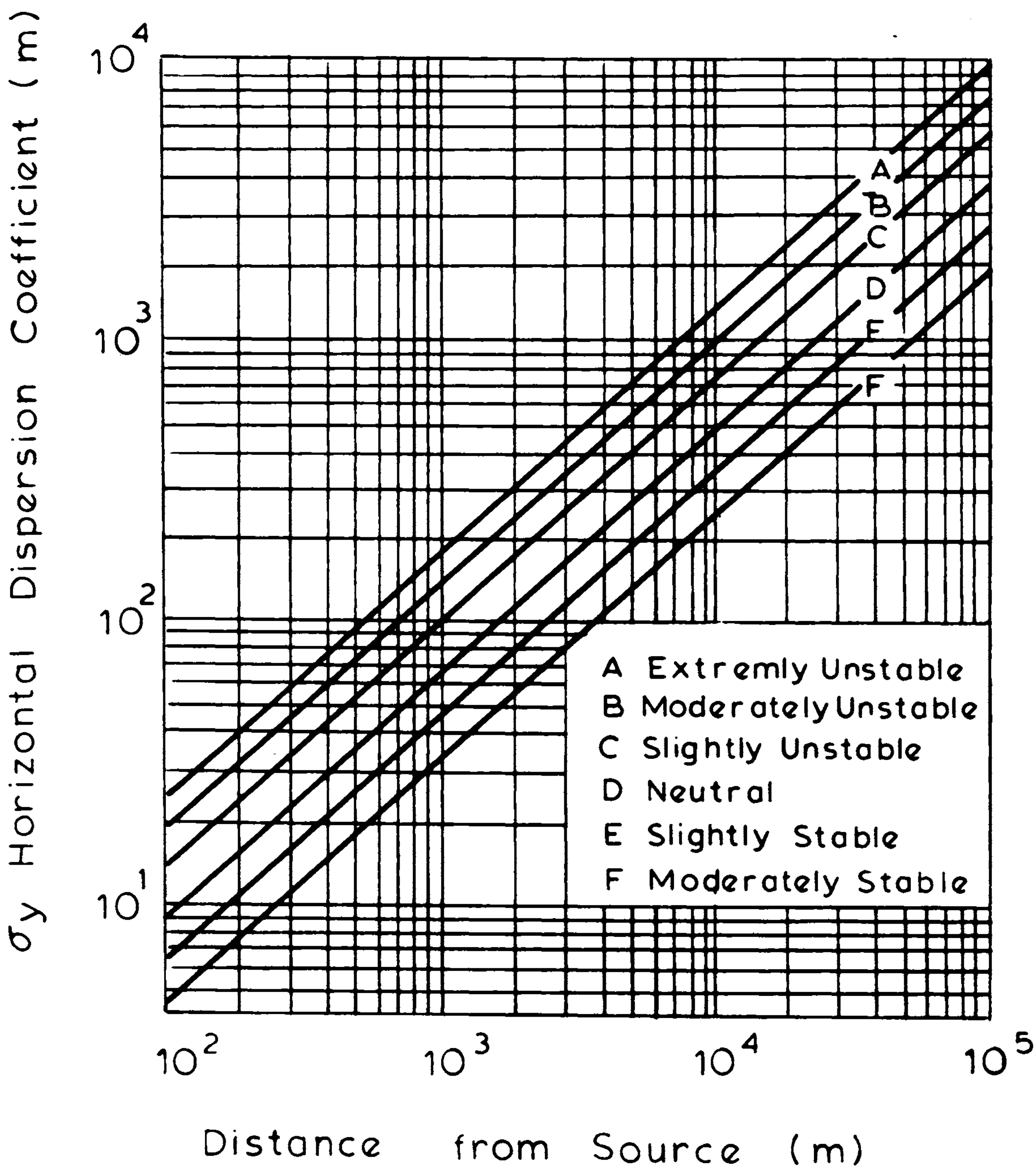


Figure 14 Gifford-Pasquill Correlation of σ_y

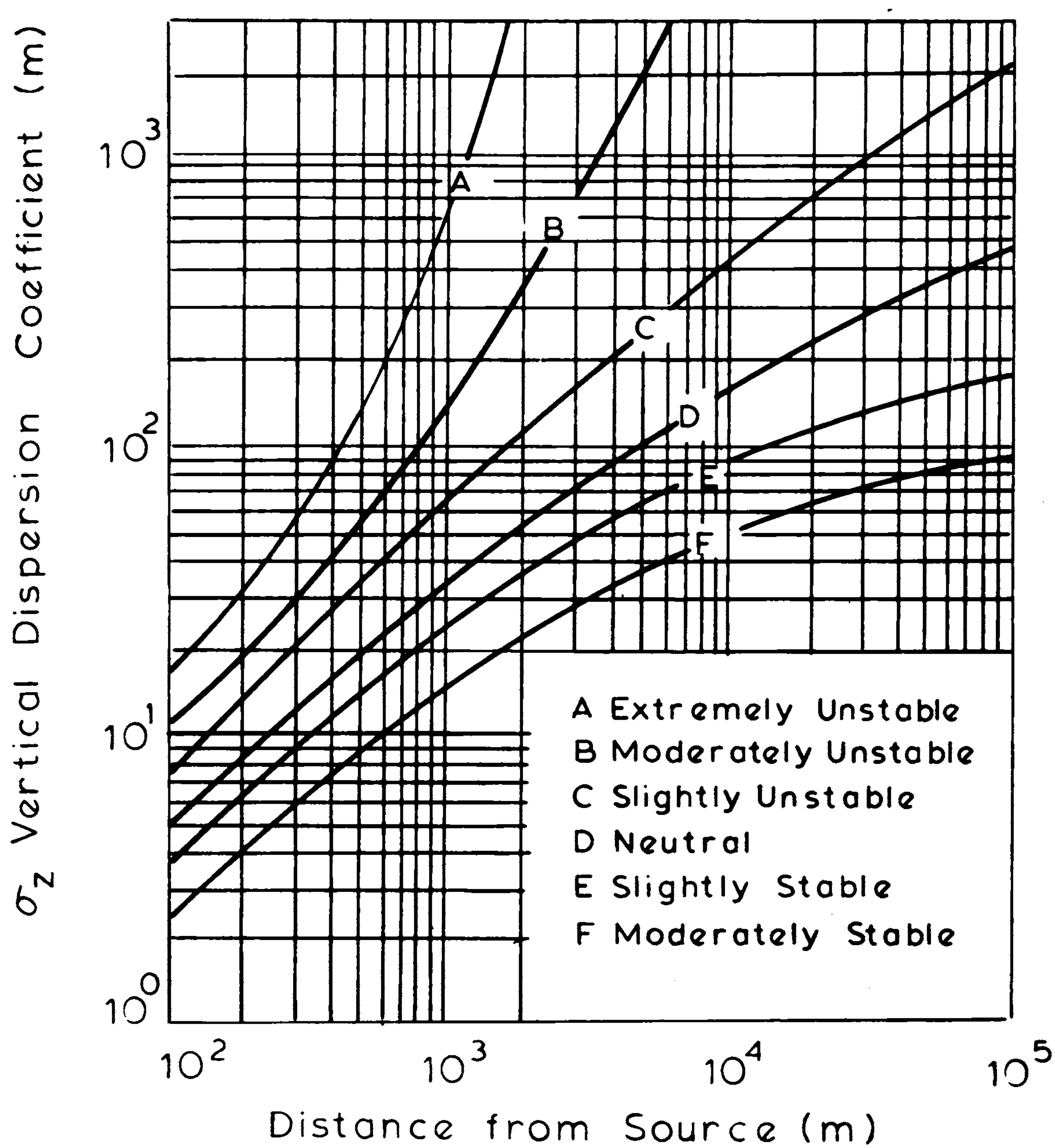


Figure 15 Gifford-Pasquill Correlation of σ_z, Vertical

Table 12 Constants for σ_y Using Equation (28)

Stability	I	J	K
A	5.357	0.8828	-0.0076
B	5.058	0.9024	-0.0096
C	4.651	0.9181	-0.0076
D	4.230	0.9222	-0.0087
E	3.922	0.9222	-0.0064
F	3.533	0.9181	-0.0070

Table 13 Constants for σ_z Using Equation (28)

Stability	I	J	K
A	6.035	2.1097	0.2770
B	4.694	1.0629	0.0136
C	4.110	0.9201	-0.0020
D	3.414	0.7371	-0.0316
E	3.057	0.6794	-0.0450
F	2.621	0.6564	-0.0540

To select an atmospheric stability, the simple rules shown in Table 14 may be helpful.

The atmospheric dispersion coefficients also may be categorized in terms of σ_θ and σ_ϕ , the standard deviations of the azimuth and elevation angles of the wind. Draxler, 1976, correlated these variables for most large-scale dispersion tests of pollutants and radioactivity and related them to σ_y and σ_z. Cramer, 1949, 1957, has also proposed the use of σ_θ and σ_ϕ to estimate the dispersion characteristics of a neutrally buoyant vapor cloud. Unfortunately, σ_θ and σ_ϕ are rarely available. However, if σ_θ is available, Beals, 1971, recommends the use of Table 15 to estimate the atmosphere category. The table is based on some 200 diffusion tests conducted in the Green Glow, Prairie Grass, Ocean Breeze, and Dry Gulch projects sponsored by the Air Force Cambridge Research Laboratories as well as projects of the Atomic Energy Commission at Idaho Falls, Idaho.

Another, completely different method has been widely used to estimate σ_y and σ_z (Singer and Smith, 1953, 1966). In this approach, dispersion data taken at Brookhaven National Laboratory were correlated with wind gustiness, and four principal categories were defined:

B_2: wind fluctuations ranging from 40-90 degrees
B_1: wind fluctuations ranging from 15-40 degrees
C: usually wind fluctuations of 0-15 degrees and a recording of the wind speed shows no large excursions
D: wind trace is essentially a line, no fluctuations greater than 15 degrees.

Such categories are, at best, very approximate and are to be applied primarily to wind fluctuations well above the ground (the authors state the height of measurement to be 106 m). For radioactive dispersal from high stacks, this method may have value, but Figures 14 and 15 are somewhat more applicable to LNG spills at grade.

On Figures 16 and 17 both the Singer-Smith and Gifford correlations have been plotted. For σ_z , the Gifford D, E, and F classes fall between the Singer-Smith C and D classes. This statement does not hold for σ_y . What is really being compared are the variances σ_y^2 and σ_z^2 of the plume with the variance in the wind. These variances are certainly related, but not in any convenient, quantitative manner.

j. Parker-Spata Model. The first to treat the vapor-dispersion hazard from LNG spilled into a diked area were Parker and Spata, 1968. The dispersion was estimated by treating an area source as a set of continuous point sources distributed over the area in question. Thus, Eq.

Table 14 Approximate Weather Stability Classes

Wind Speed m/s	Day: Incoming Solar Radiation: Strong	Moderate	Slight	Night: Thin Overcast or >½ Cover	<½ Clouds
<2	A	A-B	D	-	-
2	A-B	B	C	E	F
4	B	B-C	C	D	E
6	C	C-D	D	D	D
>6	C	D	D	D	D

Table 15 Atmosphere Classification Based on Standard Deviations of the Horizontal Wind Direction (Beals, 1977)

	Distance Downwind, x, km		
σ_Θ, degrees	x < 0.8	0.8 < x < 4	x > 4
$\leq$ 2.5	E-F	E	D-E
5	D-E	D	C-D
10	C-D	C	C
15	B	B-C	B-C
20	A-B	B	B-C
$\geq$ 25	A	A-B	B

NOTES:

1. If there is a joint category (e.g., B-C), average the values for both categories.

2. Categories A and B are not to be used at night. Category C would only be used at night with strong gusty winds that follow the passage of a cold front.

3. At night, if $\sigma_\Theta > 8$ (flat ground) or $\sigma_\Theta > 14$ (rough ground), such conditions may lead to particular wind movements so that peak concentrations, for short times, would exceed those calculated for atmosphere F.

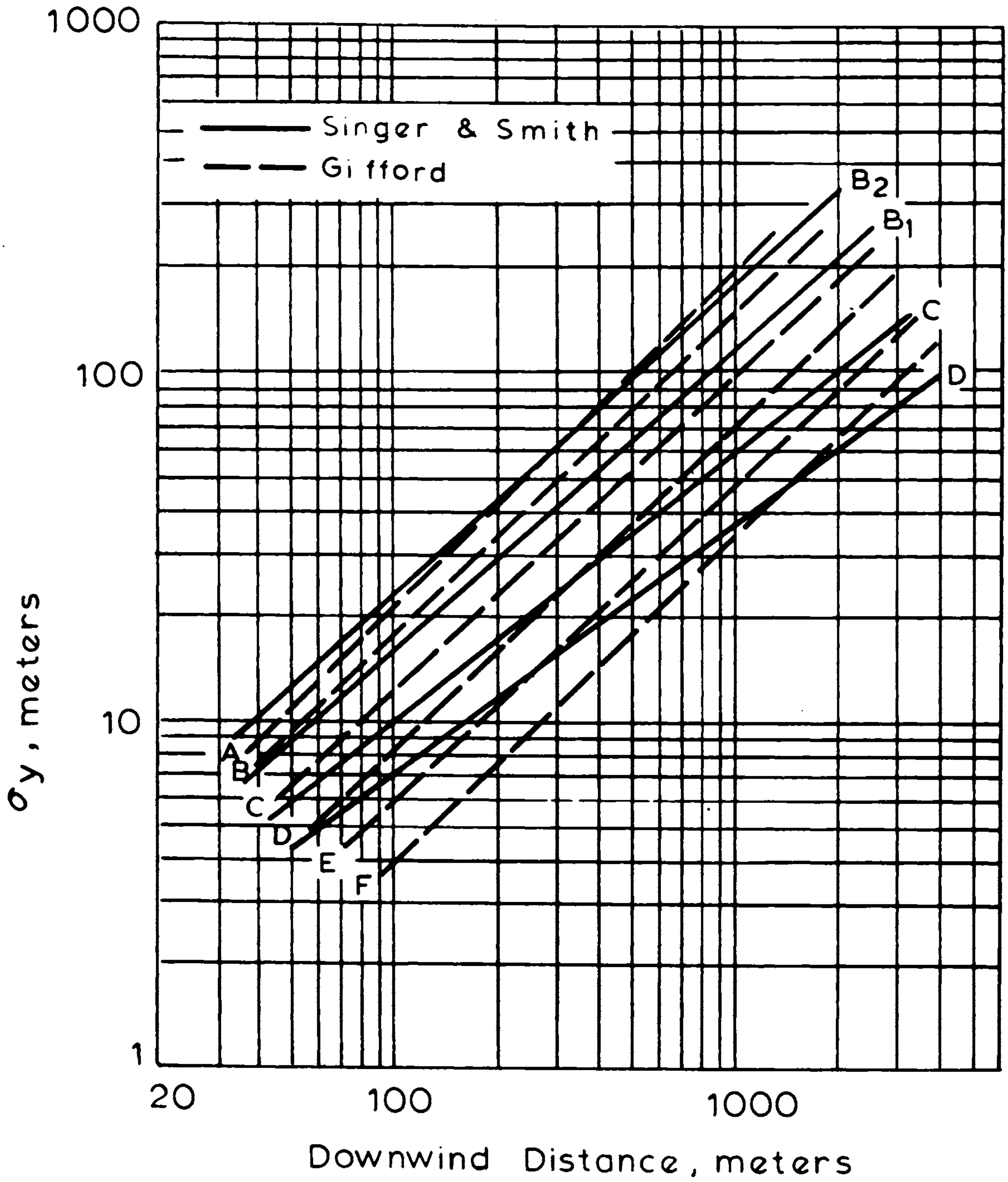


Figure 16 Comparison of the Gifford-Pasquill and Singer-Smith σ_y Parameters

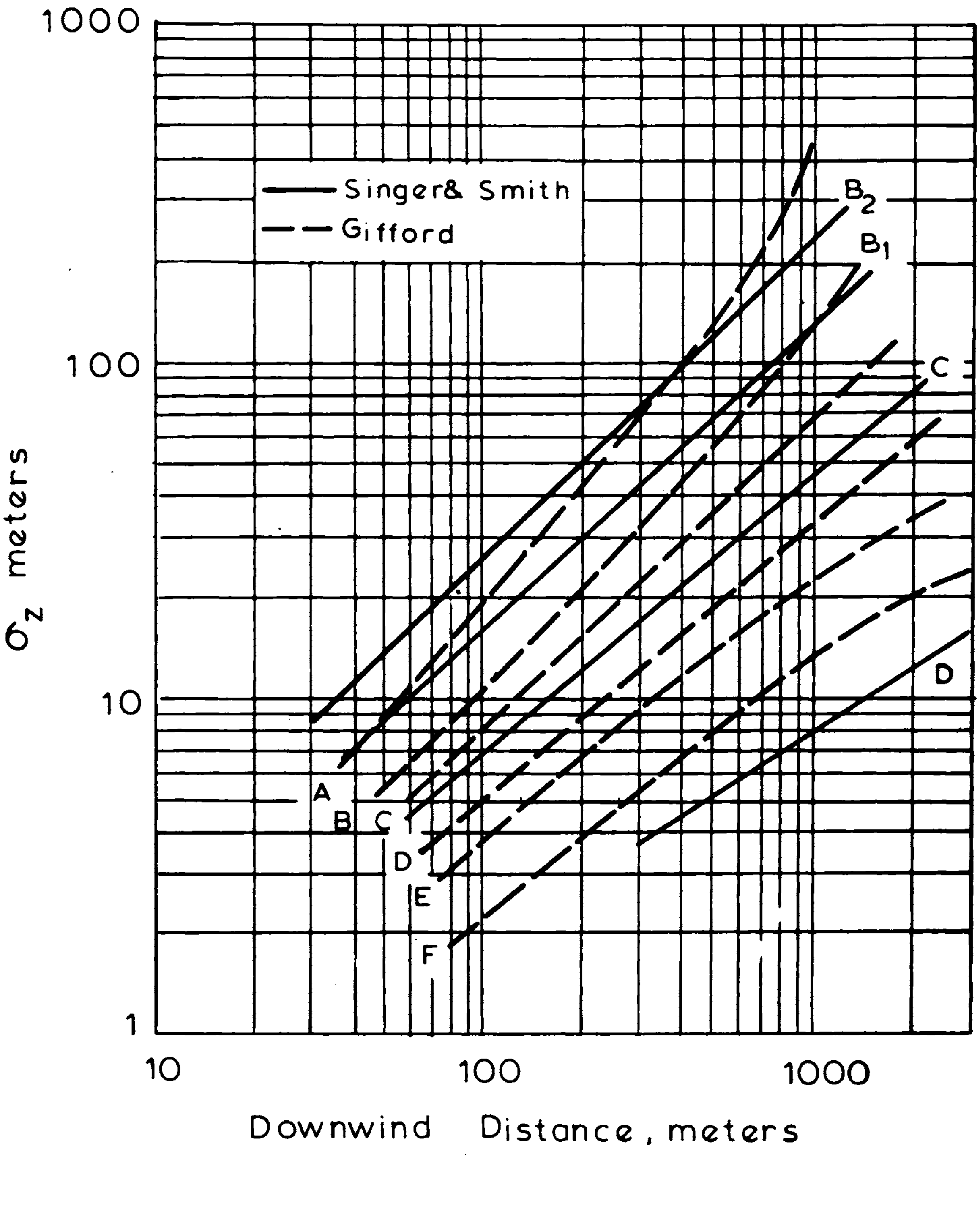


Figure 17 Comparison of the Gifford-Pasquill and Singer-Smith σ_z Parameters

(21), with the downwind point of measurement (z) as zero, becomes

$$C = \Sigma \frac{\dot{Q}_{ij}}{\pi \sigma_y \sigma_z U} \exp \left\{ - \left[\frac{y^2}{2\sigma_y^2} + \frac{H^2}{2\sigma_z^2} \right] \right\} \qquad (29)$$

where $\dot{Q}_{ij}$ is the point source for grid ij and H is the height above grade of the emission. Atmospheric category F (severe inversion, see Figures 14 and 15) was chosen to obtain σ_y and σ_z. $\dot{Q}_{ij}$ was allowed to be a function of time and was determined by a soil heat-conduction analysis with a finite surface boiling-heat-transfer coefficient.

There is an error in the method as originally presented in that a spurious 1/2 factor was introduced; Eq. (29) is correct, however. Also, work described in Section II-A suggests that a boiling coefficient is not warranted.

k. Welker, Wesson, and Sliepcevich Model. Welker et al., 1969, suggested the use of Eq. (17) with C_y and C_z from Haugen et al., 1961. Since this equation was derived only for point sources and Welker et al. desired to apply it to area sources, it was "manipulated so as to make it applicable for an area source." No further details are given. Evaporation rates were determined from a simple soil-conduction model so that the source strength decayed as $t^{-1/2}$. Average soil properties were used (see appendix of Carslaw and Jaeger, 1959). An infinite boiling heat-transfer coefficient was thereby assured.

Since the authors were concerned about worst case studies, they assumed that the spill was instantaneous and filled a 100 percent dike at grade. They also assumed an atmosphere category of F (severe inversion). The results were such that the calculated flammable zone of methane-air mixtures extended considerable distances downwind.

l. Parker Model II. A year following the Welker et al. paper, Parker, 1970, presented a new model for estimating downwind methane concentrations after an LNG spill in a dike. He modeled the dike as a set of finite line sources and employed Eq. (26) for each. That is, the dike was divided into strips and the emission for each strip was found. Then the total vapor flow at any time over the lee edge of the dike was used as a single finite line source and the dispersion determined. No dispersion was allowed over the dike area proper.

In this paper, the vaporization rate as a function of time was treated in the same manner as in the first paper except that a higher boiling coefficient was assumed. The major difference, besides the modification from point source to line source in the dike, is the use of modified dispersion parameters. It was argued that it was reasonable to increase σ_y and σ_z from their values in Figures 14 and 15 because additional turbulence would be created by the flow of the wind over the dike walls. Quantifying this suggestion, Parker replaced σ_y and σ_z with Σ_y and Σ_z where:

$$\Sigma_y = [\sigma_y{}^2 + (CA/\pi)^2]^{1/2} \quad (30)$$

$$\Sigma_z = [\sigma_z{}^2 + (CA/\pi)^2]^{1/2} \quad (31)$$

with $0.5 < C < 2$. A is the projected area of an object past which the wind blows. However, as actually used, σ_z was modified to:

$$\Sigma_z = \sigma_z + H/2 \quad (32)$$

where H is the dike height.

In a physical sense, Eq. (32) suggests that the line source at the lee edge, instead of dispersing at the dike height, H, actually disperses at a higher level, and the vertical dispersion then depends on the dike height--the higher the dike, the smaller the downwind concentration.

The use of finite line sources within the dike is a useful artifact. The ADL model also employs this procedure, as described later. It is questionable, however, whether high dikes can increase the vertical dispersion as much as indicated by Eq. (32). Unfortunately, there are no data to prove or disprove this contention.

The actual numerical calculative procedure of Parker is incorrect in that he determines concentrations at downwind locations based on the boilup rate at the real time of measurement. The correct source strength would be that at an earlier time to account for the finite time of travel of the vapor from the dike to the point of measurement. This difference can be significant in estimating the peak concentration.

m. ADL Model Arthur D. Little, Inc., developed a vapor-dispersion program to correlate the data from the AGA test at San Clemente (American Gas Association, 1974). Vapor-generation rates are computed assuming a completely wetted dike floor [Eq. (1)]. [In an earlier version of the program a correction term was used to modify Eq. (1). With a better choice of F, the experimental boilup data can be successfully correlated with Eq. (1).]. No wall-heat-transfer is allowed, but vapor holdup before overflow is allowed.

The dike is considered to be divided into a series of strips normal to the wind direction. Each contributes to the total vapor generated, but is out of step in time because the wind reaches the windward edge of the dike first and there is a finite time of travel across the dike.

The vapor-generation rate from each strip can be calculated as a function of time. However, the net flow of vapor from the lee edge of the dike is the sum of the vapor flow from all strips--each determined at a time that accounts for the travel across the dike.

Dispersion was calculated from Eq. (26), using Figures 14 and 15 to obtain σ_y and σ_z.

The final equations were modified to allow the option of introducing parameters that would better describe experimental data.

- Lateral-spreading parameter, GAMY, corrects for the buoyancy effect,

$$\sigma_y \text{ (corrected)} = \sigma_y \text{ (1 + GAMY)}$$

GAMY would be zero for plumes of neutral buoyancy, positive for nonbuoyant plumes, and negative for buoyant plumes. For correlating the San Clemente results, GAMY was found to be $\sim$ zero.

- Vertical-source-height parameter, ALM, allows one to initiate dispersal at dike height or at any other height,

$$H = \text{HDIKE (1 - ALM)}$$

Many models set ALM = 1; thus it is assumed that the cold LNG vapor falls from the dike height to the ground before beginning to disperse. Others set ALM = 0, while in the Parker II method, ALM is negative [see Eq. (32)] and dispersion is initiated at a height effectively higher than the dike.

• Vertical-dispersion parameter, GAMZ, allows one to increase or decrease the effective vertical-dispersion parameter, σ_z,

$$\sigma_z \text{ (corrected)} = \sigma_z \text{ (1 + GAMZ)}$$

Normally, GAMZ $\sim$0. For dispersion calculations following spills of LNG on water, as shown in Section III-C, GAMZ is normally set as a negative number, $-1 < \text{GAMZ} < 0$.

n. University Engineers Model. In the AGA San Clemente tests, (American Gas Association, 1974), University Engineers (UE) also proposed a predictive vapor-dispersion model. They fitted the experimental boiling rates with a modified form of Eq. (1) to give a better comparison. To estimate dispersion, Eq. (17) was used for a centerline, grade measurement ($y = z = 0$). To correct for the fact that a point-source equation was used, whereas there was actually an area source, factors are presented graphically relating the correction to the pool diameter and the ratio of the downwind distance to the pool diameter. The UE relationship then can be written:

$$C_{y=z=0} = \frac{2\dot{Q}}{\pi U C_y C_z x^{2-n}} \text{ (area factor)} \tag{33}$$

o. Gaz de France Model. Humbert-Basset and Montet, 1972, use Eq. (1) to calculate boiling rates of LNG. No vapor holdup is considered. The dike is modeled as a matrix of point sources in a manner similar to that of Parker and Spata, 1968. Eq. (21) then becomes:

$$C = \sum_i \left\{ \frac{\dot{Q}(t)}{2\pi\sigma_y(x_i)\ \sigma_z(x_i)U} \left[\exp\left(- \frac{(z-H)^2}{2\sigma_z^2(x_i)} \right) + \exp\left(- \frac{(z+H)^2}{2\sigma_z^2(x_i)} \right) \right] x \left[\sum_j \exp\left(\frac{y_j^2}{2\sigma_y^2(x_i)} \right) \right] \right\} \tag{34}$$

where $\dot{Q}_{ij}$ depends only on t, and the concentration, C, refers to the concentration at x_i downwind, at a height z, and at a lateral distance y_j between the point of measurement and the ij point source.

As in all correlations of this type, the source strength for each point in the matrix is a function of real time t. At the point of measurement, however, a time of travel, x_i/U, must be considered. Since $Q_{ij}(t)$ decreases with t, the consequence often noted is a C - x profile for the maximum C, as shown in Figure 18. At the second peak, the full dike is contributing. If the lower flammability limit (LFL) lies at A - A, one would predict an intermediate distance where the maximum methane concentration was below the LFL, but farther away the concentration again exceeds this limit. Such behavior, although reasonable, has not been observed.

Figures 14 and 15 were used to obtain σ_y and σ_z. But since experimental observations indicated that the plume rose, Humbert-Basset and Montet suggest that the vapors being evolved were not at their saturation temperature, but were warmer than might have been expected. With this line of reasoning, it was deduced that when the cloud mixed with the warm, humid, ambient air, the mixture in some cases could become buoyant. In any case, the authors corrected their dispersion equaton to provide a vertical-velocity component. A vertical velocity of 0.1 to 0.3 m/s gave the best fit to their data.

The modification to the diffusion equation was such that the apparent height of the source increased the farther downstream the point of measurement. That is, if H were the actual height of the source (for example, the dike height), then the apparent height, H', was expressed as:

$$H' = H + Vx_i/U \qquad (35)$$

where U is the wind velocity and V the vertical component of wind velocity. Thus, the estimated concentration decreased with the distance from the source, x_i, relative to the concentration predicted by the simple Gaussian model.

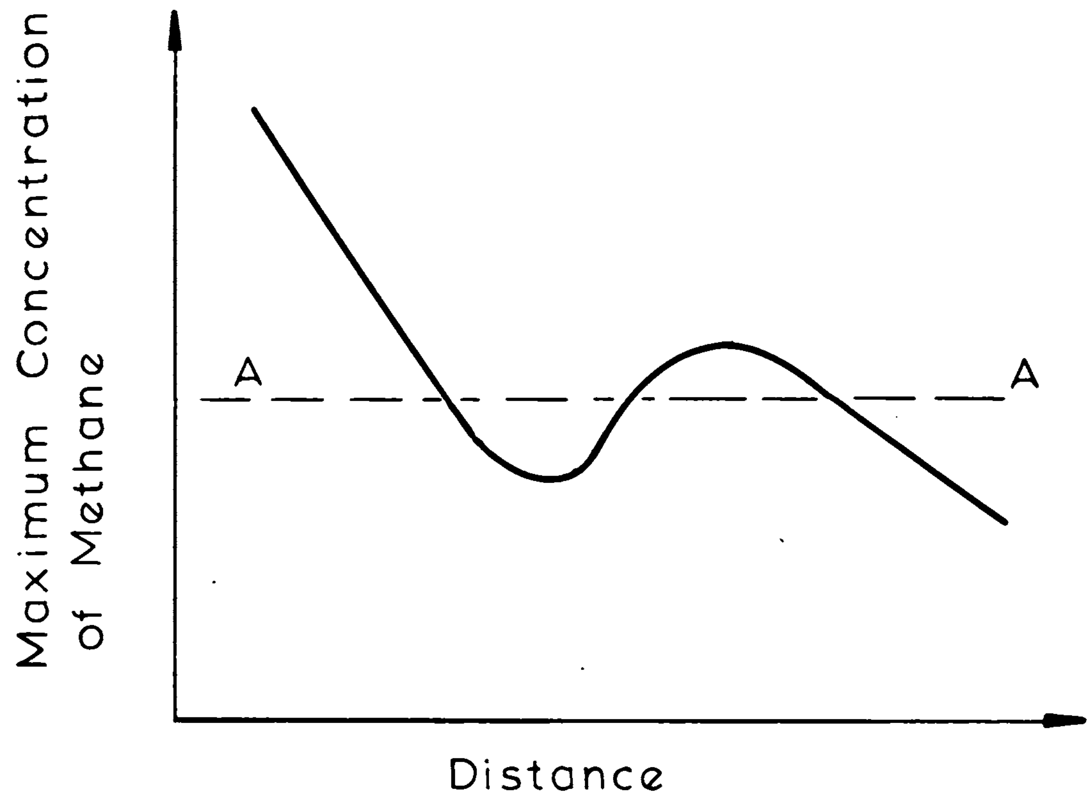


Figure 18 Gaz de France Prediction of Maximum Vapor Concentrations Downwind

In the ADL model, a similar correction (ALM) modifies the source height, but was not related to x_i or U. A correction of this type might be most logical for land spills in areas of high ambient humidity. In such cases, there is a real possibility of attaining a buoyant mixture and a correction of the type noted might well be advisable.

One final comment seems worthwhile. The Gaz de France tests were made with dike walls tapered from 0.5 to 1.5 m. For small dikes, it was concluded that the higher the walls, the smaller the measured downwind concentration. It is stated that this result "may be explained by the fact that the methane vapors require a much longer time for filling the basin before being carried away by the wind." This is reasonable. Also, if the methane concentration were measured at ground level, it should be even lower because of the vertical dispersion. However, the authors conclude that for large dikes, dike height is not an important variable unless it is very high. It is difficult to see the reasoning behind this conclusion; high dikes should be beneficial, assuming that wall conductivities are lower than floor conductivities.

p. Suppression Measures. In three Gaz de France tests, jets of water were sprayed into the vapor cloud to determine if they would add heat to the cloud and thereby accelerate the rate of rise and dilution of the plume. Qualitatively, no influence of the water spray was detected on either the visible zone or the concentration of methane. No conclusions were drawn because of the limited tests conducted. The water spray used was coarse, and one may speculate that a water fog, with its high surface area, might have given more effective heat transfer to the plume from a given quantity of water. A similar proposal was made by Martinsen et al., 1977. Little plume heating was noted in these experimental tests, but increased turbulence did aid dispersion of vapor evolved from small pools.

University Engineers studied the effect of foam for fire control of ignited LNG spills and on the dispersion of methane vapor from unignited pools (West et al., 1974). Only the dispersion is considered here. Twelve vapor-dispersion tests were run. The rate of methane vaporization was held nearly constant during a test by the addition of energy to the pool. It was reported that steady vaporization rates of between 0.04 and 0.46 mm/s were attained. The latter is a high rate that might be found in the short period immediately following the spill. The only specific example given in the paper, is for the low vaporization rate.

The authors correlate their vapor-dispersion data, with no foam addition, by plotting $CU/\dot{M}$ vs. x, where C is the percent methane measured at a distance x, U is the average wind velocity, and $\dot{M}$ is the boiling rate. The plot shown may reflect data mostly at the lower rates since, even at the largest values of U and x, the correlation would predict more than 100 percent methane. Few data are presented for the effect of foam addition on vapor dispersion, although the curves show clearly that the downwind, ground-level concentration of methane decreased, but the rate of methane boilup increased. Also, high ratios of air to foaming agent significantly enhanced the effects noted above. No explanation was tendered to explain these unusual results.

q. Van Ulden Model. Van Ulden, 1974, modeled the dispersal of Refrigerant-12 (Freon-12) vapor from 1000-kg spills (See Section II-D-1-h). The primary interest was in the spread of a heavy gas near the ground. Atmospheric turbulence and wind were neglected initially.

A rapid spill and evaporation of a cryogenic liquid is assumed to form, initially, a cylinder of vapor with a radius r_o, a height h_o, and a volume V_o. Because the vapor's initial density (ρ_o) exceeds that of air (ρ_a), the vapor spreads laterally. The volume increases because of entrainment of air and is expressed as:

$$dV/dt = 2\pi r \alpha h\ (dr/dt) \quad (36)$$

where α is a mixing coefficient.

The following quantities are expressed as functions of the radius r.

$$V(r) = \pi h(r)\ r^2 \quad (37)$$

$$u(r) = c[\Delta(r)\ g\ h(r)]^{1/2} \quad (38)$$

$$\Delta(r) = [(\rho(r) - \rho_a)/\rho(r)] \quad (39)$$

where c is a velocity coefficient and g the gravitational acceleration. u(r) is the velocity of the cylinder in the radial direction. With Eqs. (36) through (39),

$$V(r)/V_o = (r/r_o)^{2\alpha} \quad (40)$$

$$h(r)/h_o = (r/r_o)^{2(\alpha-1)} \quad (41)$$

$$\Delta(r) = \left[1 + \frac{\rho_a V(r)}{(\rho_o - \rho_a)V_o}\right]^{-1} \quad (42)$$

$$u(r) = \frac{c}{r}\left[\frac{gV_o/\pi}{(V_o/V(r)) + \rho_a/(\rho_o - \rho_a)}\right]^{1/2} \quad (43)$$

Since u(r) = dr/dt, Eq. (43) may be solved to yield r = f(t). However, to simplify the calculations, Van Ulden assumes that there is little entrainment ($\alpha \sim 0$), so $V_o \sim V(r)$ and Eq. (43) can be written as:

$$u(r) = \frac{c}{r}\left[\frac{g(\rho_o - \rho_a)V_o}{\pi\rho_o}\right]^{1/2} = \frac{dr}{dt} \quad (44)$$

integrating,

$$r^2 - r_o^2 = 2c[g(\rho_o - \rho_a)V_o/\pi\rho_o]^{1/2}\ t \quad (45)$$

Thus, the area covered by the expanding cloud increases linearly with time.

Van Ulden suggests that Eq. (44) or (45) is applicable until u(r) is about twice the friction velocity, after which time the cloud should be treated as an area source dispersing in a normal Gaussian model [e.g., Eq. (21) with a matrix of point sources or a set of line sources].

When Eq. (44) or (45) was applied to the Refrigerant-12 spill (very rapid evaporation), it predicted the trajectory of the cloud well (c was set equal to unity). Very small vertical-dispersion rates were noted, but the cloud expanded significantly in the lateral direction. In this instantaneous or puff release, a normal Gaussian model would have led to quite incorrect estimates of downwind concentrations. Figures 19a - 19c indicate the degree of dispersion and the model predictions. Clearly, the point-source Gaussian model [Eq. (21)] is not applicable.

The Van Ulden model is not unlike those described in Section III-C-2 for spills of LNG on water. It may be most applicable for the rare case of a major LNG spill in an undiked area, where spreading and evaporation would be very rapid.

r. Battelle Model. Gideon et al., 1974, have presented a graphical correlation to estimate the peak methane concentration downwind from a confined-area spill. Evaporation is assumed to occur at some constant rate. Typical experimental data from the American Gas Association test program at San Clemente and the Gaz de France tests are plotted in Figure 20. The ordinate is the downwind distance (x) divided by the diameter of the LNG pool raised to the 0.6 power. The abscissa is the product of the methane fraction, the wind velocity, and the pool diameter to the 1.2 power divided by the pool area. English units must be used. The data fall below two intersecting limit-lines which have the equations as shown. The general applicability of a correlating graph of this type is not known.

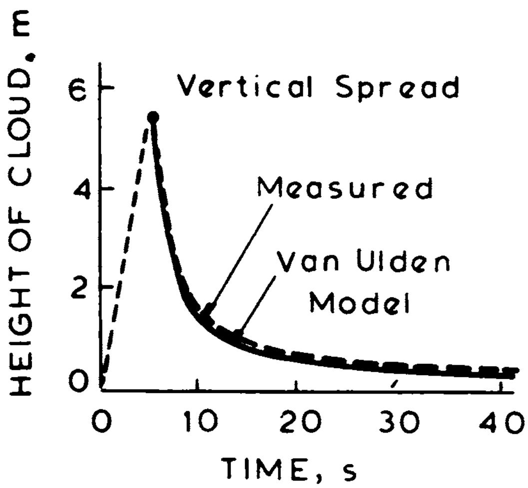


Figure 19a

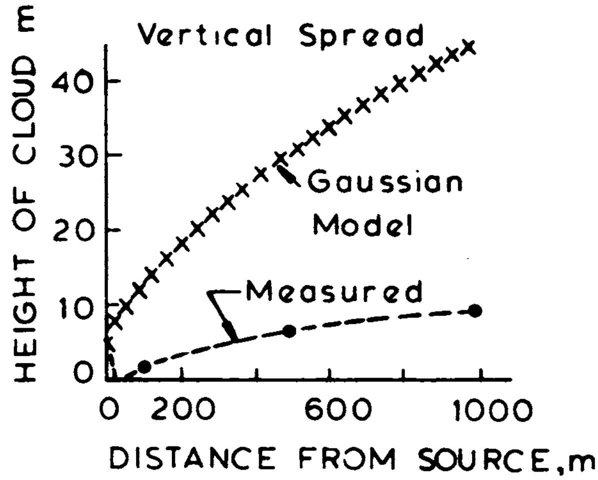


Figure 19b

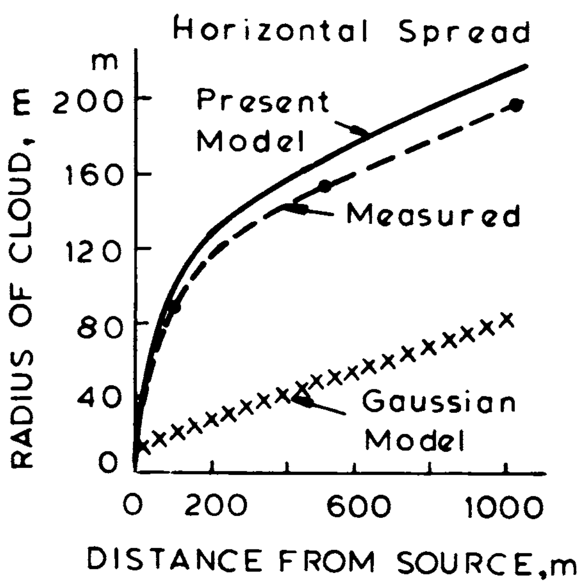
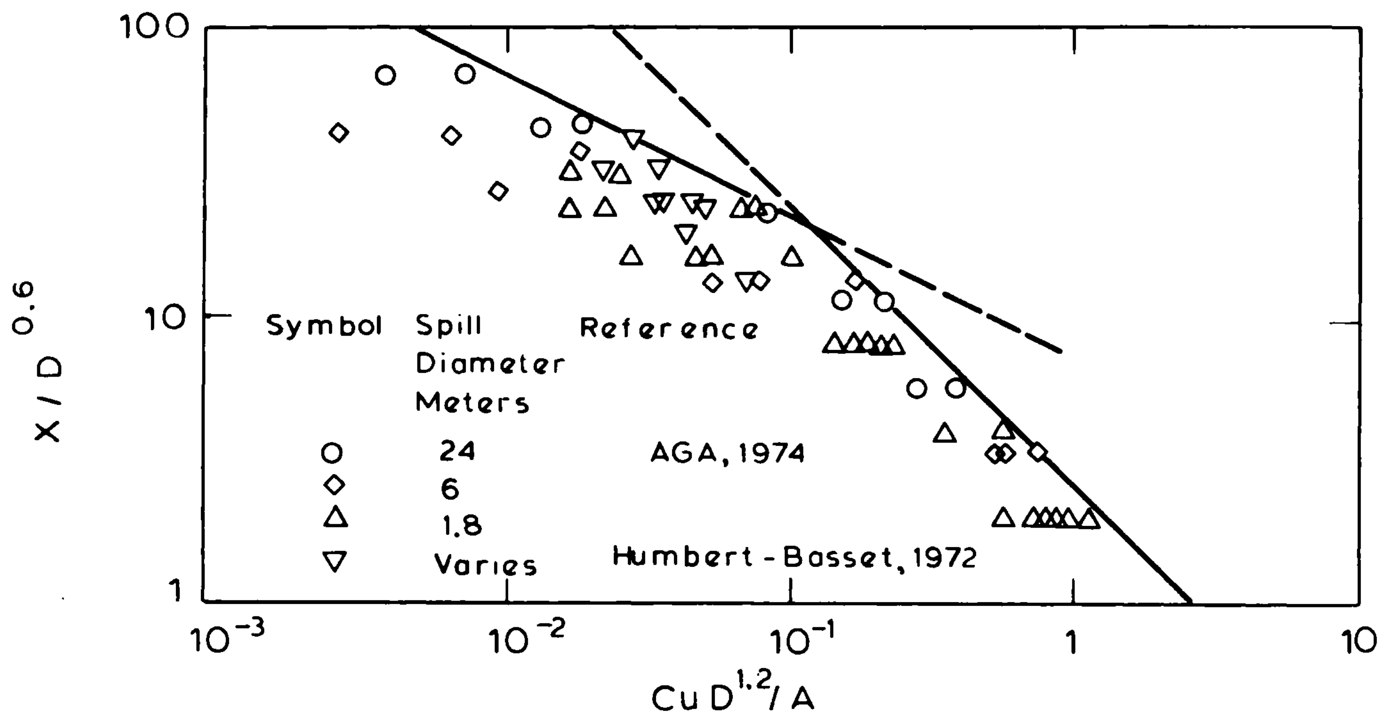


Figure 19c

Figure 19 Van Ulden Dispersion Results for a Spill of R-12



(Note x = downwind distance, ft
D = pool diameter, ft
C = methane fraction
u = wind speed, ft/s
A = pool area, ft^2

Figure 20 Battelle Correlation for Maximum Methane Concentrations After a Land Spill of LNG

3. Application of Models

Except for the Van Ulden vapor-spread model, most of the others discussed differ in relatively minor details. The British Gas Corp., 1974, 1975, compared the Gaz de France, ADL, and Parker II models in detail, using consistent boiling rates for each. As might have been expected, since the three models use some form of Eq. (21) and identical dispersion coefficients, they predicted very similar downwind concentrations as a function of time. (The Parker II method was modified to allow for the travel time of the plume.)

The Battelle correlation shown in Figure 20 (Gideon et al., 1974) may be described analytically as

$$X^2CU/A = 50 \qquad X/D^{0.6} > 20 \tag{46}$$

$$X^2CU\ D^{0.6}/A = 2.5 \qquad X/D^{0.6} < 20$$

where the notation is described in Figure 20. This very simple correlation yields the maximum methane fraction and is to be used only for low dikes, for rapid spills on soil-floors, with neutral weather.

Although most of the existing vapor-dispersion models for land spills agree reasonable well, they are not necessarily accurate. Too few data are available to allow errors to be estimated rationally. For example, in Figure 21, the predictions of the ADL model are compared with data from the American Gas Association, 1974, tests at San Clemente. In this test, the dike was 24.4 m in diameter, and the floor was packed soil with an F factor of about 0.7 $kg/m^2s^{1/2}$. The dike walls were 46 cm high. The point of measurement was 86.7 m downwind and 15 cm above grade. Since y = 0, the sensor was located as nearly as possible along the plume centerline. The wind varied from 2.7 to 8.0 m/s during the test, and standard deviations were between 16° and 30°. The measured concentrations varied considerably. Two atmospheric conditions were chosen in the ADL model, which does a reasonable job of predicting downstream concentrations. More sophisticated models would not appear to be warranted until better and more extensive experimental data become available.

Closner and Parker, 1978a, discussed accidents in LNG storage areas, but did not describe their methods of calculating vapor dispersion and boiling rates.

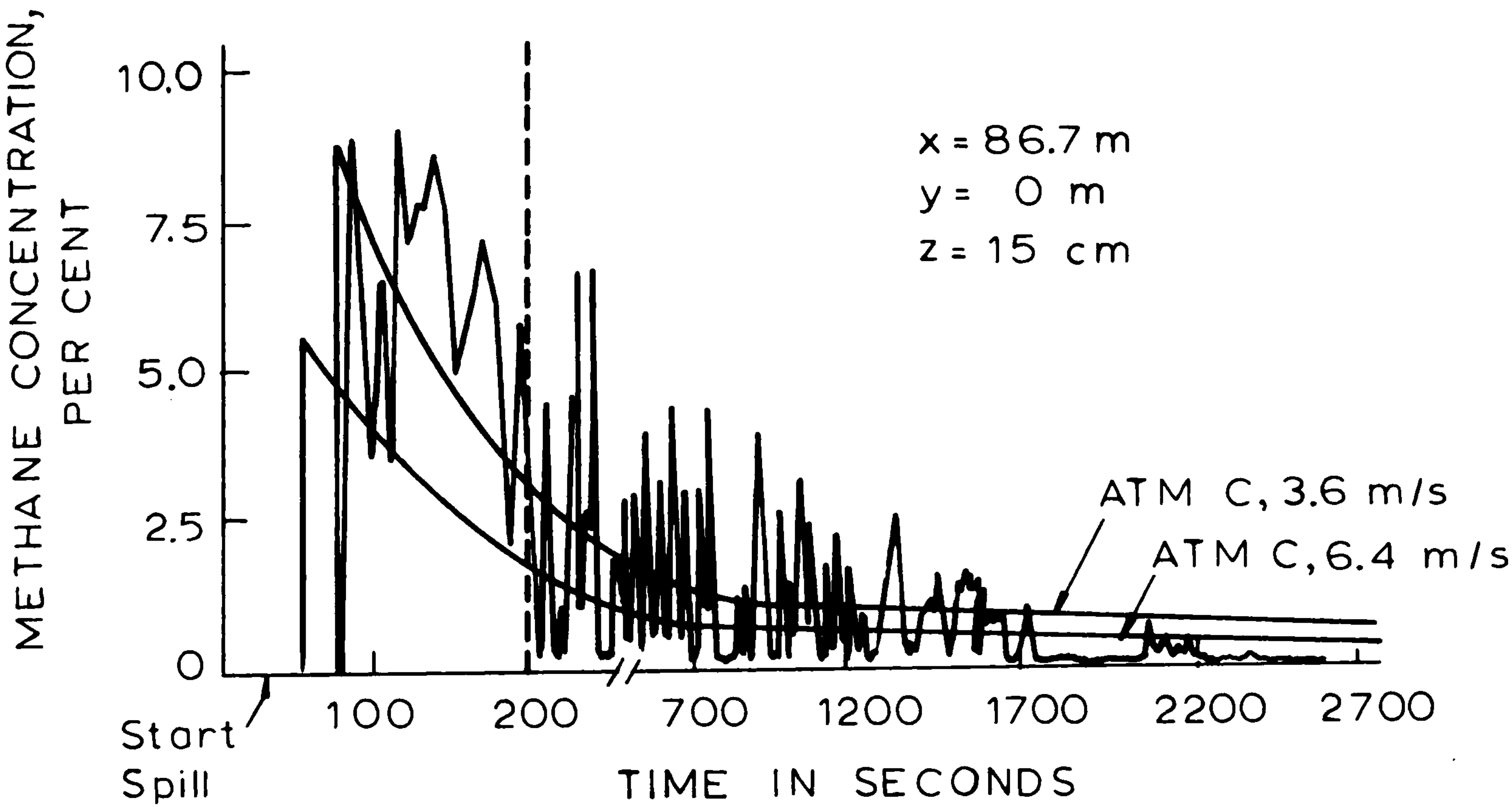


Figure 21 Typical Dispersion Data and Comparison with the ADL Model

In a subsequent paper, Closner and Parker, 1978b, discussed the relative safety of various designs of LNG storage tanks. They stress that double-walled tanks with a noncryogenic metal for the outside wall are potentially dangerous because an accident that leads to a serious leak in the inner container will allow LNG to contact the outer wall. "It may then be a question of minutes before the shell cracks due to the cold impact. It may collapse from the weight of the roof leading to loss of the roof and possible complete failure of the inner tank." (The authors suggest that even a loss of insulation may induce a significant heat leak leading to the same result, i.e., complete tank failure.) Recommended designs involve some cryogenic secondary barrier. Prestressed concrete is recommended because it can also provide significant resistance to possible external accidents (even attempted sabotage) and fire.

III. UNCONFINED LNG SPILLS ON WATER

A. MODEL SCENARIOS

Accidents involving release of LNG during marine transport can be placed in three classes.

First, with the tanker moored and receiving or discharging LNG, a malfunction may result in a spill into the harbor or onto the dock. Emergency shutoff valves presumably would limit the spill.

Second, grounding or other such emergency may require that part of the cargo be jettisoned to prevent a more serious accident from developing. The Shell Gadila tests, described later, simulated this type of scenario.

Finally, in contrast to the continuous spills noted above, there is the instantaneous spill, wherein one of the cargo tanks empties rapidly. LNG tanks are separated from the ship's hull by insulation and, in some cases, by an inert atmosphere in a dead space. Ships would have to collide with large relative kinetic energy and at appropriate angles to cause a penetration that would affect the LNG tank. The probability that such an event would occur seems small. Nevertheless, the instantaneous spill, without ignition, normally is employed as a base case for an evaluation of a major LNG catastrophe.

Usually the instantaneous spill is chosen to lie in the range of 25,000 to 30,000 m^3 of LNG. This amount would represent, typically, one tank of a large LNG carrier. The lost LNG is considered to spread radially over the water and boil. The vapor cloud, while not formed instantaneously, is generated in a period small enough--on the order of minutes--so that it can be treated in most respects as an entity that spreads, mixes with air, and eventually dissipates downwind. The evaluation is intended to determine the trajectory of the cloud of vapor with methane concentrations above some chosen value--e.g., the lower flammable limit (LFL) or some fraction thereof.

In Section III-B-1 we treat the boiling of LNG in confined areas on water, as more research has been done on this special case. The more realistic unconfined mode is discussed in Section III-B-2; few experimental data are available to confirm the predictions of the analytical models for unconfined spills. Large-scale, experimental spills of LNG on water are covered in Section III-C-1, and the various theoretical models are contrasted in Sections III-C-2 and -3. The largest experimental spill to date (198 m^3) still is far less than the design spill of 25,000 and 30,000 m^3. The few resulting data must be extrapolated over two orders of magnitude, therefore, to test theoretical models for very large spills.

B. EXPERIMENTAL BOILING-RATE STUDIES

1. Confined-Area Tests

a. Bureau of Mines. Burgess et al., 1970, 1972, at the Bureau of Mines boiled nitrogen, methane, and LNG on a water surface and measured the rate of boiling by following changes in total system mass. In the few tests reported, the boil-off rate was found to be almost constant for the first 20 to 40 s, i.e., a plot of total system mass versus time appeared to yield a straight line. Ice formation was noted in some runs. The data for different runs were not completely reproducible, but the differences normally were less than 20 percent. For nitrogen, the average initial evaporation rate was above 0.17 kg/m^2s. Multiplying this value by the heat of vaporization of nitrogen gives a heat flux of about 34 kW/m^2. Similarly, for LNG, values of 0.15 kg/m^2s and 76.7 kW/m^2 were noted. This LNG was 84 to 91 percent methane with the remainder primarily ethane. The boiling rate (and heat flux) for pure methane differed slightly from the LNG results, depending on the amount spilled. For an initial methane depth of about 2.7 cm, the boiling rate was 0.10 kg/m^2s, whereas for an initial depth of 6 cm, the value increased to 0.16 kg/m^2s. The data showed clearly that for equal quantities poured, LNG vaporized much more rapidly than either pure methane or nitrogen. A similar but less comprehensive study by Nakanishi and Reid, 1971, generally corroborated the Bureau of Mines' results.

b. Tokyo Gas Company, Ltd. Small-scale tests by the Tokyo Gas Company, Ltd., 1971, indicated a considerably lower boil-off rate of LNG (of undetermined composition) on water than noted by Burgess et al. However, the rates did increase significanty with time. The authors' studies of the effect of initial water temperature were particularly interesting. Little effect was noted for initial water temperatures between 0° and 20°C; at higher temperatures, however, the net rate of boil-off decreased appreciably. This change was attributed to the fact that ice could form more readily on the surface of the colder water. Such ice would then cool and reduce the temperature difference between the LNG and water, thus encouraging nucleate boiling with higher rates of heat transfer.

c. Shell Research. In a study on tne boiling of LNG on water, Boyle and Kneebone, 1973, and Boyle, 1973, of Shell Research, Ltd., did two types of experiments. In the first, they spilled LNG on restricted brine surfaces of 0.84 and 3.7 m² and monitored evaporation rates with load cells. They studied the effects on vaporization rates of LNG composition, amount spilled, initial water temperature, and agitation rate of water.

Except for very small spills of pure methane, all vaporization rates increased with time and, in a few cases, increased almost an order of magnitude from initial values. Boiling rates also increased when larger amounts of LNG were spilled or when the intial water temperature was decreased. In a typical run with LNG (95 percent CH_4), the intial boil-off rate, determined from taking slopes on a mass-time curve, was 0.02 to 0.03 kg/m²s. After a few seconds, the rate increased dramatically to a maximum between 0.15 and 0.20 kg/m²s. When the residual liquid was about 1.8 mm thick, the continuous LNG layer broke up, and the superficial boiling rate (based on total area) decreased abruptly.

The effect of LNG composition was also examined. It was found that small concentrations of heavier hydrocarbons (particularly ethane and butane) in methane resulted in very marked increases in boiling rates.

Boyle and Kneebone proposed that the low initial boiling rates were a result of film boiling. As soon as a thin layer of ice had formed on the surface, however, the temperature difference decreased and nucleate boiling was promoted. Only the very top layer of water cooled (temperature 5 mm below the surface remained well above 0°C), and low initial water temperatures or an increased hydrostatic head of LNG would favor ice formation. When the water was agitated, lower boil-off rates were measured, and this result was attributed to the lower rate of ice formation. To explain the enhancement of vaporization rates by addition of heavy hydrocarbons to methane, the authors proposed that the liquid was enriched in ethane and heavier ends as methane was preferentially evolved. The increase in the concentration of heavier hydrocarbons reduced the boiling temperature of the LNG near the interface and encouraged the collapse of any vapor film to form ice (and hydrates?), with subsequent nucleate boiling.

d. Vestal. In a Ph.D. thesis at the Colorado School of Mines, Vestal, 1973, measured the vaporization rates of liquefied nitrogen, methane, and LNG on water. He found that the heat fluxes for all cryogens decreased with time. Experiments were carried out in a vacuum flask, and significant wall effects may have been involved. Since these results are at variance with those of all other studies, they are not discussed further.

e. MIT. At the MIT LNG Research Center, transient boiling of liquefied light hydrocarbons on water has been studied by several groups. Jeje, 1974, as reported in Drake et al., 1975, measured boiling rates of very pure liquid nitrogen, methane, and ethane on water and also studied a few LNG mixtures. Dincer et al., 1977, investigated the effect of initial water temperature on the boiling rates of liquid nitrogen. Valencia, 1978, extended Jeje's work by concentrating on a wide range of LNG compositions. Reid and Smith, 1978, reported on the transient boiling of liquid propane and liquefied petroleum gas on a surface of confined area.

In all these studies, calorimeters were constructed of several concentric cylinders of thin, smooth, plastic film. Adjacent cylinders were separated by thin polyurethane spacers. By this means, side-wall heat leaks were made negligibly small. The plastic-film cylinders were fixed to a base and filled to various depths with water. The completed assemblies were placed on a load cell and the cryogen spill made. A data-acquisition computer recorded changes of mass with time and temperatures in the vapor and liquid phases could be followed continuously when desired. Further details are available in Drake et al., 1975, and Valencia, 1978.

Boil-off rates of liquid nitrogen were strongly sensitive to the initial hydrostatic head of cryogen, but largely insensitive to the initial water temperature. Ice was visible within a short time, but did not always form a continuous layer. The interface was quite rough except in the areas covered by ice. Water temperatures a few millimeters below the surface changed very little, which supports the hypothesis that most of the energy is extracted from the top layer of water. Nitrogen vapors were quite superheated. The superheat ranged from 40° to 50°C with large spills, but from 90° to 100°C with small spills.

Boiling rates of liquid methane and ethane showed little sensitivity to the amount of hydrocarbon spilled as contrasted with the rates for nitrogen. The initial water temperature, as with nitrogen, had little effect. Ice formed with both hydrocarbons, but far more rapidly with ethane. Again, the temperature of the water a few millimeters below the interface did not change significantly. The vapor superheat for methane was on the order of 10° to 30°C, but none was detected for ethane. These vapor-superheat data seem to indicate that nitrogen and probably methane on water undergo film boiling initially, whereas ethane undergoes nucleate boiling. This argument is further supported by the rapid formation of ice--which would promote nucleate boiling--in ethane spills.

Typical boiling-flux curves derived from the data of Valencia, 1978, are shown in Figure 22. Ultrapure liquid methane boils at a relatively low rate initially, but the rate increases rapidly to a maximum at about 40 s and decreases steadily thereafter. If ethane is added to the methane, the peak-boiling flux increases and is attained in a shorter time. The peak flux for pure ethane is not known, but apparently is reached within five seconds. When propane was added, no maximum could be discerned but very high initial heat fluxes (>150 kW/m^2) were measured.

When LNG mixtures are boiled on water, as noted above, the boiling rate is high initially, but then decreases. A second peak normally is found after the LNG has been depleted in methane, as shown in Figure 23. The surface ice remains near the boiling temperature of methane while significant amounts of methane are present. However, this surface temperature must readjust to the boiling point of ethane as that component becomes predominant. During this period, the boiling essentially ceases and then resumes as ethane begins to boil. In tests such as shown in Figure 23 (or with the methane-ethane mixtures in Figure 22), extensive foaming occurred immediately following the spill.

Thermal fluctuations in water and their effects on the boiling rates of methane and nitrogen were investigated by Dincer et al., 1977. Boil-off rates for liquid nitrogen were the same as those found by Jeje. These rates were found to increase with the initial hydrostatic head of cryogen and to decrease with time. The initial water temperature did not affect boil-off rates significantly. Ice formed after 30 seconds at initial water temperatures of 30°C and above; ice formed within a few seconds at initial water temperatures below 20°C.

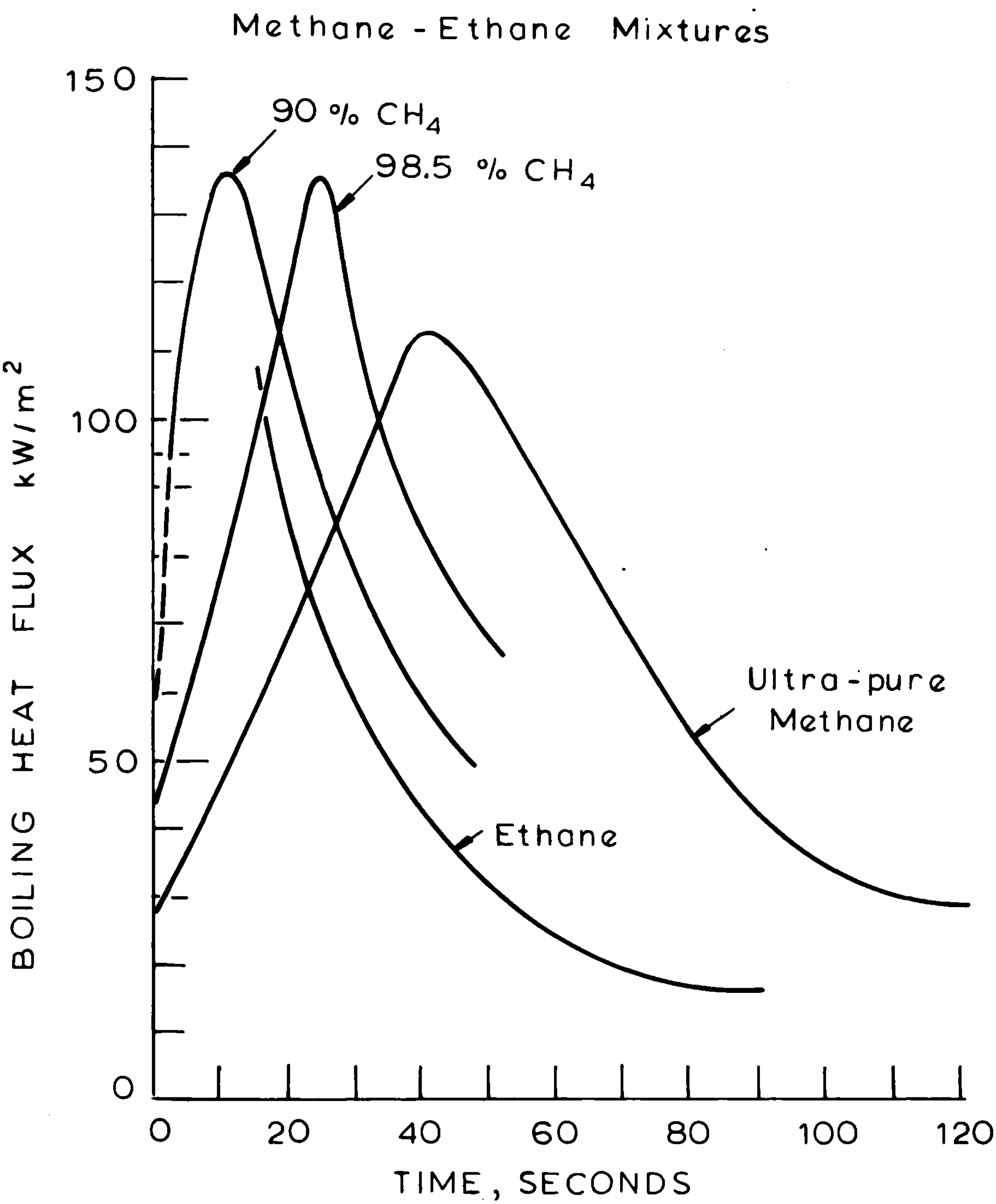


Figure 22 Typical Boiling-Rate Curves for Methane and Ethane on Water

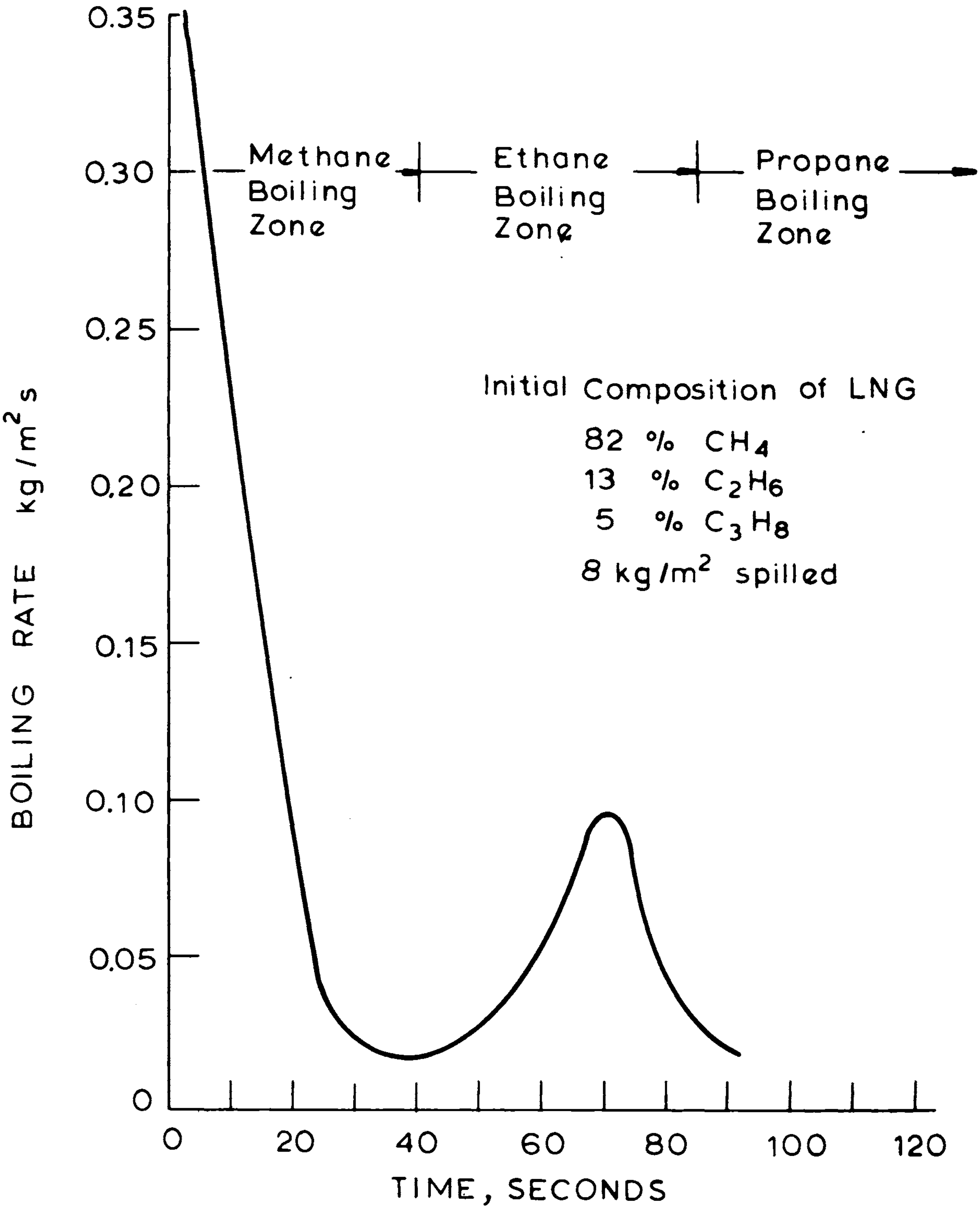


Figure 23 Preferential Boiling Curve for LNG

Dincer's boil-off rates for liquid methane were higher than those reported by Jeje. This discrepancy is easily explained however, by the fact that Dincer used methane containing some higher hydrocarbons as impurities, whereas Jeje used ultrapure (>99.98 percent) methane.

Work is continuing at the MIT LNG Research Center to delineate more clearly the effect of composition on the boiling rates of LNG. A computer model is being prepared to account for the change in boiling regimes as ice is formed. This program also follows the changes in composition and temperature of the LNG as it weathers by losing its more volatile components (Valencia, 1978).

f. Summary of Confined-Area Spill Tests With LNG and Other Cryogenic Liquids. A summary of the experimental results obtained in the confined-area spills is presented in Tables 16, 17, and 18.

All investigators agree that the boiling rates of liquid nitrogen are sensitive to the liquid head but almost independent of the initial water temperatures. The rates decrease with time. No foaming is noted, and the interface is turbulent. The vapor is superheated from 40° to 100°K above the saturation temperature.

Burgess et al. report that the boiling rate of pure, liquid methane increases with an increase in liquid head. This finding is disputed by Drake et al., Dincer et al., and Valencia. All but Vestal state that the boiling rate increases initially with time. The initial water temperature has essentially no effect. The boiling interface is not particularly turbulent, and the vapor is superheated from 0° to 30°K, depending on the quantity of methane spilled.

Finally, for LNG spills on water, the boiling rates may increase as the initial water temperature decreases or if the amount of cryogen spilled increases. Drake et al. report that the vaporization rate increases with time; Vestal indicates a decrease; Burgess et al. say there is no effect; Boyle and Kneebone and Valencia show an increase followed by a decrease. The boiling interface is smooth, and there is negligible superheat.

2. Unconfined-Area Tests

Only a few data are available to describe simultaneous boiling and spreading rates after an LNG spill on water. Burgess et al., 1970, 1972, used an overhead camera to study a few LNG spills on an open pond. They reported that the liquid spread at a constant velocity of about 1.25 ft/s (0.38 m/s). With a constant radial spread velocity of u, the pool diameter d and the pool area A are:

Table 16 Boiling of Liquid Methane on Water

Investigator		Burgess et al., 1970, 1972	Vestal, 1973	Drake et al., 1975	Dincer et al., 1977	Valencia, 1978
Q	High	82 (avg.)	197	95		110
(kW/m^2)	Low (avg.)	51 (avg.)		30	*	
Effect on Q due to an increase in:						
Water temperature		-	same	same	same	same
Cryogen mass		up	-	same	same	same
Time		up	down	up	up	up/down
Area		-	-	-	-	-
Foaming?		-	yes	no	-	no
Rough interface?		-	no	no	-	no
Vapor superheat?		-	-	10-30K	-	0-20K

*Dincer's boil-off rates were 25% higher than those reported by Drake. If we assume the same contribution of vapor superheat to the total heat flux, then Dincer's heat fluxes would be 25% higher than Drake's.

Table 17 Boiling of Liquefied Nitrogen on Water

Investigator		Burgess et al., 1970, 1972	Vestal, 1973	Drake et al., 1975	Dincer et al., 1977
Q	High	68	88 (60°C)*	50	**
(kW/m^2)	Low (avg.)	(26)	28 (10°C)*	20	**
Effect on Q due to an increase in:					
Water temperature		-	up	same	same
Cryogen mass		-	-	up	up
Time		-	down	down	down
Area		-	-	-	-
Foaming?		no	no	no	-
Rough interface?		yes	yes	yes	-
Vapor superheat?		-	-	40-100 K	-

*Number in parenthesis refers to initial water temperatures.

**Dincer's boil-off rates were the same as those reported by Drake. If the same vapor superheats are assumed, then Dincer's heat fluxes are the same as Drake's.

Table 18 Boiling of LNG on Water

Investigator		Burgess et al., 1970, 1972		Boyle and Kneebone, 1973	Drake et al., 1975		Vestal, 1973	Valencia, 1978
Q	High		153	100	120	150	550	>150
(kW/m^2)	Low (avg.)	(92)	(77)		50	50		-
	C_1	94.5	92	94.7	98.2	89.4	92.58	wide range studied
	C_2	3.4	6.3	4.5	1.6	8.2	6.27	
	C_3	0.9	0.1	0.1	0.11	2.0	0.40	
	C_4	-	-	0.2	0.07	0.4		
	Other	1.2	1.6	0.5			0.77	
Effect on Q due to an increase in:								
Water temperature		-		down	down		slightly up(?)	same
Cryogen mass		same		up	up		-	same
Time		same		up then down	up		down	up then down
Water agitation		-		down	-		-	-
Foaming?		yes		-	yes		yes	yes
Rough interface?		no		-	no		no	no
Vapor superheat?		-		-	5-10 K		-	small

$$d = 2ut \tag{47}$$

$$A = (\pi/4)(d^2) = (\pi/4)(2ut)^2 \tag{48}$$

A constant boiling heat-flux $\dot{q}$ was assumed. Thus, the volume of LNG evaporated at time τ is:

$$V = \int_0^\tau (\dot{q}A/\Delta H_v \rho_L)\, dt = \pi \dot{q} u^2 \tau^3 / 3\rho_L \Delta H_v \tag{49}$$

where ρ_L is the density of the liquid and ΔH_V the enthalpy of vaporization. The time to evaporate an initial volume of LNG, V_o is

$$\tau = (3\Delta H_v \rho_L V / \pi \dot{q} u^2)^{1/3} \tag{50}$$

Burgess chose $\dot{q} \sim 0.18$ kg/m^{2}s = 92,500 W/m^2. With $\rho_L \sim$ 420 kg/m^3 and ΔH_v = 511 x 10^3 J/kg,

$$\tau = [(3)(511 \times 10^3)(420)(V_0)/(\pi)(92{,}400)(0.38)^2]^{1/3}$$

$$= 24.8\ V_o^{1/3}\ (V_o \text{ in m}^3,\ \tau \text{ in s}) \tag{51}$$

As an example, a 50-gal (0.19-m^3) spill would evaporate completely in $\sim$14 s; at this time, the pool diameter would be $\sim$11 m.

Experimental data taken by Burgess et al. show maximum pool diameters as a function of time for spills of LNG up to 360 lb ($\sim$0.40 m^3). In general, the relationship

$$d = (2)(0.38)\tau = 0.76\ t(m) \tag{52}$$

Table 19 Boyle and Kneebone Spread/Boil Data for LNG

Spill size, m^3	2.29×10^{-2}	4.57×10^{-2}	9.15×10^{-2}
Pool diam at breakup, m	3.96	5.64	7.32
Time to pool breakup, s	2.8	4.5	9.5
Time to evaporate completely, s	24	33	35
Average spreading rate, m/s	0.71	0.63	0.39
Time to evaporate, Burgess et al. model, [see Eq. (51)], s	7.0	8.9	11
Maximum pool diam, Burgess et al. model, m	5.3	6.8	8.4

is obeyed in the early part of the test, but the data show clearly that the spreading rate diminishes with time, so Eq. (52) is only an approximation.

Boyle and Kneebone, 1973, made three spills of LNG on a pond and measured the diameter of the pool when it began to break into discrete patches. Their data are shown in Table 19.

Several points should be noted. The Burgess et al. model predicts a time that is between that found by Boyle and Kneebone to achieve breakup and to evaporate completely. The latter authors claim that when the thickness of LNG reaches ∿1.8 mm, there is no longer a coherent layer and discrete discs or patches of LNG form spontaneously. With this hypothesis, they compute the average vaporization rate required to produce a layer ∿1.8 mm thick at the experimentally observed time for pool breakup. The rate is less than 0.049 kg/m², equivalent to a heat flux of less than 25 kW/m². Note that this flux is significantly below the 92.4 kW/m² used by Burgess et al. in their study.

Boyle and Kneebone interpret their low vaporization rate as follows. In contrast to a confined-area spill of LNG, where surface ice forms rapidly, they claim that little or no ice forms in a free, unconfined spill. Boiling is then limited to the film-boiling regime with concomitant low heat fluxes. Thus, they would claim that the confined-area heat flux employed by Burgess et al. would be incorrect.

The Burgess et al. and Boyle and Kneebone studies comprise all the available experimental data, although boiling/spreading experiments are under way at the LNG Research Center at MIT.

Other studies of the boiling/spreading of cryogenic liquids on water have been theoretical and based predominantly on results from spreading of nonvolatile oil. Otterman, 1975, has reviewed the various analytical models. Essentially all are based on derivations which assume that in the period soon after a spill, gravity causes spreading while being opposed by inertial forces. In such cases, with no evaporation,

$$r = k(gV_o\Delta)^{1/4}\ t^{1/2} \tag{53}$$

where g is the gravitational constant, V_0 the initial volume spilled, and Δ is a density parameter defined as:

$$\Delta = (\rho_{H_2O} - \rho_{cryogen})/\rho_{H_2O} \tag{54}$$

k is a dimensionless constant which, from experiment and theory, is about 1.14.

Note that the radial spreading velocity would then be predicted to vary as $t^{-1/2}$ rather than being a constant [Eq. (52)] in the Burgess et al. study. Using Eq. (53) in a model which assumes a constant heat flux, the analog to Eq. (50) is

$$\tau = (8\rho_L^2 \Delta H_v^2 V_o / \pi^2 \dot{q}^2 g\Delta)^{1/4} \tag{55}$$

With $\dot{q} \sim 92{,}400\ W/m^2$, for LNG

$$\tau \sim 30\ V_o^{1/4}\ (V_o \text{ in } m^3,\ \tau \text{ in s}) \tag{56}$$

Eq. (56) predicts higher values of τ than Eq. (51) and, therefore, is in even poorer agreement with the Boyle and Kneebone data cited earlier.

The most thorough analysis of the boiling/spreading rates of LNG spills on water is reported by Raj and Kalelkar, 1974. Both one-dimensional and radial spills were considered. Differential momentum, energy, and material balances were written and solved in closed form. However, two key assumptions reduce the generality of the results. First, a constant boiling flux was assumed; as noted earlier, neither the validity of this assumption nor the appropriate value of heat flux are known at present. The other assumption is involved in the basic model where a "mean film thickness" of LNG is employed to characterize the LNG layer at any given time. Thus no thickness profiles can be introduced.

For a two-dimensional spill of V_o (cubic meters) in a trough of constant width (meters) with τ (seconds) as the time for complete evaporation and x (meters) as the maximum travel distance (assuming flow in only one direction),

$$x = 1.59 \left[\frac{(V_o/w)^3 (g\Delta)}{(\dot{q}/\rho\ \Delta H_v)^2} \right]^{1/5} \tag{57}$$

$$\tau = 1.09 \left[\frac{(V_o/w)^2}{(g\Delta)(\dot{q}/\rho\ \Delta H_v)^3} \right]^{1/5} \tag{58}$$

For a radial spill with the same notation but using the maximum radial dimension as r (meters),

$$r = [(\Delta H_v \rho/\dot{q})^2\ V_o^{\,3}(g\Delta)]^{1/8} \qquad (59)$$

$$\tau = 0.675\ [\Delta H_v \rho/\dot{q})^2 (V_o/g\Delta)]^{1/4} \qquad (60)$$

For LNG,

ρ = liquid density ∿420 kg/m^3

ΔH_v = heat of vaporization ∿511 x 10^3 J/kg

$\Delta = (\rho_{H_2O} - \rho_{LNG})/\rho_{H_2O}$ ∿ 0.58

g = acceleration due to gravity = 9.81 m/s^2

As noted earlier, the heat-transfer rate for unconfined spills is not known. If we use a typical value for confined spills (Drake et al., 1975; Dincer et al., 1977), $\dot{q}$ ∿92,000 W/m^2.

Then, for example, Eqs. (59) and (60) become:

$$r = 8.6\ V_o^{\,3/8}\text{, meters} \qquad (59a)$$

$$\tau = 21.0\ V_o^{\,1/4}\text{, seconds} \qquad (60a)$$

If Eq. (60a) is substituted in Eq. (53), then $r = 8.1\ V_o^{3/8}$ which is in good agreement with Eq. (59a).

Equations (59) and (60) have not been verified, and careful experimental work is necessary to indicate their validity. They were used by Opschoor, 1977, to model the spreading and evaporation of LNG in unconfined spills, but he assumed a constant heat flux of 23,000 W/m² rather than the 92,000 W/m² used in Eqs. (59a) and (60a).

Georgakis et al., 1978, suggest that a radial model for LNG spills may not be realistic if a hole is opened at the waterline of an LNG tanker. They suggest a model that predicts long elliptical shapes for the LNG pool. (Instantaneous ignition was assumed, but is reflected simply in a higher vaporization rate.) The physical aspects of the model are difficult to accept, and the scenario proposed is limited to one type of tank penetration. The authors are correct, however, in their criticism of previous models which have allowed no directionality of the outflow of LNG. More work is needed to delineate more realistically how an LNG spill would behave.

C. VAPOR DISPERSION

1. Review of Test Programs

The few small-scale tests of unconfined LNG spills on water were described in Section III-B-2. Only two large-scale tests have been made, and even these did not represent very rapid spills on water. The Shell Gadila spills simulated jettison, and the LNG evaporated completely before contacting the water. In the Esso tests, a jet of LNG was sprayed in an arc onto the water, but there may have been significant vaporization before contact (Gideon et al.,1974).

a. Shell-Gadila. Kneebone and Prew, 1974, described the jettison of LNG from the 75,000-m³ tanker Gadila. The only previous tests of a similar nature were made with the Methane Pioneer in 1959 when 20 m³ were jettisoned at a rate of 160 m³/h. The ship was moving at 10 knots in a wind of 11 to 16 knots.

The Gadila tests were made with a relatively heavy LNG (87 percent methane). Spills ranged from 27 to 200 m³ and pumping rates from 162 to 1160 m³/h. In some instances the ship was stationary. Winds ranged from 4 to 11 knots. The jettison line formed an extension of the stern loading manifold; the inside diameter of the line was 20 cm, but the exit nozzles were either 5 or 10 cm in diameter.

Entrainment of air led to rapid evaporization, and liquid was barely detectable in the exit flow. Visual observations, confirmed by overhead infrared cameras, showed that few, if any, LNG pools formed on the water surface. No ice was noted. The vapor clouds formed were low and readily visible in the high-humidity environment until methane concentrations dropped below 0.5 percent. The thickness of the cloud seldom exceeded 10 to 12 m; generally, the ratio of the cloud half-width to its thickness was in the neighborhood of ∿25.

b. Esso Tests at Matagorda Bay. Esso Research and Engineering Co. carried out the most comprehensive tests yet made with LNG on water (May et al., 1973a, 1973b). These experiments were made in Matagorda Bay, Texas, several miles from land. The spill sizes were 250 and 2500 gallons (0.95 and 9.5 m^3). Pumping rates were set at about 1140 m^3/h in an attempt to simulate an instantaneous spill. The LNG was forced through nozzles on a barge, and the liquid traversed a wide arc before reaching the water. Extensive photographic coverage, both surface and air, was employed. Sampling stations were moored downwind. For all runs, sensors were set near the waterline in a main line normal to the wind and at intervals appropriate to the size of spill to be made. Other sensors were placed at various heights to obtain vertical-dispersion data. Temperatures were also measured.

2. Mathematical Modeling

a. Background. In Section II-D-2, the theory of atmospheric dispersion was reviewed briefly. For LNG spills on land, a continuous-plume model was deemed most appropriate, and the basic Gaussian equation [Eq. (21)] was used in all theoretical models for land spills.

For spills of LNG on water, analytical models usually can be broken into three phases. First, there is the spreading/boiling phase that generates a discrete cloud of cold, dense vapor. This phase would be analogous to the boiling of LNG on dike floors. Second, the large cloud that would be formed from a ∿25,000-m^3 spill drifts downwind, spreading laterally because of its negative buoyancy, perhaps mixing with air, and being heated to some extent by the underlying ocean. Dispersion occurs in the third phase.

The dispersion step normally is based on an instantaneous or puff model. As presented by Sutton, 1953, assuming a source of vapor Q, the downwind concentration at a position x, y, z (relative to the release point) at time t is given by:

$$C = \frac{Q(2\pi)^{-3/2}}{\sigma_{xI}\sigma_{yI}\sigma_{zI}} \exp\left\{-\frac{1}{2}\left[\frac{(x - Ut)^2}{(\sigma_{xI})^2} + \frac{y^2}{(\sigma_{yI})^2} + \frac{z^2}{(\sigma_{zI})^2}\right]\right\} \qquad (61)$$

As before, U is the wind speed. The dispersion parameters (σ) have a subscript, I, to indicate that they are for instantaneous spills and are not necessarily equal to those for continuous spills (e.g., Figures 14 and 15).

Eq. (61) does not include gravity effects or heat transfer and simply describes the dispersion of the cloud as it moves downwind.

The maximum concentration in the cloud is at the center, where x = Ut, y = 0, z = 0, and, for this point,

$$C_{max} = \frac{2Q(2\pi)^{-3/2}}{\sigma_{xI}\sigma_{yI}\sigma_{zI}} \quad (62)$$

The factor of 2 allows for reflection of the cloud from the water surface.

The comparable equation for estimating C_{max} if the cloud were assumed to be emitted from a continuous source would be

$$c_{max} = \dot{Q}/\pi\sigma_y\sigma_z U \quad (63)$$

Many analytical models have been suggested to predict downwind concentrations of methane from a major spill of LNG on water. Most have been reviewed by Havens, 1977. As will be noted later, they differ among themselves in assuming instantaneous spills [Eq. (62)] or continuous spills [Eq. (63)], in treating the spreading of liquid and cloud in various ways, in the choice of different dispersion parameters, etc.

b. Fay and Lewis Model. Fay and Lewis, 1975, adopt the view suggested by Fay, 1973, that following a massive spill of LNG on water, vaporization leads to a pancake-shaped cloud of pure methane vapor. This cloud expands radially in a gravity-spread phase with little or not mixing with air. The vapor cloud's dimensions at the completion of vaporization and gravity-spread are somewhat uncertain. In the initial boiling and spreading phase, Fay, 1973, decouples the liquid-spreading from the boiling process. First, the spreading liquid is assumed not to boil, thereby conserving volume. The rate of spread is viewed as a density intrusion with

$$dr/dt = (2gh\Delta)^{1/2} \tag{64}$$

r is the pool radius at time t. Δ is the same density parameter defined in Eq. (54) and h is the pool thickness. With no boiling

$$h = V_o/\pi r^2 \tag{65}$$

where V_o the volume of the spill. Integrating Eq. (64),

$$r = (8gV_o t^2 \Delta/\pi)^{1/4} \tag{66}$$

The LNG pool with the radius given by Eq. (66) is then assumed to boil by cooling and forming a slab of ice. Solving this heat balance yields an expression for the vaporization time which then may be substituted in Eq. (66) to obtain the maximum pool diameter. This procedure is based on ice being formed under the LNG--an assertion that is not borne out by experimental data.

However, the maximum pool radius is not an important variable in the Fay and Lewis model. More important is their subsequent assumption that the vapor cloud also spreads in a manner given by Eq. (66) except that the volume $V_o = V_v$, the volume of the saturated methane vapor, and Δ becomes Δ_v as given by

$$\Delta_v = -(\rho_{air} - \rho_{LNG\ vapor})/\rho_{air} \tag{67}$$

The maximum radius of the vapor cloud is then determined by assuming heat transfer from the water to the cloud until neutral buoyancy is achieved.

The final result is

$$r_{vm} = (T_b V_v \Delta_v/\pi N_{ST} \Delta T)^{1/3} \tag{68}$$

where T_b is the boiling temperature of the LNG, ΔT is the temperature difference between saturated methane vapor and water, and N_{ST} is the Stanton number. N_{ST} was estimated to be $\sim 10^{-3}$. For example, with $T_b = 111°K$, $\Delta_v = 0.46$, $\Delta T = 182°K$, $N_{ST} = 10^{-3}$, and $V_v = 6.0 \times 10^6$ m³,* then r_{vm} $\sim$810 m. The thickness of the cloud at the end of the spreading phase depends on the temperature of the cloud. If it were saturated vapor, then

$$h_{vm} = 6 \times 10^6/(\pi \times 810^2) = 2.9 \text{ m}$$

This is the value used by Havens, 1977. However, Fay, 1973, clearly indicates that with $r = r_{vm}$, the cloud is neutrally buoyant, so $T \sim 162°K$. The cloud volume is then (162/111) x (6×10^6) = 8.8×10^6 m³ and h = 4.3 m. But, in correspondence to Havens, 1977, Fay suggests that it would be preferable to assume the cloud was at 0°C. In this case, h = 7.2 m.

Obviously, there remain some bothersome inconsistencies in the estimation of the radius, thickness, and temperature of the LNG cloud at the completion of the gravity-spread phase.

Fay and Lewis assume that dispersion begins after the end of the gravity-spread phase [$r = r_{vm}$ as given in Eq. (68) and $h - h_v = V_v/\pi r_{vm}^2$]. They suggest that Eq. (62) is applicable at long distances from the spill. Also, it was assumed that x = Ut and $\sigma_{xI} = \sigma_{yI}$. Since,

$$V_v = Q = \pi r_{vm}^2 h_v \tag{69}$$

Eq. (62) may be written as

$$C_{max} = (2\pi)^{-\frac{1}{2}}(r_{vm}/\sigma_{yI})^2(h_v/\sigma_{zI}) \tag{70}$$

---

*A 25,000-m³ liquid spill was assumed; since $\rho_{sat\ liq}/\rho_{sat\ vap}$ $\sim$ 240, $V_v = 240 \times 25{,}000 = 6 \times 10^6$ m³.

At distances closer to the source, Fay and Lewis assume that only vertical dispersion occurs. The corresponding dispersion equation for C_{max} is then written as

$$C_{max} - (2/\pi)^{\frac{1}{2}}(h_v/\sigma_{zI}) \qquad (71)$$

Finally, they argue that at the source, $C_{max} = 1.0$. To consolidate the various relations for C_{max} into a single equation, Fay and Lewis suggest:

$$C_{max} = \left[\frac{r_{vm}}{r_{vm} + \sqrt{2}\ \sigma_{yI}}\right]^2 \left[\frac{h_v}{h_v + (\pi/2)^{1/2}\sigma_{zI}}\right] \qquad (72)$$

An intermediate distance is defined as one where $\sigma_{yI} << r_{vm}$ and $\sigma_{zI} >> h_v$. With these restrictions, Eq. (72) yields Eq. (71). A long distance is defined as one where $\sigma_{yI} >> r_{vm}$ and $\sigma_{zI} >> h_v$. Under such constraints, Eq. (72) gives Eq. (70).

The problem with Eqs. (70) through (72) lies in the relationship of σ_{yI} and σ_{zI} to r_{vm}. Using, for example, the very stable atmospheric conditions of Högstrom, 1964,

$$\sigma_{yI} \simeq 0.02\ x^{0.89} \qquad (73)$$

$$\sigma_{zI} \simeq 0.05\ x^{0.61}$$

with σ and x in meters, the following values of C_{max} are determined. (In the calculations, $r_{vm} = 810$ m, $h_v = 7.2$ m, and C_{max} is the methane fraction .)

Very Stable Weather

Downwind Distance, x (m)	σ_{yI} (m)	σ_{zI} (m)	C_{max} Intermediate [Eq. (71)]	C_{max} Long [Eq. (70)]	C_{max} All-Purpose [Eq. (72)]
10^3	9.3	3.4	>1	>>1	0.61
10^4	72.6	13.8	0.42	>1	0.23
10^5	560	56.1	0.10	0.11	0.024
10^6	4400	230	0.025	4.3×10^{-4}	3.3×10^{-4}
1.4×10^5	760	68.8	0.083	0.047	0.0141

The intermediate range appears to be $\sim 10^4$ m($\sim$6.3 miles) and the long range $\sim >10^6$ m ($\sim$625 miles.) As the latter is far larger than would ever be of interest, only the intermediate range should be considered. But in this range, Eq. (71) is certainly not a Gaussian type of dispersion. The Gaussian form is Eq. (70); use of this relationship yields large values of C_{max} except at very long distances. It would predict a $C_{max} \sim 0.05$ (the LFL) at x $\sim$ 1.4×10^5 m ($\sim$87.5 miles.) Such a long distance results from the low values of the dispersion parameters.

c. Germeles and Drake Model. The model of Germeles and Drake, 1975, has elements of similarity and dissimiliarity when compared to that of Fay and Lewis. The spreading and boiling of the LNG are treated simultaneously, and Eqs. (59) and (60) are used to estimate the initial size of the pure methane cloud and the time for evaporation. The thickness at this time is determined form a volume balance where the cloud is assumed to be saturated vapor at 111°K. For a 25,000-m³ spill, from Eq. (59a), r = 390 m and h = $[25{,}000/(\pi \times 383^2)]$ (240) = 13 m. τ = 264 seconds.

Let the outer radius of the cloud be R and the thickness H. This pancake-like mass then is assumed to spread radially and entrain air. The variation in R with time is given by Eq. (64) with $\Delta = \Delta_v$ as in Eq. (67).

$$dR/dt = (2gH\Delta_v)^{1/2} \tag{74}$$

The spreading vapor cloud entrains air by the shearing action between the moving cloud and the air above. By using experimental data from Lofquist, 1960, who studied the mixing of a layer of salt water beneath fresh water, Germeles and Drake show that there can be significant turbulence at the methane-air interface and choose an entrainment coefficient of 0.1. [Entrainment also was used in the Van Ulden Model--see Eq. (36).] Then for any annular area, $2\pi r'dr'$, in the cloud, the volume of air entrained in unit time is dQ_e,

$$dQ_e = \alpha U_{r'}(2\pi r'dr') \tag{75}$$

where α is the entrainment coefficient ($\sim$0.1) and $U_{r'}$ is the characteristic local entrainment velocity at position r'. Ur' is assumed to vary linearly with r',

$$U_{r'} = (r'/R)(dR/dt) \tag{76}$$

With Eq. (76), Eq. (75) may be integrated from r' = 0 to r' = R to give Q_e, the total volume of air entrained by the vapor per unit time,

$$Q_e = (2\pi/3)\ \alpha R^2\ (dR/dt) \tag{77}$$

Eq. (77) is used in a mass conservation equation with M = mass of material in the cloud and ρ_{air} = density of the entrained air,

$$dM/dt = \rho_{air}\ Q_e \tag{78}$$

Eq. (77) also is used in an energy conservation equation,

$$d(CMT)/dt = C_{air}\ \rho_{air}\ Q_e\ T_{air} + Q_v + Q_w \qquad (79)$$

In Eq. (79),

C = heat capacity of the methane-air cloud

T = temperature of the methane-air cloud

C_{air} = heat capacity of the entrained air

T_{air} = air temperature

Q_v = the heat-transfer rate for any moisture condensed (and frozen, if appropriate); it may be either positive or negative--especially as the cloud warms toward neutral buoyancy

Q_w = the heat-transfer rate between the cloud and the water; both natural and forced convection are considered.

Germeles and Drake solve the differential equations represented by Eqs. (74), (78), and (79) by a numerical procedure to yield the time-dependence of the radius, thickness, density, temperature, and concentration of the cloud. (No scalar gradients are considered to exist within the cloud.) The computation is terminated when the cloud attains neutral buoyancy under a no-wind condition or at a time when $dR/dt \sim U$, the assumed wind speed. In Figures 24 and 25, typical results are shown for a 25,000-m³ liquid spill (Havens, 1977). The ambient conditions chosen for this example are shown in the figures. Germeles and Drake also show results for a similar spill--except that the wind speed is 10 mph instead of the 5 mph of Figures 24 and 25. In this case the cloud radius when spreading ceases is only 700 m and the methane concentration at this time is $\sim$40 percent, as opposed to the 950 m and $\approx$22 percent of Figures 24 and 25.

The most significant difference between the Fay-Lewis model and the Germeles-Drake model--to this point--is the assumption in the latter that air can be entrained during the gravity-spread phase of the cloud.

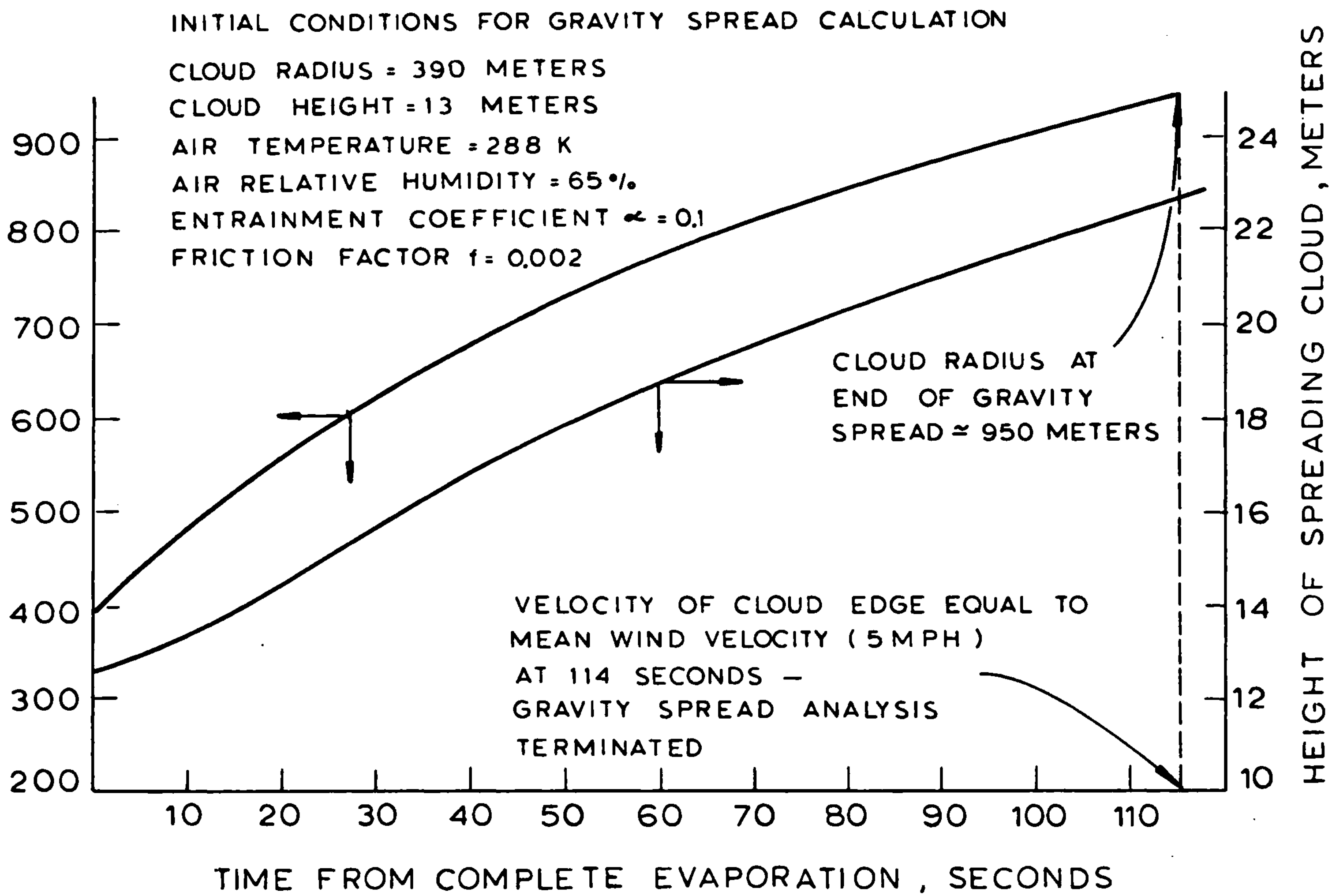


Figure 24 Cloud Radius and Height vs. Time; Gravity-Spread Phase (Germeles and Drake) from Havens, 1977

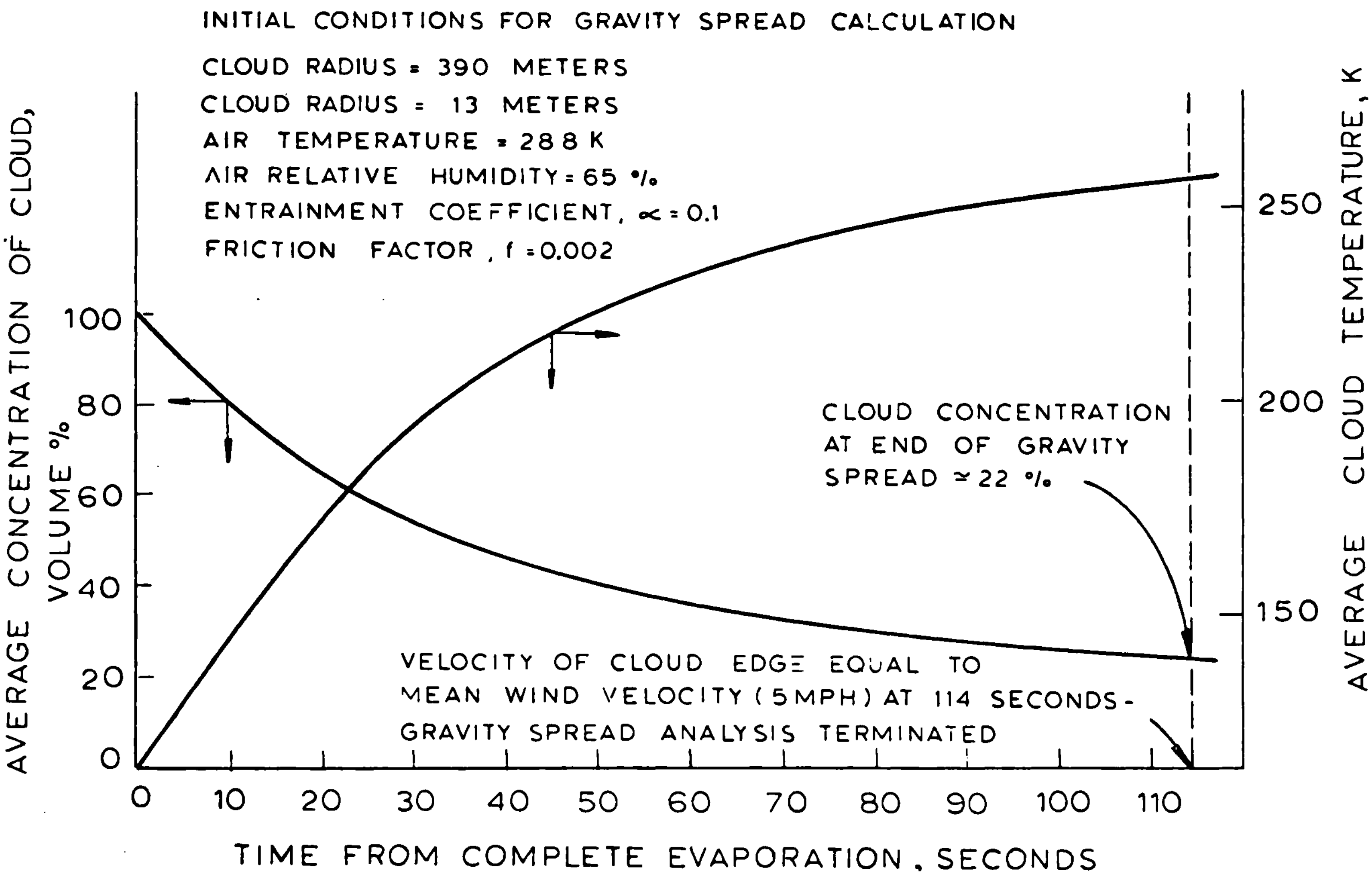


Figure 25 Cloud Concentration and Temperature vs. Time; Gravity-Spread Phase (Germeles and Drake) from Havens, 1977

In the dispersion phase of the Germeles-Drake model, air-entrainment is treated by a virtual-source technique, i.e., an upwind distance is estimated such that, when dispersion is computed,the methane concentration would agree with that calculated from the air-entrainment computations described above. Fay [in the Appendix to Havens, 1977] criticizes the use of a virtual-source technique, pointing out that even at the virtual source, the cloud is still large.

In any case, Germeles and Drake use Eq. (62) to estimate the maximum downwind concentration (from the virtual source). It is not clear what value of Q (the total vapor evolved) they used; from their paper, it would appear that Q should correspond to the saturated methane vapor corresponding the vaporized liquid. Havens, 1977, however, states that they used pure methane vapor at ∿300°K. The dispersion coefficients were those shown in Figures 14 and 15. The authors argue that instantaneous dispersion coefficients (used by Fay and Lewis) are not representative since σ_{yI} and σ_{zI}, as given by Högstrom, 1964, were obtained from 30-s bursts of oil fog released from tall (87-m) towers in tests conducted shortly after dawn on days when there was a pronounced temperature inversion.

With the sample case shown in Figures 24 and 25, with D-weather and σ_y and σ_z from Figures 14 and 15, Havens, 1977, computes the distance from the cloud to the virtual source to be ∿5000 m. [This is the distance required to reduce the methane concentration to ∿22 percent (see Figure 20)]. Similarly, a distance of ∿9800 m is necessary to attain the LFL of 5 percent. Thus, from the spill site, the cloud has a C_{max} > 5 percent for a distance of 9800 - 5000 = 4800 m (3 miles). This distance increases to 11 miles if F weather is chosen. (Oakley in an appendix to Havens, 1977, states that F weather is not realistic in view of the present restrictions on when LNG tankers may enter a port.)

In summary, the Germeles-Drake model is similar to the Fay-Lewis model, but differs from it in three major ways:

- Air entrainment is allowed during the gravity-spread phase of the cloud
- Larger dispersion coefficients are employed
- A more complete heat-transfer analysis is used to estimate the temperature time history of the cloud.

d. Raj and Kalelkar Model. Raj and Kalelkar, 1974, developed a simplified model for analyzing a spill of LNG as part of a comprehensive hazard assessment analysis related to spills of chemicals on water [The CHRIS program (Chemical Hazards Response Information System).] They used Eq. (59)

or Eq. (59a) to estimate the maximum pool radius when evaporation is complete. (For a 25,000-m^3 spill, this radius is then 390 m.) A virtual source is located five pool diameters upwind, and dispersion is assumed to begin from this point. Eq. (62) is employed (with $\sigma_{xI} = \sigma_{yI}$) to compute C_{max} downwind of the virtual source. Also, σ_{yI} and σ_{zI} were obtained from Figures 14 and 15, i.e., continuous dispersion coefficients were selected. Finally, the source term, Q, in Eq. (62) was chosen as the volume of the vaporized methane at ∿300°K.

The Raj-Kalelkar model is not dissimilar to the Germeles-Drake model, but it is greatly simplified to allow estimates to be made rapidly. The deletion of the gravity-spread phase of the cloud, however, leads to a less realistic model; also, the arbitrary selection of the position of the virtual source can be criticized (see correspondence from Fay in the appendix to Havens, 1977).

e. Burgess et al. Model. In contrast to models described to this point, Burgess et al., 1970, 1972, treat the vaporizing LNG as a continuous source. As discussed under Eq. (50), a constant evaporation rate of 0.18 kg/m^2s was chosen. The maximum pool area is determined by combining Eqs. (51) and (52) to yield

$$A_{max} = \pi d^2 = \pi(0.76\tau)^2 = \pi(0.76 \times 24.8)^2 V_o^{2/3} = 1116 V_o^{2/3} \qquad (80)$$

With a spill of 25,000 m^3, the maximum evaporation rate would then be $(0.18)(1116)(25{,}000)^{2/3} = 1.72 \times 10^5$ kg/s, but the average rate would be only 1.45 x 10 kg/s.* Burgess et al. consider that the LNG is then to be treated as a continuous source with a rate of vapor evolution ∿1.5 x 10^4 kg/s--or perhaps somewhat higher. (An upper value of 3.8 x 10^4 kg/s was used by Havens, 1977.)

Dispersion rates are calculated from Eq. (21), but for C_{max}, H = y = z = 0 and Eq. (63) results. The dispersion parameter σ_y was obtained from the Singer-Smith correlation (Figure 11), but to account for the pronounced layering of the dense cloud, σ_z was determined from

*$\tau = 24.8\, V_o^{1/3} = 725$ s; thus the average rate is 25,000 x 420/775 = 1.45×10^4 kg/s.

$$\sigma_z \sim 0.2\ \sigma_y \qquad (81)$$

No provision is made for the vaporized LNG's being an area source.

f. FPC Model. The Federal Power Commission, 1976, described an LNG-spill and-dispersion model which has elements of similarity to those described above but is unique in other ways.

The pool-spreading phase is analyzed in a manner identical to that used by Germeles and Drake and by Raj and Kalelkar, i.e., Eq. (59) or (59a) is employed to obtain the maximum pool diameter, and Eq. (60) or (60a) then gives the time for evaporation. (For a 25,000-m^3 spill, as noted earlier, r = 390 m and τ = 264 s.) The cloud is a pancake 13 m thick, as the vapor is chosen to be saturated at 111°K. This pure methane cloud begins a gravity-spread phase in a manner very similar to that described in the Fay-Lewis model. Eq. (66) is used with $\Delta = \Delta_v$ from Eq. (67). The similarity continues as heat transfer from the underlying water to the cold methane cloud is allowed to take place. Both the FPC and the Fay-Lewis models stop the gravity-spread phase when neutral buoyancy is achieved, i.e., when $T \sim 162$°K. However, the rate of heat transfer is calculated quite differently in the two models. Fay and Lewis used essentially an order-of-magnitude approach to obtain Eq. (68). The FPC was more definitive, taking into account heat transfer between the cloud and both the surrounding air and the water. However, the FPC analysis seems suspect because the rate-limiting step for heat transfer to the water was chosen to be conduction in the water phase. This choice seems unusual in view of the mixing and turbulence that normally occur in the sea.

In any case, by choosing V_v in Eq. (66) to be the arithmetical average of the initial volume of saturated vapor (111°K) and the volume when neutral buoyancy has been achieved and with the gravity-spread time given by a solution of the energy balance for cloud warming, the FPC can predict a cloud radius and height when neutral buoyancy is attained.

The FPC and Fay-Lewis results for a 25,000-m^3 spill are compared in Table 20.

Table 20 Comparison of FPC and Fay-Lewis Results for a 25,000-m^3 Spill

	At the End of the Gravity-Spread Phase with Neutral Buoyancy	
	Radius of Cloud, m	Height of Cloud, m
Fay and Lewis	810	7.2*
FPC	577	8.5

*Assuming T = 294°K

The differences are not small, but probably are not significant in view of the many assumptions made.

The FPC model does, however, differ greatly from all others in its treatment of vapor dispersion. The authors assume that their pancake cloud at the spill site, which is not neutrally buoyant, releases vapor downwind only from its top surface. The rate of release is estimated from heat-transfer considerations such that $\dot{Q}$ [in Eq. (21)] is given by

$$\dot{Q} = hA/C \tag{82}$$

with

h = heat-transfer coefficient between the cloud and the ambient air = $\sim 5.7\ W/m^{2}{}^{\circ}K$ ($\sim 1\ Btu/h\text{-}ft^{2}\text{-}{}^{\circ}F$)

A = the cloud area (from the discussion above, $A = \pi(577)^2 = 1.05 \times 10^6\ m^2$)

C = heat capacity of the vapor cloud, $\sim 2.1\ J/g\ {}^{\circ}K$

Eq. (82) predicts a source strength of only 2.8×10^3 kg/s. One may compare this value to that estimated in the Burgess et al. model, where $\dot{Q} \sim 1.5 \times 10^4$ to 3.8×10^4 kg/s.

Dispersion is computed using Eq. (21) with σ_y and σ_z from Figures 14 and 15, and downwind concentrations are based on a virtual source located upwind at a distance x* which is numerically equivalent to the cloud radius (at neutral buoyancy) divided by ~ 2.1.

Finally, and very significantly, when Eq. (21) is used to compute C_{max}, y and z are set equal to zero, but the source height H is retained, so that the actual dispersion equation used is:

$$C_{max} = (\dot{Q}/\pi\sigma_y\sigma_z)\ \exp(-H^2/2\sigma_z{}^2) \tag{83}$$

H is approximated as the effective emission height and is computed from

$$H = V_{av}/\pi r_{av}^2 \tag{84}$$

with V_{av} and r_{av} as the arithmetical averages of the cloud volume and radius during the gravity-spread phase. For the

25,000-m³ spill being used as an example, H ∿10 m (Havens, 1977). This emission height is large and the use of it in Eq. (83) will reduce greatly the maximum downwind concentration.

g. Esso Model. The Esso model (May et al., 1973a, 1973b), while described almost last among those that have been published was the first attempt to model a large-scale spill of LNG on water. And as far as possible, the various steps were based on experimental observation (See Section III-C-1-b.) Many of the models described previously have used ideas originally developed by May et al.

If the spill is large and rapid, the first step in the model is to estimate the maximum vapor-evolution rate, W_{max}, kg/s, from the liquid pool. In this calculation, the method is similar to that proposed by Burgess et al. (1970, 1972) (Section III-B-2) except for one important difference described below. The velocity of spread in the radial direction was chosen as 0.64 m/s, and the boiling rate was assumed to be constant at 0.195 kg/m²s. (Note that Burgess used similar values--0.38 m/s and 0.18 kg/m²s.) May et al. obtained their values from an examination of the Esso test data. Thus at any time, t,

$$r = 0.64\ t \tag{85}$$

$$A = \pi r^2 = 1.287\ t^2 \tag{86}$$

Spreading was assumed to continue until a limiting average thickness, δ, was achieved. By an empirical correlation, again using the Esso test data as a guide,

$$\delta = 1.49 \times 10^{-3}\ r^{0.56} \tag{87}$$

with δ and r in meters. Thus at the end of the liquid-spread and boiling period, when the pool diameter was a maximum,

$$V_{\text{liquid remaining}} = \delta A = 1.49 \times 10^{-3}\ t^{2.56} \tag{88}$$

$$= V_o - V_{\text{vaporized}} \tag{89}$$

with $\dot{V}_o$ as the volume of the spill, m³. Eq. (50) can be used to estimate the time required to vaporize a given amount of LNG. Rewriting this expression,

$$t = [3\rho_L V_{vaporized}/\pi(\dot{q}/\Delta H_v)\ u^2]^{1/3} \quad (90)$$

with ρ_L (as chosen by May et al.) =457 kg/m³, u=0.64 m/s, and ($\dot{q}/\Delta H_v$) = 0.195 kg/m²s. Then

$$t = 17.61\ V^{1/3}_{vaporized} \quad (91)$$

Substituting Eq. (91) into Eqs. (88) and (89) yields

$$2.30\ V^{0.853}_{vaporized} = V_o - V_{vaporized} \quad (92)$$

Solving Eq. (92) for $V_{vaporized}$, t can then be found from Eq. (91) and the maximum pool radius from Eq. (85). For a 25,000-m³ spill, $V_{vaporized}$ = 1.61 x 10⁴ m³, t= 445 s, and r_{max} = 285 m. Thus the maximum evaporation rate is

$$\dot{W}_{max} = (0.195)(\pi)(285)^2 \sim 50,000 \text{ kg/s} \quad (93)$$

It was necessary to determine $\dot{W}_{max}$ because the vapor flow downwind, q, is based on $\dot{W}_{max}$ (as well as wind speed), as shown in the empirical correlation given in Figure 26. Thus since $q < \dot{W}_{max}$, vapor accumulates over the spill site. For example, if the wind speed were 2.24 m/s (5 mph), $q/\dot{W}_{max} \sim 0.2$, so the maximum downwind vapor flow would be ∿10000 kg/s if $\dot{W}_{max}$ were equal to the value shown in Eq. (93).

The gravity-spread phase of the Esso model does not differ greatly from that described in the Germeles-Drake model; entrainment of air is allowed, and heat is exchanged with the environment by mechanisms that include the condensation of water vapor in the air. The method uses

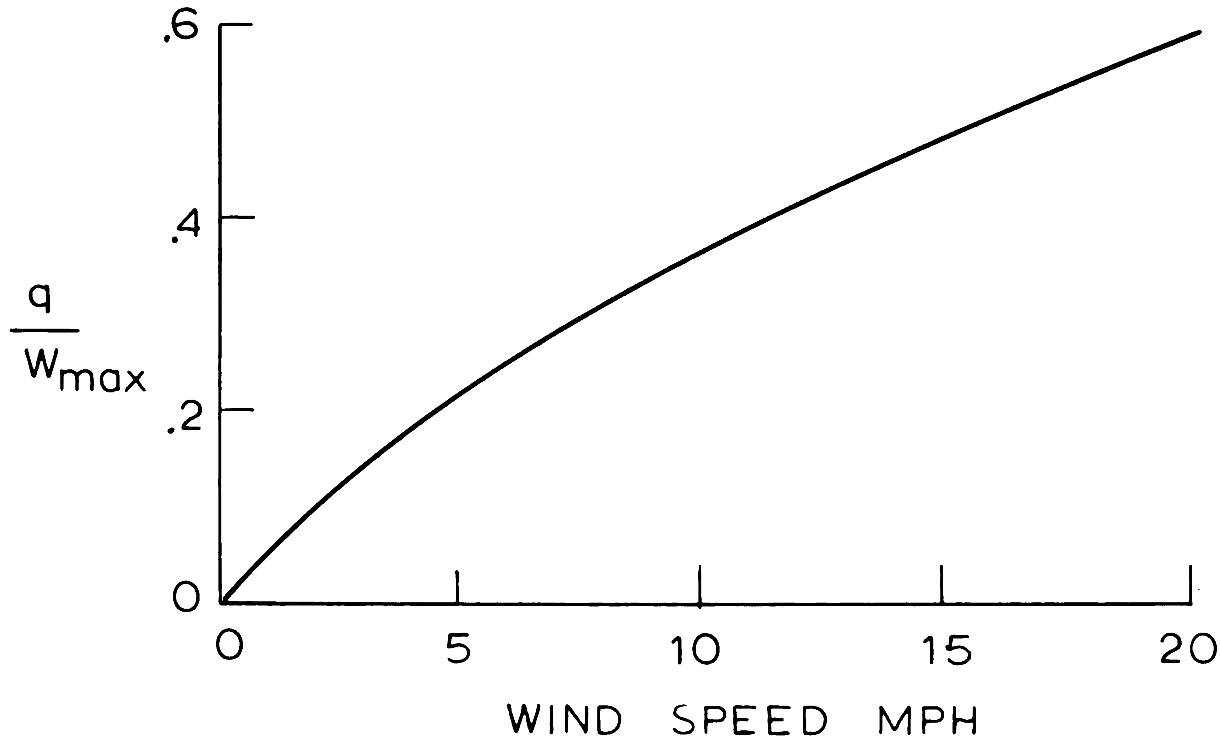


Figure 26 Effect of Wind Speed for Instantaneous Spills; May et al., 1973a, 1973b (from Havens, 1977)

correlations developed from Esso's experimental data. Interestingly enough, the plume height is taken to be a constant during the gravity-spread phase. Since most models predict rather low plume heights, it is probably reasonable to neglect small variations in this parameter during vapor-cloud spreading. (The calculative details of the spreading phase of the Esso model are detailed in Appendix 7 of May et al., 1972.) The gravity-spread phase of the moving cloud (with the maximum methane flow as q) is terminated when neutral buoyancy is achieved. For the 25,000-m^3 example, Havens, 1977, shows that the cloud is then about 300 m wide, 12 m thick and ∿360 m downwind of the spill site. The methane concentration is ∿22 percent for a 5-mph wind. Note that the Germeles-Drake model gave the same concentration at the end of the gravity-spread phase, but gave a radius of ∿ 950 m (1900 m wide). The difference lies in the fact that the Esso Model limits the amount of vapor that can move downwind from the spill site. In this sense, the Esso model bears some similarity to the FPC model.

After the cloud stops spreading, dispersion is assumed to begin. Rather than introduce a virtual source, May et al. propose that the cloud disperses much like a line source. However, instead of using Eq (26), they postulate 11 equidistant point-sources along the cloud front, each serving as a point-source for one-eleventh of the total vapor flow. Thus Eq. (21) is used with z = H = 0 to give

$$C_{max}(x,y) = \sum_{j=1}^{11} \frac{\dot{Q}_j}{\pi \sigma_{y_j} \sigma_z U} \exp\left[- \frac{y_j^{\,2}}{2\sigma_j^{\,2}} \right] \tag{94}$$

where $\dot{Q}_j$ is the vapor flow corresponding to q/11. (For the example being used, q ∿ 10^4 kg/s ∿ 1.5 x 10^4 m^3 of gas at 1 bar and 294°K.) The dispersion coefficients σ_{y_j} were obtained using Atmosphere C in Figure 14, while σ_z was selected for Atmosphere D in Figure 17. These choices were made to give the best fit of experimental data to predictions from the model.

The Esso model is the most difficult to visualize in detail because it is based on theory wherever possible, but, also contains several empirical steps introduced to improve the match between the model and Esso's experimental results. The model is interesting because it introduces the quite plausible concept that the LNG cloud will begin to stream downwind and spread simultaneously. Most other models do not allow the cloud to move downwind during gravity spreading. The FPC model maintains the cloud as a discrete form during spreading, but then peels away vapor at a low rate to determine dispersion.

h. Kneebone and Prew Model. Kneebone and Prew, 1974, correlated their data from the Shell jettison tests with the tanker Gadila (see Section III-C-1-a) with a continuous-plume model [Eq. (21)]. The LNG vaporized before contacting water and, therefore, could be considered a steady source. (Obviously, some dilution occurred at the nozzle and during evaporation, but the use of a virtual source to account for this dilution was shown to have little effect on far-downwind distances where significant dispersion had occurred.) Modified dispersion parameters were necessary however. The best fit to the data was obtained from the relationships,

$$\sigma_y = 1.384\ x^{0.705} \tag{95}$$

$$\sigma_z = \sigma_y/25 \tag{96}$$

where σ_y, σ_z and x are in meters.

The measured wind speed at 30 m above the surface was corrected by the 1/7-law to give values at 5 m.

$$U_{30}/U_5 = (30/5)^{1/7} = 1.3 \tag{97}$$

The model was then used to estimate concentration profiles downwind. The predicted value of the 0.5 percent methane contour is shown in Figure 27 for a test where the LNG was discharged at a rate of 1160 m^3/h. This rate corresponds to a rate of 151 kg/s, as the liquid's density was about 470 kg/m^3. The wind speed was 3 m/s at 5 m above the surface. Good agreement is shown between the model predictions and the estimated 0.5 percent-methane fringe.

To illustrate a different approach to correlating the Shell-Gadila data, Drake, 1977, used a line-source, continuous-plume model [Eq. (26)] to predict a concentration-contour diagram for the test shown in Figure 27. However, she chose "C" weather and obtained the dispersion parameters from Figures 14 and 15 rather than from Eqs. (95) and (96). The downwind axis was tilted to match the true cloud shape, and the boundaries were determined for various concentrations of methane. It was found that a boundary corresponding to 0.25 percent methane gave an excellent fit to the observed cloud boundaries (Figure 28).

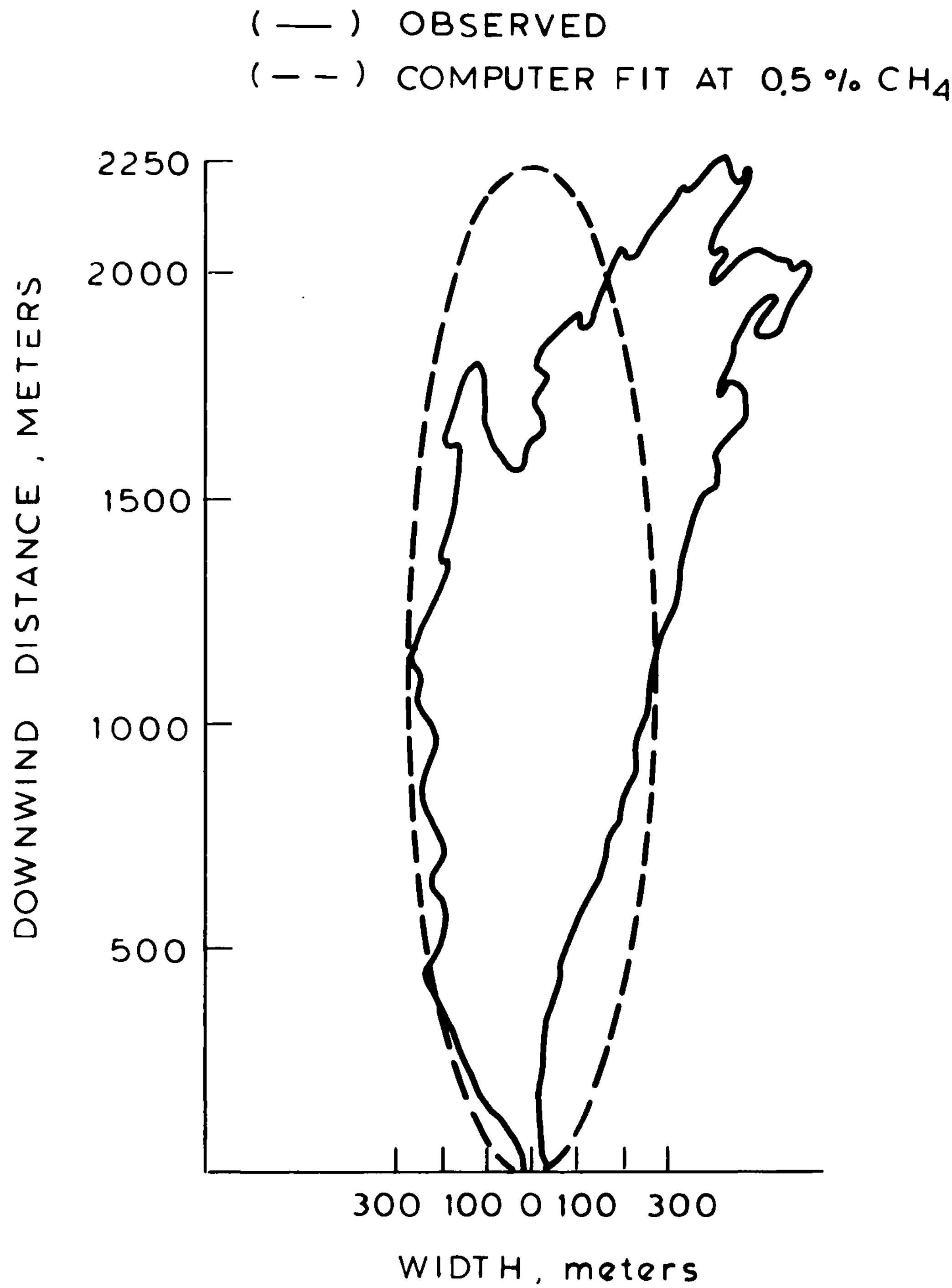


Figure 27 Calculated and Observed Plume Shape for the Gadila Tests

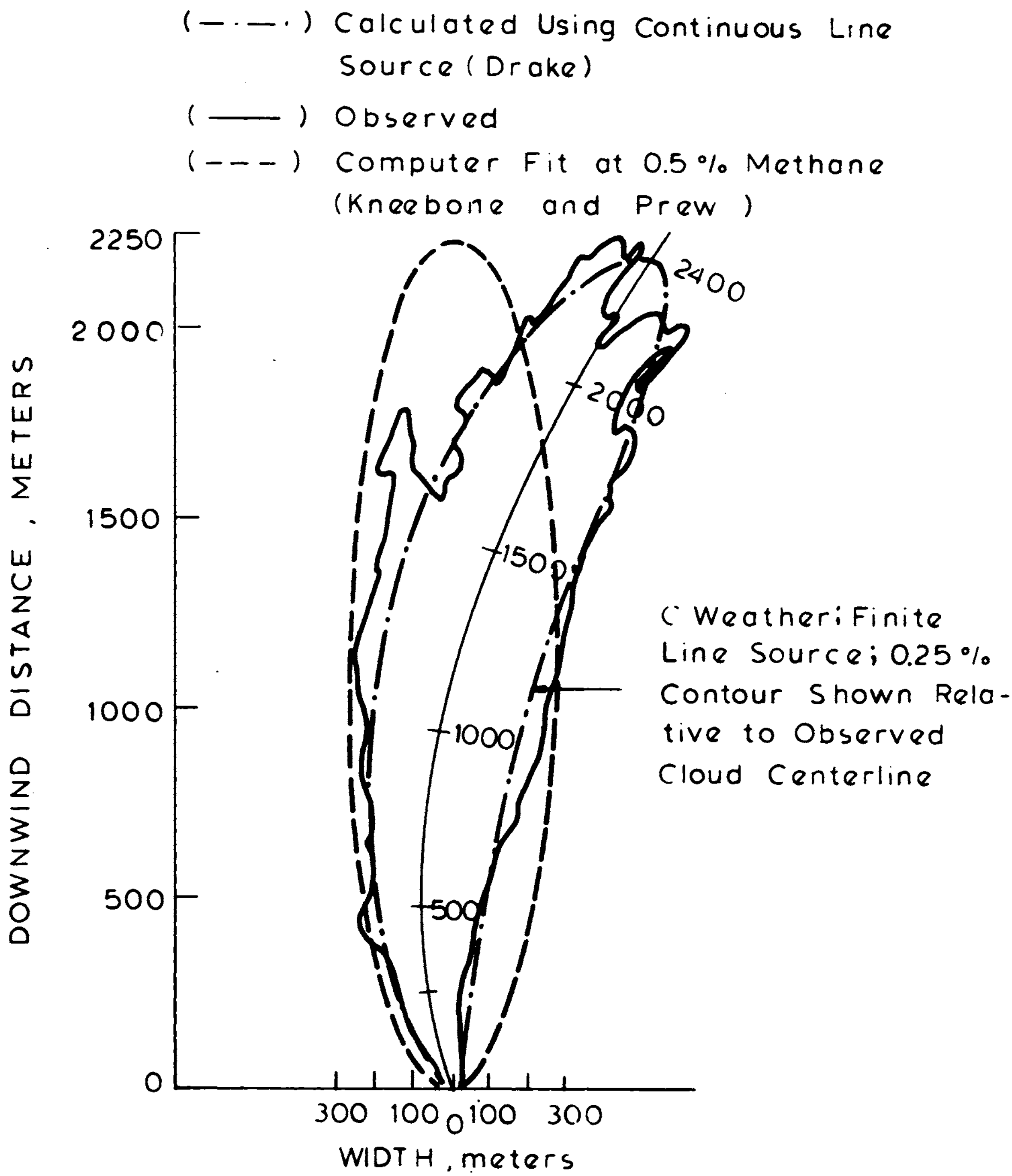


Figure 28 Drake's Estimate of Gadila Plume

Although Kneebone and Prew used 0.5 percent methane and Drake 0.25 percent methane, both values are well within the scatter of data that have been used to define the visible outline of a dispersing cloud.

i. SAI Model. Science Applications, Inc., 1975, has developed a complex model to allow predictions to be made for the dispersion of LNG vapor from a large spill. The approach involves the solution of a detailed system of equations representing the conservation of mass, momentum, and energy associated with the dispersion. Havens, 1977, presents a summary of the theory involved. He states that Eq. (64) is employed to relate the pool radius to time after a spill. He then indicates that Eq. (87) was used to delineate the critical thickness of LNG at which to stop the liquid spread. Then he states that the Esso evaporation rate (constant at 0.195 kg/m^{2}s) was chosen. But Eq. (64), in the Fay-Lewis model, does not consider evaporation during spreading(?).

The method used by SAI to calculate vapor spreading, air entrainment, heat transfer, and eventually dispersion has never been released. However, a summary is available (England et al., 1978).

3. Discussion and Comparison

Three of the models described here treated a vaporized LNG cloud as an instantaneous source (Fay and Lewis; Germeles and Drake; Raj and Kalelkar). Four other models assumed that the dispersion may be handled as though the LNG came from a continuous source (Burgess et al.; Esso; FPC; Kneebone and Prew). The technique suggested by SAI does not employ normal dispersion models and attempts a more fundamental approach.

All but the Kneebone-Prew method were discussed and compared in a detailed report by Havens, 1977. He chose a base-case spill of 25,000 m^3 of liquid LNG. The same report includes a selection of replies from the authors of most methods. In some instances the replies introduce new ideas and interpretations.

Each model except that of Kneebone and Prew assumes that initially the spilled LNG spreads radially and boils. However, the analytical approaches differ. Fay and Lewis decouple the spreading from the boiling; the former is described by Eq. (66), while the latter is based on cooling of a shield of ice. The actual pool dimensions do not play an important role in the Fay-Lewis model. The Germeles-Drake, Raj-Kalelkar, and FPC models treat the spreading and boiling of liquid with Eqs. (59) and (60). Burgess et al. use essentially an average evaporation rate computed from the spill volume and the time for evaporation as given by Eq. (51). The Esso model employs a constant spreading rate and a constant boiling rate (per unit area) until a limiting average pool thickness (which depends on pool diameter) is attained. The SAI treatment of pool boiling and spreading is not clear.

Even though different methods were used, as shown by Havens, 1977, the calculated size of the liquid pool and thickness of the vapor cloud at the end of the evaporation phase do not differ greatly in most cases (Table 21).

All but the Raj-Kalelkar, Kneebone-Prew, and Burgess et al. models next invoke a cloud resulting from the fact that the LNG vapor is denser than air. During this period, and depending on the model, air may be entrained and energy may be added from the underlying water, from the atmosphere, and from condensation of water in the atmosphere. Different criteria are used to define the end of this spreading phase; usually it ends when the cloud attains neutral buoyancy--but in the Germeles-Drake model, it ends when the spreading rate becomes equal to the local wind speed. Some of the results for a 25,000-m^3 spill, as given by Havens, 1977, are shown in Table 22.

The final step in the models is to allow the cloud to disperse downwind. Fay-Lewis, Germeles-Drake, and Raj-Kalelkar use an instantaneous, point-source dispersion relationship, whereas Burgess et al., Esso, FPC, and Kneebone-Prew employ a continuous-plume model. In some cases the large cloud area was treated by the use of a virtual source; in others the area effect was neglected, empirical equations were used, or a pseudo-line source was adopted. Two other variations in the dispersion calculations greatly affect the prediction of downwind concentrations. One is the choice of typical weather and appropriate dispersion coefficients, and the other is the rate of flow of vapor allowed to move downwind. The results from the dispersion phase are summarized in Table 23.

Each model has its particularities. Some seem reasonable; others are hard to defend. The very slow emission of vapor from the LNG cloud by heating (FPC model) is difficult to justify. There appears to be a real question as to the extent of air entrainment or mixing within the LNG cloud during the gravity-spread phase. The Germeles-Drake model assumes moderate mixing, and the SAI model is believed to predict considerable turbulence--so much, in fact, that the ultimate vapor-dispersion results are not highly sensitive to the prevailing weather.

The most important differences in the models, as noted above, relate to the choice of source strength and dispersion coefficients. The very small downwind hazard

Table 21 Liquid-Spread and Boiling-Phase Dimensions (25,000-m^3 Spill of LNG)

Model	Pool Diam, m	Vapor-Cloud Thickness, m	Time for Vaporization, s
Fay-Lewis	864	10.4	316
Germeles-Drake	765	13.1	270
Raj-Kalelkar	765	13.1	270
FPC	765	13.7	270
Burgess et al.	549	-	714
Esso	620.6	20.2	900

Table 22 Gravity-Spread of Vapor Cloud
($25,000-m^3$ Spill of LNG)

	Fay-Lewis	Germeles-Drake	FPC	Esso
Diameter at end of cloud spreading, m	1632	1900	1150	300
Height at end of cloud spreading, m	7.2	23	8.5	20.2
Mole % methane at end of spreading	100	22	100	22
Air entrained ?	no	yes	no	yes
Temperature of cloud after spreading, °K	294	255	151	-
Heat transfer to:				
Water	yes	yes	yes	yes
Air	no	yes	yes	yes
Condensation of water	no	yes	no	yes
Criterion for end of spreading	neutral buoyancy	equal to wind speed	neutral buoyancy	neutral buoyancy
Wind speed, mph	-	5	-	5

Table 23 Dispersion Results (25,000-m^3 Spill of LNG)

	Fay-Lewis	Germeles-Drake	Raj-Kalelkar	Burgess et al.	FPC	Esso	Kneebone-Prew
Continuous/point-source ?	Point	Point	Point	Continuous	Continuous	Continuous	Continuous
Virtual source used ?	*	yes	yes	no	no	no	no
σ_y	Eq. (73)	Figure 14	Figure 14	Figure 16	Figure 14	Figure 14	Eq. (95)
σ_z	Eq. (73)	Figure 15	Figure 15	Eq. (81)	Figure 15	Figure 17	Eq. (96)
Flow rate of vapor m^3/s	-	-	-	21,000	4,000	17,000	-
Atmosphere	very stable	F	F	D(σ_y)	D	C(σ_y)/D(σ_z)	-
Distance to reach LFL, km	28	18	26	40	1.2	8.3	-

*An empirical relation was used to force the concentration at the source to be unity.

distance predicted by the FPC model is due to the small vapor-flow rate, the choice of D weather, and the use of an elevated source. On the other hand, Burgess et al. use a large vapor-flow rate and quite low dispersion coefficients.

The two models that seem most plausible are those of Germeles-Drake and Esso. The use of a virtual source in the former and the empirical corrections in the latter are their weakest points. The fact that large LNG vapor clouds may control the local weather actually makes suspect any of the models that have been based on small spills. Only by thorough theoretical analysis or actual spill tests involving large quantities of LNG can the reliability of any of the existing models be assessed. For a more complete discussion of the existing models, the comprehensive report by Havens, 1977, is recommended. An earlier comparison was published by the British Gas Corp., 1975, Part 2.

IV. PEAK-TO-AVERAGE CRITERIA

A. BACKGROUND

LNG vapors generated by a spill on land or water disperse by mixing with air, but the methane concentration within the cloud is not uniform. Atmospheric turbulence is characterized by eddy circulations ranging in size from molecular motions to large storm systems. Consequently, the cloud contains local regions where the concentrations of methane are above or below the average. Vapor-dispersion models described earlier provide estimates only of average concentrations.

To establish criteria for safe dispersal of flammable vapors, one must consider the fact that certain portions of the vapor cloud may be flammable when average concentrations are below the lower flammable limit (LFL). In evaluating the flammable width of a dispersing vapor cloud, one is interested in two questions: (1) where do large (tens of meters) flammable pockets cease to occur?; and (2) where is the boundary where ignition will result only in local burning? In estimating maximum downwind travel for an unignited vapor cloud, one is concerned only with the distance at which major flammable pockets disappear.

Atmospheric mixing of vapor occurs in three dimensions. With a release near sea or ground level, the solid boundary suppresses vertical circulations. Lateral eddy motions produce concentration fluctuations as concentrated regions of a dispersing plume mix with air on the periphery. This type of fluctuation was reported by Burgess et al., 1975, for measurements downwind from a small, continuous LNG spill. Burgess observed variations in peak-to-average (P/A) concentration as high as 20:1. However, these tests were conducted in gusty weather, and fluctuations caused by meandering--lateral movement of the vapor-plume centerline--back and forth over the fixed sensors contributed much to the variability. In a vapor mass of large width, lateral mixing produces significant dilution only at the edges of the cloud. In central regions, lateral motions cause mixing only with vapors of approximately the same average concentration.

In this Section, it is shown that meandering fluctuations should be excluded from P/A criteria for maximum downwind travel of unignited clouds of LNG vapor. Even at the edges of the cloud, the predominant effect of meandering is the shifting of the cloud to different areas; the effect on the actual flammable width of the plume is less significant.

B. CONCEPT OF SAMPLE TIMES

Consider a point source that is continuous and steady. The material emitted is dispersed downwind. Even though the weather conditions do not change, and the wind direction and speed remain at some average value, the concentration of the emitted material is not constant when monitored at some downwind station. There are fluctuatons that appear to be random.

In some instances, the very long-time average is the concentration desired. However, in many cases it is important to be able to delineate peak concentrations, especially if they exceed greatly the average value. If one could express the true instantaneous concentration-time values mathematically, it would be relatively easy to determine peak concentrations and their frequency and duration. However, although we know that such an instantaneous concentration-time relationship exists, it can never really be measured. In all cases, there is a finite sampling time, which often can significantly affect the estimation of P/A values.

Still considering an ideal steady-state point source, assume that the true concentration-time relationship is as shown in Figure 29. If the sampling time is from 0 to t_1, some average value, $\bar{C}$, is obtained. This value gives no information about the microstructure of the concentration-time spectrum.

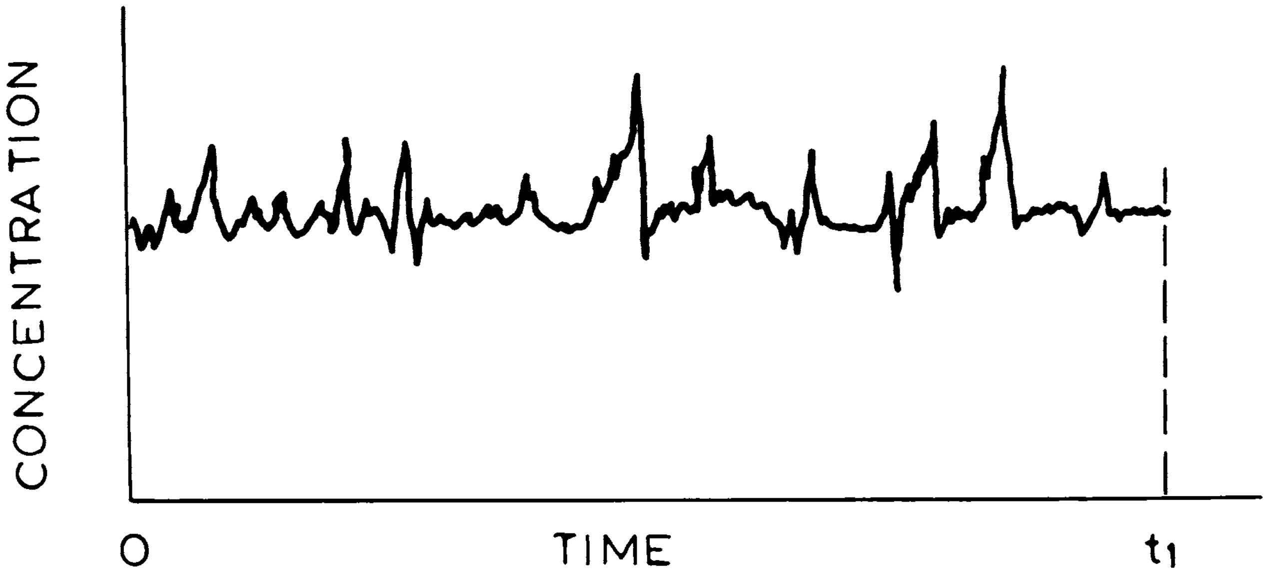


Figure 29 An Ideal Instantaneous Sensor Response

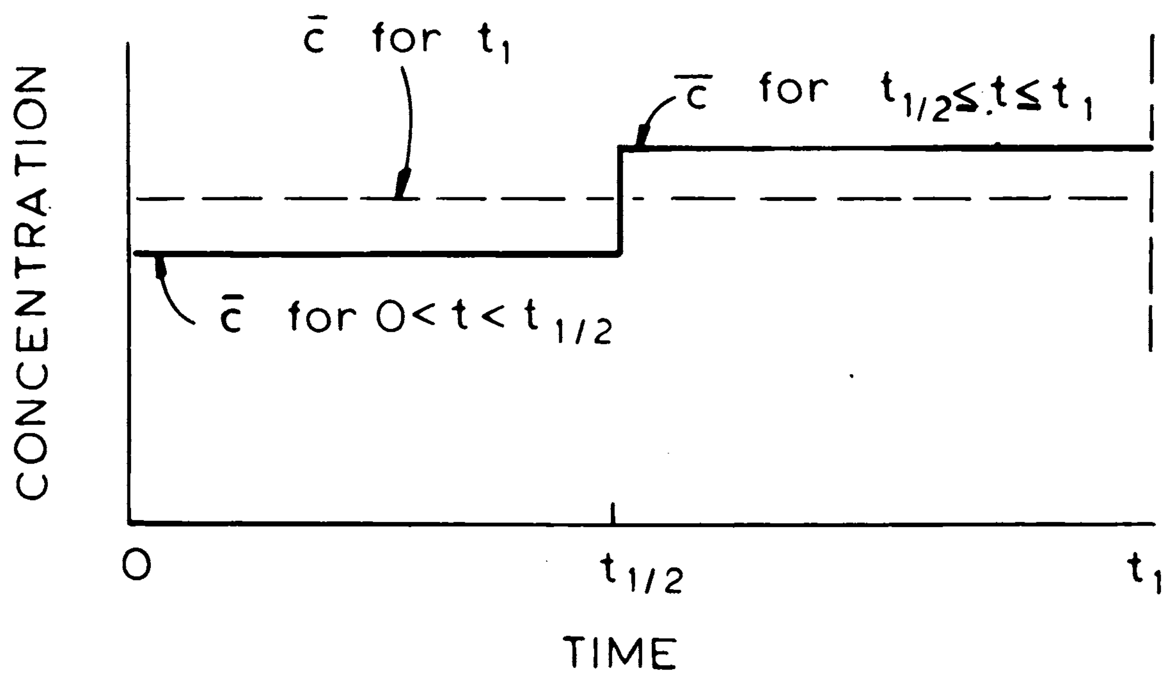


Figure 30 Average Concentrations for Two Sampling Periods

If the sampling time were halved, one would obtain two average concentrations, each over an interval $t_1/_2$. They might appear as shown in Figure 30. The average concentrations for the two sampling periods are somewhat different, although their average must still equal $\overline{C}$.

From Figure 30, the P/A value for $t > t_{1/2}$ and $t < t_1$ would be computed as:

$$\overline{C} \text{ for } t_{1/2} \leq t \leq t_1 / \overline{C} \text{ for } 0 < t < t_{1/2} \tag{98}$$

and would be > 1.

It is clear that, by this method, the P/A ratio may increase as the sampling period, t, decreases. Some authors have suggested that the relationship may be quantified by the proportion

$$P/A \propto t^{-p}, \text{ for } t > 0 \tag{99}$$

where p varies but is near 0.2 (Slade, 1968; Turner, 1969). Thus, given a P/A value for one sampling time, it is possible to estimate values for other times. Unfortunately, this procedure can never give the true P/A, but only a value relative to the base value chosen. Usually it is desirable to choose a long time interval and, over this time, assume P/A $\sim$ 1, i.e., the true average is indeed the one measured. Then, other P/A values are scaled from the choice. Other authors disagree with Equation (99) and indicate that it does not yield good estimates, although they, too, find that the P/A value increases as sampling time decreases.

Most sampling times have been greater than 10 s in experimental measurements of P/A ratios in LNG-vapor clouds. Values on the plume centerline, however, rarely exceed 3 to 4. At shorter sensor-response times, higher P/A values could be found. However, the concentrated pockets become smaller as instrument-response times are decreased. In a dispersing LNG-vapor cloud, the very small flammable pockets at the downwind extremities pose little danger.

C. PLUME MEANDER

The foregoing comments pertain largely to P/A values at the plume centerline. Experiments have indicated that much larger values may be found off-center. This would seem reasonable for point sources, because plume meander could significantly change the average values at points where the average concentration was much less than the centerline concentration. The same arguments would hold if there were a large difference in evaluation between source and sensor (Slade, 1968).

Where data are available, however, the product of the off-center P/A and the off-center average concentration is always less than the centerline P/A times the average centerline concentration. This result means that the highest peaks occur near the centerline, and we will confine our remarks to centerline values. Burgess et al., 1975, in fact, have reported P/A values of 20 for continuous point sources of methane when the instrument is located so that the plume can meander relative to it. Effects of plume meander, and puff meander for instantaneous spills, are depicted in Figure 31.

An example of the effect of meandering appears in Figure 32, which shows measured gas concentration downwind of a large LNG-spill test (AGA, 1974) into a dike 24.4 m in diameter. The concentration fluctuations at grade and at the centerline of the plume demonstrate P/A ratios in the range of 2:1 (the solid line superimposed on the data is based on the ADL vapor dispersion model, Section II-D-2). At $y = \pm 48.8$ m, the P/A ratios are extremely high, since the peaks are due to meandering of the plume centerline. It is clear from the data that peaks occur only on one side at a time. When predicting flammable areas, one does not wish to include variations caused by meandering of a plume of a known flammable area, since the meander only shifts the location of the flammable area without changing the extent of the flammable zone.

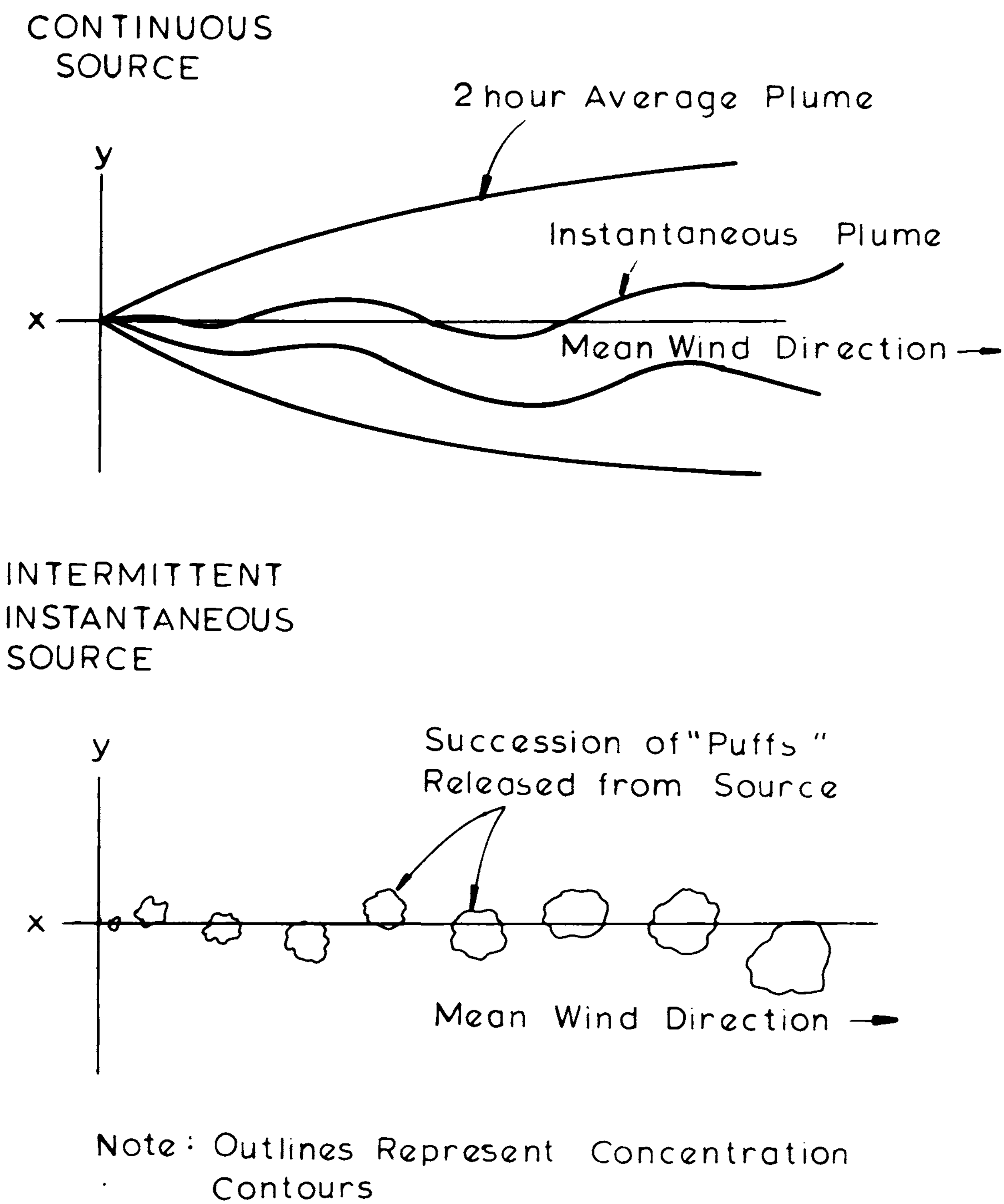


Figure 31 Illustrative Examples of Dispersion Showing the Effects of Meandering

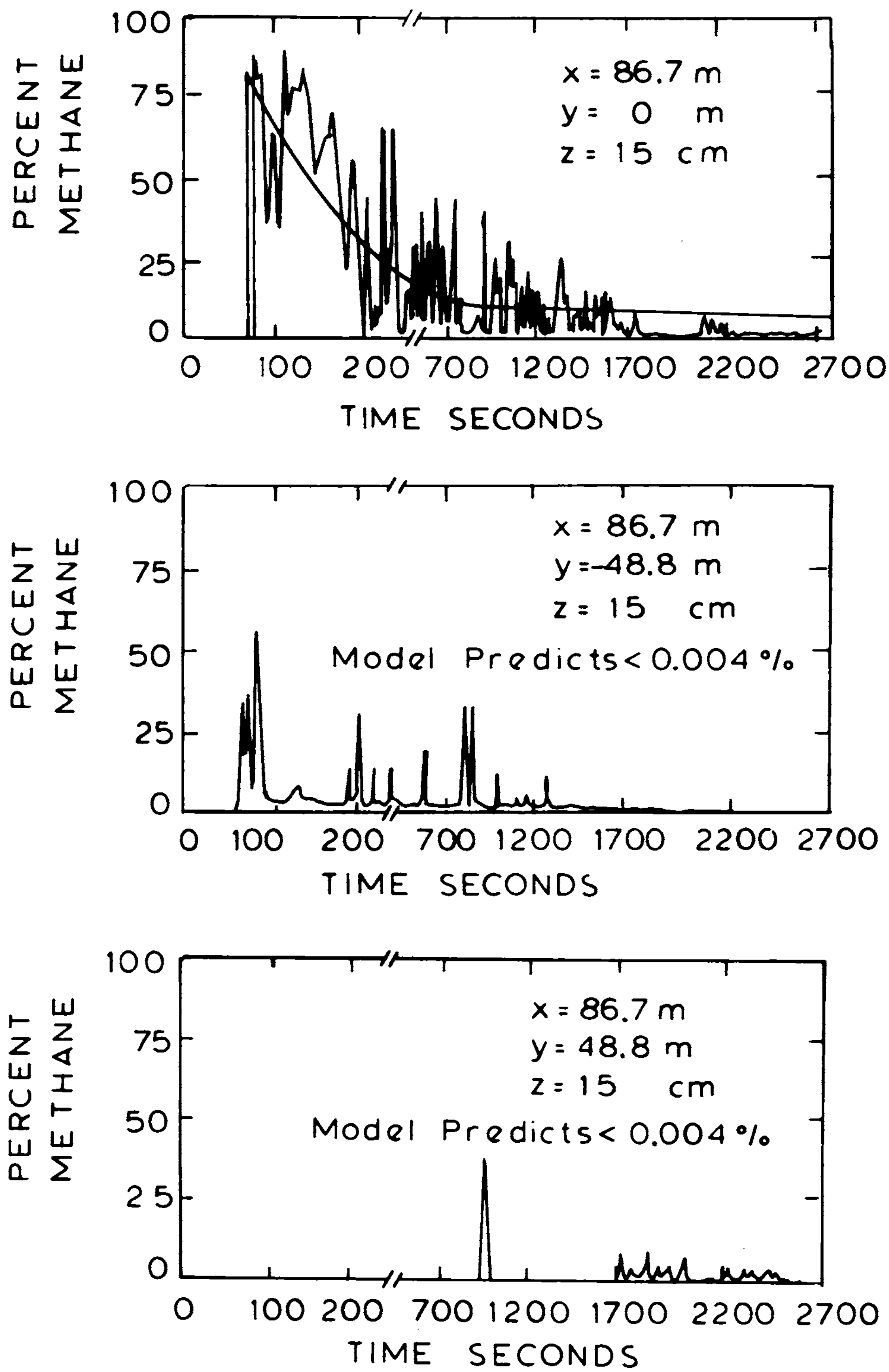


Figure 32 Example of Centerline and Lateral Concentrations at y = ± 48.8 m

D. AREA EFFECT

A most important point, which has often been neglected, is the effect of a large area on central P/A ratios. It would seem very logical, from our understanding of the physical causes of P/A values greater than unity, that if one replaced a small source by a very wide source, the P/A values at the centerline should decrease. In the central portions of such a cloud, lateral motions cause mixing among regions of similar concentration so that mixing inhomogenieties are greatly suppressed. Large LNG spills are more appropriately modeled as area (or line) sources; the net result is that the centerline P/A values should be much lower than those from a small source. Vertical fluctuations would be the major contributor to variations in concentration.

E. TRANSIENT SOURCES

Most LNG spills with vaporization are transient, and the strength of the vapor source varies with time. This fact introduces serious problems in defining and estimating a P/A value. Consider Figure 33. The downwind sensor for the methane vapor records zero until the leading edge of the plume arrives at the sensor. The concentration rises as the plume approaches and tails off as the plume strength decreases. Over the period of interest, the detected methane had been evolved at different rates. One could define an average concentration over the time interval, or one could define a time-dependent average which reflects the time average if the source has remained constant at the value it had at a particular time.

It is clear that the choice of one average or the other is very important in delineating P/A ratios. The time-independent average concentration is incorrect, although it is easy to determine from an experimental concentration-time profile. The time-dependent average concentration cannot be found from the profile, but must be inferred from theory or obtained from data in which the source rate is held constant at many different values and measurements made at each rate. The latter type of data is not available. Therefore, one must use dispersion theory to predict time-dependent average concentrations and compare these values with experimental profiles to estimate P/A ratios.

The approach used by Lewis, 1974, with the Esso spill-test data (Section III-C-1-B) to determine peak-to-average occurrence frequencies neglects the spill transient. Vapor clouds were generated from spills of 2 to 3 seconds'

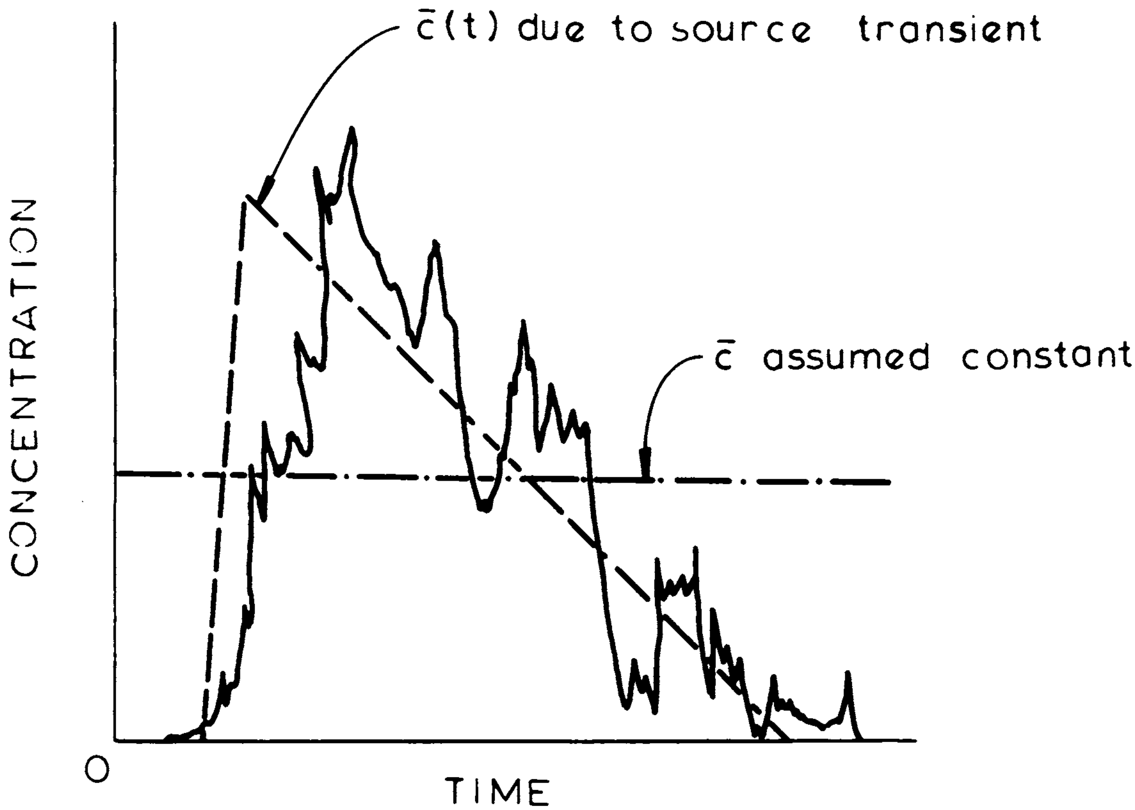


Figure 33 Influence of Concentration Transients on P/A Estimates

duration and passed over a fixed array of sensors. The sensors were at downwind points where concentrations near the lower flammability limit were expected.

Let us suppose that the Esso vapor cloud had a Gaussian or normal probability distribution of concentrations in the axial direction (Figure 34), as would be predicted by an instantaneous model for vapor dispersion. The transient response of a downwind sensor would be Gaussian. If we neglected turbulent fluctuations, and treated the Gaussian curve in the way that Lewis treated the Esso results, we would establish a C_{MIN} (minimum detectable concentration) and find the time, T, that the sensor registered concentrations above this value. Then we would estimate an average concentration

$$\bar{C} = (1/T) \int_{-T/2}^{T/2} C dt \qquad (100)$$

Lewis, 1974, shows the probability distribution of the times that normalized vapor concentrations exceeded $C/\bar{C}$. If we pick C_{MIN} so that 95 percent of the Gaussian transient is detected, we obtain the curve that is superimposed on Lewis' figure in Figure 35. If a still higher percentage of mass were detected, the computed distribution function for the Gaussian would be extended to higher and lower limiting values of $C/\bar{C}$. Therefore, in analyzing the Esso data, Lewis has not separated turbulent P/A effects from transient effects resulting from variations in concentration with time as a consequence of the spill transient itself.

Also shown on Figure 35 are P/A distributions reported by Ramsdell and Hinds, 1971. The curve represents conditions near the mean centerline of a continuous plume from a small source. The authors observe that while P/A ratios as high as 5:1 occur less than 1/2 percent of the time at the plume centerline, they are observed more than 6 percent of the time near the edge of the mean plume. Since we are concerned with maximum concentrations, the P/A ratio of interest is necessarily the one in the center of the plume.

Two other curves on Figure 35 were calculated from the correlations given by Csanady, 1969, for the probability of obtaining dosages greater than the average for instantaneous, ground-level spills. While a dosage (D) is an integrated sum of concentrations as the cloud passes over a point of measurement, there is clearly a reasonable analogy between $D/\bar{D}$ and $C/\bar{C}$. The two curves bracket the extremes discussed by Csanady. The steeper curve is for

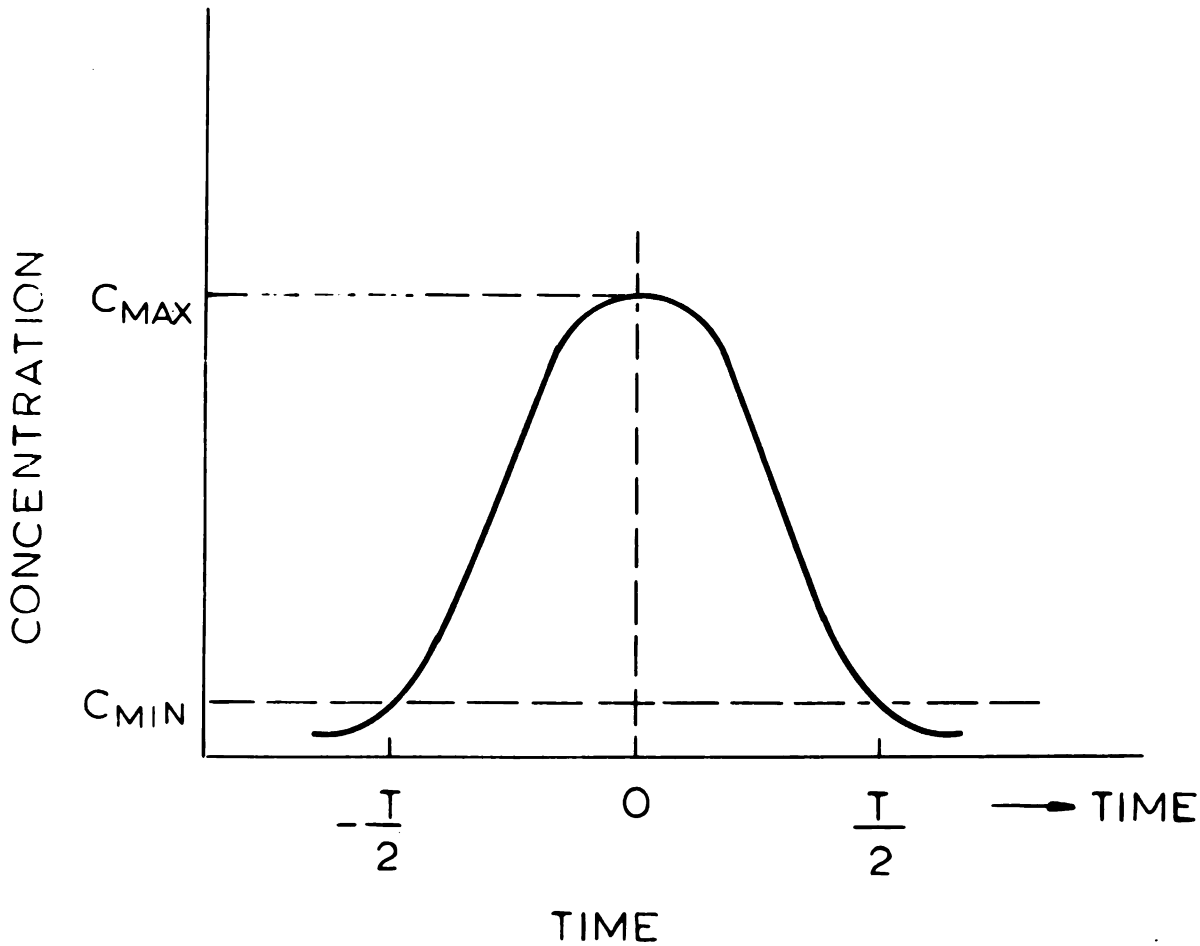


Figure 34 Sketch of Concentration-Time Response for a Gaussian Vapor Cloud at a Downwind Location

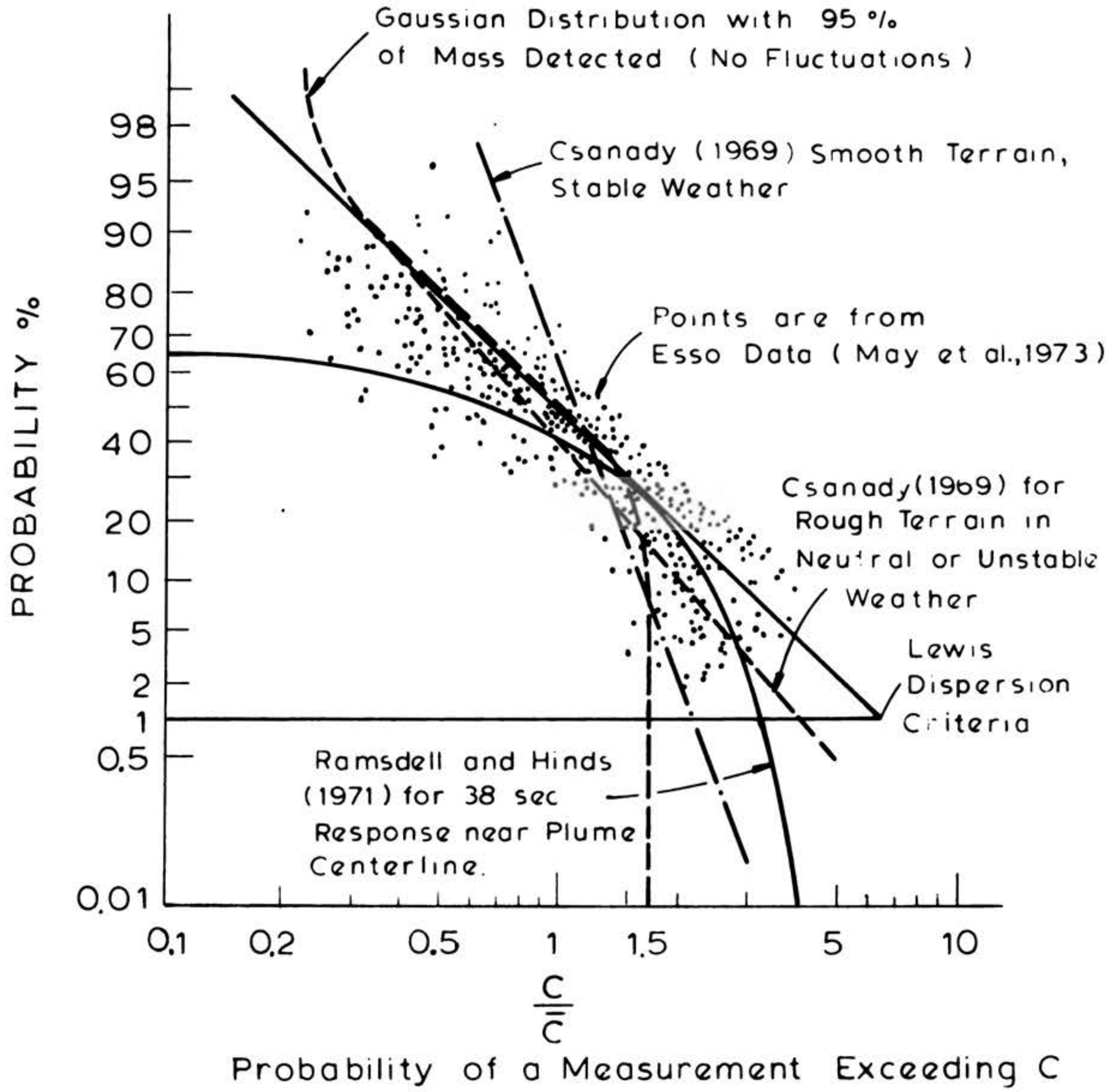


Figure 35 Comparison of the Lewis Analysis with Other Results

stable weather and a smooth terrain; the other curve is for rough terrain and neutral or stable weather. The former is probably more applicable for LNG spills on water when estimating the downwind P/A ratios.

The significance of Csanady's results is the small probability that dosages (or concentrations) will differ much from the mean if the weather is stable and the downwind terrain is smooth. It should also be noted that these results are independent of the plume meander, because Csanady employed the plume centerline as a reference rather than a fixed coordinate oriented in the mean wind direction.

F. CONCLUSIONS

- Experimental studies of P/A values in a dispersing plume have almost always used small or point sources. With a large-area source, centerline P/A values would be expected to be much less. The large-area source is more typical of an accidental LNG spill.

- Point-source P/A values are lowest on the plume centerline, at the same elevation as the source, and in stable weather. With these restraints, P/A values would rarely, if ever, exceed 3 or 4. This conclusion does not agree with Burgess et al., 1975, who measured larger values of P/A. In the Burgess study, however, meandering of the plume undoubtedly increased P/A values, especially since the experiments were conducted in B_2 gustiness. With C, D, E, or F weather, much lower P/A values would be expected (Slade, 1968).

- P/A values increase as sampling time decreases. Sampling times for methane vapor are normally in the range of three to five seconds.

- Caution must be used in computing P/A values for transient spills. The technique employed by Lewis, 1974, is in error and, upon extrapolation, yields significantly higher probabilities for high P/A values than those reported by Ramsdell and Hinds, 1971.

- Rough terrain, trees, buildings, etc., can increase experimental P/A values. For LNG spills on water, however, these effects would not be significant. P/A values increase with atmospheric turbulence. The lowest values result from stable atmospheres, for which the dispersion time is greatest, i.e., it is an exaggeration to superimpose a P/A value for gusty weather on a downwind-travel distance computed for stable weather.

• For large LNG-vapor clouds in stable or neutral weather, P/A values above 2:1 would be expected near the center of the cloud only about 10 percent of the time. Higher peaks would occur, but at much lower frequency. At a 1 percent occurrence level, a P/A of 3 would be appropriate.

• The P/A ratios of around 2:1 suggested from the Esso results and also from land-spill tests (American Gas Association, 1974) seem to be realistic for assessing LNG hazard zones for large spills on water using conventional vapor-dispersion models.

NOTATION

a	parameter in Eq. (9), $m/s^{1/4}$
A	area, m^2
b	picket width, m (Figure 10)
C	heat capacity, kJ/kg°K
C	concentration, kg/m^3 or dimensionless if expressed as a fraction
C_t	concentration average over time t
$\bar{C}$	average concentration
C_y, C_z	dispersion parameters for Eqs. (15) and (16), m^n
d	diameter of pool, m
D	dosage, kg•s
F	boiling parameter $(k\rho C/\pi)^{1/2}\ \Delta T/\Delta H_v$, $kg/m^2s^{1/2}$
g	acceleration due to gravity, 9.801 m/s^2
h	height of pool or cloud, m
H	height of source, m; height of vapor cloud
H'	corrected height [Eq. (35)]
ΔH_v	enthalpy of vaporization, kJ/k mol or kJ/kg
k	thermal conductivity, W/m°K
K_x, K_y, K_z	dispersion parameters, m/s
M	mass of vapor cloud, kg
$\dot{M}$, $\dot{M}_e$	boiling rate, kg/s
$\dot{M}_\ell$	leak rate, kg/s
N_{ST}	Stanton number

n	parameter in Eqs. (15) and (16), dimensionless
p	picket spacing, (Figure 5); power-law exponent in Eq. (19)
P/A	peak-to-average concentration
q	vapor flow rate, kg/s
$\dot{q}$	boiling rate, kg/m^2s
Q	source, kg; heat transfer terms in Eq. (79)
$\dot{Q}$	source, kg/s
$\dot{Q}_L$	line source, kg/m·s
$\dot{Q}_{ij}$	source from matrix element ij, kg/s
r, R	radius, m
t	time, s
T	temperature, °K; also time, s
ΔT	temperature difference, °K
u	pool velocity of spreading, m/s
U	wind speed, m/s
V	volume, m^3; V_o, liquid spilled; V_v, vapor cloud
w	width, m
$\dot{W}$	mass flow rate, kg/s
x	downwind distance, m
y	lateral distance, m
Y*	parameter in Eq. (27)
z	vertical distance, m
Z*	parameter in Eq. (22)

Greek

α	entrainment coefficient
δ	thickness, m
Δ, Δ_v	density parameter, Eqs. (38) and (67)
ρ	density, kg/m^3
τ	time, s
θ	angle, degrees
σ_x, σ_y, σ_z	dispersion parameters, m
Σ_y, Σ_z	modified dispersion parameters, m [Eqs. (30) and (31)]

Subscripts

b	boiling point
I	instantaneous
a, air	air
e	entering
l	leaving
L	liquid
o	original
ov	overflow time
vm	vapor, maximum
v	vapor

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APPENDIX C

SLOSHING EFFECTS IN LNG CARGO TANKS

A. HISTORY

Sloshing of liquid cargo or ballast water became a problem when oil tankers became larger and the size of individual tanks increased correspondingly (Abrahamsen, 1962; Hagiwara, 1963). In the late 1960s, ore-bulk-oil (OBO) combination tankers reached the critical size (Olsen, 1973), and Bureau Veritas planned a program of systematic research. This program was modified at Gaz Transport's request to address sloshing of LNG in membrane tanks. The request stemmed from two incidents aboard the 71,500-m^3 LNG carriers Polar Alaska and Arctic Tokyo, which were operating on the Alaska-Japan route.

In December 1969, on Polar Alaska's first ballast trip, electric cables broke in tank #1. The tank was about 20 percent full, and its contents were used to cool the other tanks. Tests by Det Norske Veritas on a model tank subject to roll showed small overpressures, so partial filling was resumed after cable supports were reinforced on both ships.

In September 1971, Arctic Tokyo, operating at exactly the same ballast condition and tank-filling ratio, encountered a very heavy sea resulting from two typhoons. Gas was detected in tank #1 intermediate space upon arrival. The Invar primary membrane was found to be deformed at several points on the forward bulkhead at about the height of the liquid level and close to the starboard corner. In one of these deformed areas, a manual weld had fractured.

The Bureau Veritas tests were performed in Liege, Belgium. They led to a more thorough understanding of sloshing phenomena, including resonance and wave shapes occurring at various filling ratios, but the overpressures measured were still too low to account for the damage observed on the Arctic Tokyo. However, tests by Sogreah-Alsthom in Grenoble showed that, in boiling liquids, the pressure peaks were enhanced by a factor of 2 to 3 when using a water-air emulsion and of 6 to 10 when using a water-water vapor mixture. The latter was associated with bubble-collapse shocks, which are well-known in cavitation.

As a result of such tests and others performed on the Technigaz membrane, conservative filling restrictions were imposed on membrane tanks. The restrictions were: maximum heel, 5 percent of tank length; minimum fill, 90 percent of tank height as a rule, with case by case modifications allowed (e.g. 10 -90 percent exclusion on the Ben Franklin) after due theoretical and experimental justification. Freestanding tanks were able to avoid such filling restrictions, either because of their shape (spheres) or their heavy framing and swash-bulkheads (Conch rectangular). The matter had been felt to be settled when an incident in March 1978 affected the upper corner bulkhead of the El Paso Sonatrach, a 125,000-m^3 vessel of the Invar (Gaz Transport) membrane technique, and drew renewed attention to the sloshing phenomenon. The U.S. Coast Guard currently has a research program on the subject at Southwest Research Institute.

B. RESULTS OF THE FRENCH TEST PROGRAMS (Gaz Transport, 1977)

The results of sloshing in LNG tanks are difficult to predict accurately because of the random effects introduced by bubble-collapse in a boiling liquid and by the localized character of peak pressures. Even the simpler underlying resonance phenomenon can be quite complex, as it requires the synchronism of:

(a) The natural frequency of liquid surface waves in pitching, heaving, rolling, or any combination. This frequency depends on:

- The shape and internal structure of the tank
- The filling height of the liquid and its density and viscosity
- The excitation motion: frequency, amplitude, and center of rotation

(b) The natural roll and pitch-heave periods of the ships, which depend on:

- The hull form and the loading condition of the vessel
- The ship speed
- The wave-frequency spectrum and orientation

At very low-frequency excitation motion, the liquid surface remains horizontal. At very high frequencies, the liquid surface stays parallel to the tank bottom at low filling ratios. At high filling ratios, the liquid

surface goes through a series of declining resonance modes separated by stages of little motion vis-à-vis the tank bottom as the excitation frequency increases. The first mode of resonance is of interest in the typical 7-second (pitch) to 15-second (roll) periods of normal ship excitation.
Despite these drawbacks, the model tests have provided some quantitative answers. For example, in the case of tank #1 of the Arctic Tokyo:

- A 5 percent ratio gave a resonance overpressure 1/55th of that at 20 percent filling ratio. This result appears to be linked to the fact that, below 10 percent filling ratios, the resonance waves are of the breaking type, while at filling ratios between 15 percent and 60 percent the resonance waves do not break in their back-and-forth movement. However, the waves splash in the corners, where overpressure has been found to be 50 percent greater than at mid-bulkhead.

- At filling ratios of 90 percent or more, overpressures disappear as the resonance wave becomes stationary (its length equal to twice the tank length) and liquid velocity is parallel to the tank walls at the transverse bulkhead.

- The foregoing results concern pitching, and rolling is much less critical: the rotation axis is in the tank, and for filling ratios outside the 10 to 90 percent range, sloping walls dampen completely the much reduced overpressure.

Computer models and tank tests have been combined to estimate the critical range of filling ratios in spite of the above-mentioned scaling difficulties, for example:

Ship capacity, m^3	71,500	125,000	130,000
Lower filling ratio, %	10	19	23
Higher filling ratio, %	28	54	78
Tank length, m	23.2	33.2	36.8

C. CONCLUSIONS AND RECOMMENDATIONS

The complexity of the sloshing phenomenon, and the incident of March 1978 on the El Paso Sonatrach, suggest that further research is warranted as membrane tankers, particularly of the Gaz Transport Invar technique, are received or built in the U.S. It is expected that U.S.-built tanks, if any, will use somewhat stronger supporting insulation: 3-D reinforced polyurethane instead of perlite-filled plywood boxes, but the membrane itself has suffered on the Arctic Tokyo.

Suggested areas for investigation include:

- Effect of rolling and heaving in combination with the main pitching excitation

- Effect of boiling liquids of different composition (e.g., liquid methane versus propane-rich LNG)

- Attention to local effects which may require larger model tanks and/or instrumentation of shipboard forward tanks

- More stringent interim filling restrictions on the technique(s) shown to be particularly prone to sloshing damage.

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