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F. W. MURRAY
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W. S. KING

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PREFACE

One of the major new programs emerging to satisfy the nation's requirements for energy is the importation of natural gas in liquefied form. This new industry will require an entirely new technology, with attendant hazards that might well differ both in nature and magnitude from those of related industries, such as the shipping of crude oil. Since plans for the construction of large tankers and port facilities are in an advanced stage, a program to assess the hazards is an immediate necessity. Because hazard-assessment activities already undertaken have been conducted on much too small a scale and have omitted important factors, many of these projects and facilities have been marred by controversy over their safety.

As a part of Rand's continuing interest in public policy affecting energy programs, the work reported here was carried out under the Corporation's own sponsorship, primarily from April to December 1974. The study was meant to provide a brief overview of the field, recommending fruitful areas for further research. It is hoped that the report will spur the development of a comprehensive and independent program to assess hazards that may attend the importation of liquefied natural gas.

Much of the material in the text has previously appeared in the following Rand papers:

Possibilities and Probabilities in Assessment of the Hazards of the Importation of Liquefied Natural Gas, by D. L. Jaquette, The Rand Corporation, P-5411, April 1975.

On the Fluid Mechanics and Heat Transfer of Liquified Natural Gas Spills, by W. S. King, The Rand Corporation, P-5396, June 1975.

Atmospheric Dispersion of Vaporized Liquefied Natural Gas, by F. W. Murray, The Rand Corporation, P-5360, February 1975.

Phenomenology of LNG Accidents: A Selected Bibliography, by Ines Siscoe, The Rand Corporation, P-5295, September 1974.

This material has been revised and integrated into the present report to provide a single up-to-date publication covering all aspects of the investigation.

SUMMARY

An increasing demand for natural gas combined with decreasing rates of domestic production has led to plans for importing large quantities of natural gas from Alaska and several foreign countries. To transport the gas in tanker ships, it is liquefied by cooling it below its boiling point, which at normal atmospheric pressure is about 111 K (-259°F). Handling large quantities of this highly volatile cryogenic substance will entail unique hazards of a nature and scope not previously encountered in large-scale transportation of hazardous materials.

The report lists and discusses some probable causes of accidental spills of liquefied natural gas (LNG) and the hazards surrounding them, and describes methods of estimating the probabilities of major accidents. It shows that the state of knowledge indicated by the LNG facility environmental impact statements and other technical reports currently available is deficient in a number of critical areas.

When a spill occurs, a decision as to the proper course of action will depend on knowledge of the rate of vaporization and the way the vapor cloud interacts with the atmosphere. Since the models heretofore used for these phenomena are inadequate for large spills, the report suggests ways to develop better models for the fluid mechanics and heat transfer of a pool of LNG on water and for atmospheric dispersion of the vapor cloud.

One conclusion of the study is that even though the physical models available are inadequate and the history of shipment of LNG is as yet too brief to develop meaningful statistics, the evidence indicates that serious hazards will exist. The prudent course of action would be to locate all facilities for handling LNG at remote sites until better estimates of risk can be made and determined to be low. These better estimates might derive from better modeling, from the accumulation of experience, or, more appropriately, from a combination of the two. Unfortunately, it will be some years before adequate models can be developed, and even longer for proper experiments to be conducted and data to be

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collected to validate these models. Meanwhile, the fact that current plans for handling LNG are not limited to remote sites makes it possible that experience may be accumulated at enormous cost.

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I. INTRODUCTION

The rapid increase in demand for energy in the United States, the progressive depletion of domestic sources of natural gas, and the failure to develop increased quantities of such substitutes as petroleum, nuclear power, and others have led to proposals and plans to import large quantities of natural gas from Alaska and several foreign countries. Transporting natural gas involves refrigerating the gas until it liquefies (at approximately 111 K or -259°F), pumping it aboard specially designed and insulated tankers, transporting it to a destination port, and pumping it to a shore facility, in which it is again vaporized by warming and fed into the pipeline system.[1] While in transit, the liquefied natural gas (LNG) is kept near atmospheric pressure. Because of insulation the amount of boil-off is small; what occurs can be used to power the tanker.

One of the major hazards of this procedure consists of spills, which can occur either on land in the port facilities, at sea, or in the harbor, especially during transfer procedures. Spills can be caused in countless ways: ship collisions and groundings, sabotage, natural disasters, design faults, construction or fabrication error, or human error, for example. The source, the cause, and the location of the spill determine the subsequent progress of containment and control.

At sea or in the harbor, a tanker can cause a release on water of

1. Cold dense vapor through safety vents in the event of overpressurization of the LNG tank.
2. LNG itself through piping, hoses, vents, compressors, or pumps.
3. LNG through a crack in the tank. Thermal stress failure, fabrication defect, collision, and sabotage are all possible causes.
4. LNG from all tanks. Sinking would cause rupture of tanks as a result of the heating of the LNG.

Shore facility release of LNG on land can be caused by

1. Failure or mismanagement of piping, hoses, pumps, etc.
2. Structural tank failure.
3. Overpressurization, resulting in release of cold dense vapor through safety vents.

Once LNG spills, it evaporates and produces a cold dense cloud of gas (largely methane) that can be transported by the winds and mix with the atmosphere. Unless there is sufficient admixture of oxygen, the gas cannot burn, but in atmospheric concentrations of about 5 to 14 percent the gas becomes highly flammable.

Although a nonburning vapor cloud can produce biological damage by freezing and by asphyxiation, the major hazards to property and people are ignition and the resulting fire, which usually burns back to the source. Virtually no effort has been made to determine where and when a cloud of vaporized LNG might ignite. Many researchers have assumed that ignition would occur during any significant release of LNG, but that it would is in fact uncertain. No research has addressed this important open question.[2] A burning spill is of almost no hazard to any distant population, but it obviously destroys or significantly damages the ship or facility from which the spill occurred. If a spill has not already become accidently ignited, those charged with maintaining safety must decide to ignite or not to ignite, weighing the expected damage to the facility if they burn against the possible damage elsewhere should the vapor cloud drift away and then somehow become ignited. Speculatively, one can imagine a situation in which the cloud is moving into a populated area, and a decision is made to sacrifice the ship and/or facility by igniting the spreading cloud.* Possibly because there has been no conclusive research on the dispersion of LNG vapor cloud, the burn/no burn decision problem has not been formally addressed.

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*A much simplified version of the necessary decision model implied here is one that takes into consideration spill geometry (size, rate, etc.), weather factors, and local geography and population densities, and, in some real-time decision mode, concludes that the expected loss (or some utility of loss) will be better by controlled ignition of the cloud than by no external control.

The dispersion problem has two major parts: the rate at which vapor is produced from spilled LNG and the way in which this vapor is transported by the winds and mixed with the atmosphere. Insofar as these matters have been studied, it has been in the framework of other technologies, such as oil spills and atmospheric pollution from factory stacks. However, oil spills do not involve boiling, and stack effluents are not cold, dense gases, so it would appear that LNG spills differ sufficiently from these other phenomena to warrant a new approach to the subject, emphasizing the unique features of LNG and its vapor cloud. Some suggested lines of research are discussed elsewhere in this report. The degree of hazard resulting from a spill cannot reasonably be assessed without reference to the physics of vaporization and atmospheric dispersion; however, we shall first consider the possibilities and probabilities of accidental LNG release, for no hazard exists unless that occurs.

II. POSSIBILITIES AND PROBABILITIES OF LNG SPILLS

Several paths of analysis can be taken to determine the risks of any LNG operation. Virtually all approaches to risk assessment claim to yield an upper bound of risk; that is, they state that the probability that a certain class of accident will happen is no larger than so much, or that the average fatality rate is less than so much. Decisionmakers want these upper bounds, which state that the risk cannot be greater than some given number. However, important components of the risk can inadvertently be omitted, models of the physical phenomena can be inappropriate, data parameters can be inaccurately estimated, etc., all of which can easily increase the true risk of any operation well above the claimed upper bounds. The weight placed by decisionmakers on such a study of operational risks must consider the level of effort and the completeness and accuracy of the analysis. In assessing risks of LNG operations, the best we could conclude is that not enough evidence has been collected to prove that it is so unsafe as to warrant its abandonment nor does enough evidence exist to prove its safety.

Accident scenarios for various situations that might occur, together with the associated probabilities, are excellent descriptors that can be used as either inputs or outputs to risk assessment. Conditions that might bear upon the hazard assessment include location of the spill (land or water), rate of release, and quantity of release.

On land most facilities will be diked for containment and control of spills, which will limit the area available for evaporation; the low heat capacity of the underlying soil and loss of heat by the top layer of the soil through freezing will cause boil-off to proceed slowly. The use of a chemical foam blanket can further reduce the rate of boil-off, so it is conceivable that the parameters governing boil-off could be controlled in such a way that the vapor cloud could warm sufficiently to have positive buoyancy and thereby be dispersed harmlessly upward through the air.

Spills on water are more complex than those on land. First, the pool of LNG is unconfined, and can spread into a thin layer of large area. Second, the high heat capacity of water transfers heat more rapidly to the LNG. Both circumstances lead to more rapid vaporization. These processes are considered at greater length in Section III.

Earlier thinking[3] was that the total quantity of release was a better determinant of hazard, or at least an adequate and much more readily available determinant, than rate of release. However, the rate of vaporization is certainly a central factor in the atmospheric dispersion problem, and a careful study of the rate of evaporation (as is advocated in Section III) should take into account the rate of release. Nevertheless, it is probably a valid procedure, at least as a first approximation, to classify the hazard of a spill in terms of its magnitude.

The magnitude of a spill can vary from the entire capacity of the ship (130,000 m^3 is currently the maximum size planned) and that of the entire shore facility (Pacific Lighting's proposed Los Angeles Harbor facility is to have two 550,000-bbl tanks or about 175,000 m^3 maximum in storage) down to scarcely measurable quantities. A careful analysis could be conducted to determine a classification system based on the size of a spill and its potential hazard. A probability distribution in terms of yearly (or per trip, etc.) rates by release size, category, and origin is desirable, but virtually inestimable at this level of refinement from information now available.

METHODS FOR ESTIMATING SPILL PROBABILITIES

History of LNG Operatons

One straightforward way to estimate spill probabilities is to use the available operating experience of LNG tankers and facilities. The history of the LNG vessel operations begins in 1959 with the *Methane Pioneer*. By 1974 there were 14 vessels in the world LNG fleet with combined experience of more than 800 voyages. Throughout the 16-year history of such operations there have been no significant accidents.

Such a simplistic approach would be in error for three reasons. First, during these 16 years of operating experience, the average size of the ships was 50,000 m^3, about one-third the capacity of currently planned ships. Using the available data to make safety statements about the new tankers is an extrapolation that has not yet been justified. It can be argued that the bigger ships are safer because of improved technology and operating standards, or

that they are more dangerous because of a lack of maneuverability, certain engineering design features, heavier traffic, etc. No definitive case has been presented to indicate the accuracy of these predictions.

Second, the lack of any significant LNG accident during this period is consistent at some specified confidence level with a wide range of probabilities. An Environmental Impact Statement (EIS)[2] prepared for the Staten Island LNG terminal by the Federal Power Commission (FPC) estimates 2.144×10^{-7} as the probability for a serious LNG accident in each trip. If we accept that figure, the probability of 800 voyages with no accidents is 0.99983.* At a much larger probability, of say 2.144×10^{-4}, the probability of no serious accident in 800 trips would be 0.8424. Thus, the actual record is also consistent with this larger probability with a confidence limit of 84 percent. Simply stated, the 800 accident-free voyages do not represent enough data to justify making estimates in this range of accident probabilities near zero. Testimony presented by Professor Fairley in hearings held by the FPC on the EIS pointed out that "the record, while *consistent* with very low values, does not prove that the values *are* low."[4]

The third reason that existing LNG operational data do not apply is that these probabilities are site-dependent. Each harbor has unique characteristics (meteorological, geographic, oceanographic, etc.) as well as different competing traffic of tankers, cargo vessels, fishing boats, and so forth. Any estimates drawn from world operations of similar vessels must be supplemented by information for a particular locale, and decision-makers must have estimates of these probabilities in choosing among various candidate sites.

History of LPG Operations

A second set of data which may be relevant to estimating LNG accident probabilities is the operating history of the 120 or so liquefied petroleum

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*Accidents of a serious nature are defined in the EIS as "undesirable events." Such an event includes but is not restricted to an accident causing 300 deaths. If we suppose that serious accidents occur independently per trip with a probability p, then the number of such serious accidents is a sum of Bernoulli trials, which is a binomial random variable. The probability of exactly k serious accidents in n voyages is $p^k(1 - p)^{n-k}\binom{n}{k}$.

gas (LPG) carriers operating throughout the world in 1972. While some of the same technology and operating care are presumably used in LPG tankers, the average LPG tanker is smaller than the existing LNG tanker (and about one-fourth the displacement of the LNG tankers planned for service in the next few years). Thus, relevant operations and factors must be carefully studied before any release estimates are transferred to LNG operations. The hazards of LPG transportation differ from those of LNG transportation in two major respects: (1) vaporized LPG, even when warmed to ambient temperature, is heavier than air, does not mix well, and tends to stay near the surface and move into low areas; and (2) ordinarily storage tanks are pressurized in order to maintain the LPG in liquid form at ambient temperature. Because there are no cryogenic problems as with LNG, the ships are quite different in construction and operation. Hence statistics from LPG carrier operations can be criticized as being both inadequate and inapplicable.

History of Oil Tanker Operations

The approach taken by researchers preparing the Staten Island EIS[2] was to use the considerable existing data on crude oil spills. Files on the nature of accidents and the frequency and size of tanker landings are available from the U.S. Coast Guard, the Maritime Administration, Army Corps of Engineers, and individual harbor commissions for each of the harbors in the United States. Crewmen and operators on LNG vessels will come from the oil tanker industry, and ships are of similar size and shape, except for draft (60 ft or more for supertankers versus 30 ft for LNG tankers).

There are, however, differences between oil spills and LNG spills that make extrapolation by analogy risky. As shown in Section III, the difference in evaporation rates makes the fluid dynamics of oil slicks and LNG spills on water substantially different. In addition, there are special problems unique to an LNG spill. The release of cryogenic liquid into contact with the hull may cause brittle fracture, thus further aggravating the problem and accelerating the release. Because of the known hazard, small releases may be uncontrolled and worsen the situation as the crew panics or abandons

ship.* Also, if a ship carrying LNG is disabled or grounded, it is unlikely that the cargo can be offloaded into another ship.

Additional equipment, training of the men on board, and general emphasis on safety in design, construction, and maintenance will undoubtedly help to improve the safety of operating LNG import facilities, but whether this makes a hazardous operation just as safe as the operation of crude oil tankers, or more safe, or less, is a completely open question. The Staten Island EIS used the analogy with crude oil tankers to claim that engineering design improvements reduced the probability of a serious LNG event by a factor of five. Furthermore, the fact that the tanks do not run the whole length of the ship (only two-thirds) yields another factor of 1.5. Only one collision in one hundred was judged to produce a serious LNG spill. Improved navigation and positive control (such as air traffic control) over movement of LNG vessels were predicted to decrease accident probabilities by another factor of five. Unfortunately, the effects of these improvements on accident probabilities are not detailed by the EIS and appear to be based on intuition. In contrast, the U.S. Coast Guard has predicted that additional precautions taken within harbors to put all ships under a traffic control system will reduce collisions and groundings by a factor of only two.[5]

Oil operation spill sizes averaged 13,000 bbl, considered a spill of high magnitude. Yet, a majority of spills (86 percent) contributed but 17 percent of the total release,[6] which indicates the distribution of spill size is skewed to the right, with many more small spills and a few very large spills significantly larger than the average. If this skewed performance can be transferred to LNG operations, one could expect most spills to be quite small, with only a few catastrophic ones. Based on the skewed distribution, we might want to aggregate LNG spills of 1000 m^3 or less together as minor spills and categorize those above 1000 m^3 as major spills.

As with LNG, crude oil statistics are fraught with the difficulties already mentioned. To date no significant attempt has been made

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*Noel Mostert, in his book *Supership* (Alfred E. Knopf, 1974, pp. 376-77), describes an LPG tanker collision after which the crew abandoned ship even though no fire or sinking actually transpired. The empty ship drifted ashore. Later during salvage and transfer of the cargo a hose sprang a leak and a vast cloud of gas formed. The captain of the ship receiving the gas cargo steamed away, rupturing hoses and pipelines, thus increasing the hazard.

to justify element by element the needed comparisons. With little else to go by, analysis of the appropriateness of such comparisons seems crucial to estimating LNG release probabilities.

Underwriting Experience

Finally, one last source of an estimate of these elusive probabilities is the insurance industry. Insurance rates for oil tankers, when compared with the rates for LNG tankers, should indicate how the insurance underwriters have weighted the existing safety record of oil tankers with a projected record of LNG tankers. In contacts with underwriters in the Oil Insurance Association we find that LNG is viewed as a "shade more hazardous."[7] Rates are quoted in yearly costs as a percentage of dollar cost of the vessel. The rate per dollar of tanker value per year for LNG tankers is about 80 percent of that for crude oil vessels, but because each ship is from 50 to 100 percent more expensive, the total premium is higher. Rates are apparently based on educated guesses made by experienced insurance executives with the help of reports from consultants and the oil industry. Many of the safety features incorporated in the design of shore facilities and tankers have been added because of the insurance industry studies and recommendations of their consultants.

In any insurance business the greater the uncertainty of the risk the higher the premium. During the early phases of operation of LNG importation facilities, rates are likely to be higher than indicated by simple expected values. As operating experience is gained and more data are seen, insurance rates will be adjusted to reflect more accurately the expected loss rates (i.e., the true probabilities or risks). Because early estimates indicate LNG to be a "shade more hazardous," we must conclude that the insurance industry expects the loss rate in dollar terms to be only slightly above that of crude oil transportation.

It should be noted that the rates mentioned are rates for losses to the insured, such as the material and construction costs of a facility, but do not include liability for property losses or personal injury to the public. Study could be made of the LNG terminal operator's liability insurance to estimate the potential liability risks for effects of spills beyond the

perimeter of the facility. If, indeed, the hardware loss rate in dollar terms is nearly equal to the crude oil loss rates and (as has been suggested by both industry consultants and intervenors) spills that damage the hardware present an unusually high risk to surrounding property and inhabitants, then one must conclude that remote siting of LNG facilities is the only rational choice in light of the high potential for property damage and loss of life.

SABOTAGE AND TERRORISM

One of the most important elements of safety analysis of LNG operations has for the most part been ignored by researchers. Sabotage and acts of terrorism have, unfortunately, become significant possibilities even in the United States. Who would have thought in preparing an EIS for commercial jet aircraft in the late 1950s that the hijacking of jet aircraft would occur as frequently as it did in the 1960s? The Staten Island EIS virtually ignores this possibility for LNG operations.

Many analysts believe that potential acts of terrorism and sabotage contribute significantly more probability to LNG risks than do the design and operation considerations. An example of the effect sabotage can have on the estimation of probability is presented in testimony by W. B. Fairley.[4] He shows that if an event has a low probability of occurring naturally, but a much higher probability of occurring as a result of cheating or sabotage, the actual probability is effectively the larger of the two. Thus sabotage *could* dominate the probability of tanker sinking at berth in an LNG terminal. Fairley refuses to speculate on the absolute magnitude of such probabilities, but properly argues for including them in decisionmaking and risk analysis, since just because "the probability of an unconventional or unexpected event is not well determined does not mean that it is zero." Certainly a risk analysis of LNG safety should address the sabotage and terrorism issue directly in spite of all the practical difficulties, even if only to determine whether physical, engineering, human, or natural accidents do in fact comprise the major part of the risk of such operations.

CONFIDENCE LIMITS

An important technique omitted in the research conducted heretofore is the estimation of error bounds or confidence limits on each of the point

estimates of release probabilities and contributing subsystem events. These bounds would represent, for example, the 90-percent confidence interval within which the true estimate of the probability will fall. They would provide decisionmakers with a better idea of the accuracy of the numbers generated in the risk assessment.

When a series of events must transpire in order that a larger catastrophic event occur and probability estimates and confidence intervals for the series of events are obtained, the proper combination of each of these to obtain the probability and confidence interval for the catastrophic accident must include careful analysis of possible statistical dependencies that may exist.*

As an example of the error of failing to include such dependencies, consider manufacturing defects. Parallel pressure relief valves provide redundancy. If these valves have a failure probability of 10^{-3}/yr with error bounds of 90-percent confidence of 10^{-2} to 10^{-4}, then the composite estimate of failure (if the operation of one valve is sufficient to relieve pressure) would be 10^{-6}/yr, with error bounds of between $10^{-4.586}$ and $10^{-7.414}$. If the valves were of identical manufacture and the principal components of failure were some manufacturing fabrication error or design effect, the valves could have totally dependent failure rates. In this case the proper error bounds would be 10^{-4} to 10^{-8}. While this may not seem like much difference from the independent failure assumptions, it serves to suggest that consistently ignoring dependent failure modes in complex systems will lead to an overoptimistic estimate of confidence in the ultimate estimate of total system failure.

FAULT TREE ANALYSIS

A design study by Ecosystems, Inc.,[8] funded by the Center for Environmental Quality, to devise a methodological procedure for risk analysis of LNG operations indicated that "fault tree analysis" could be used here. In fault and event tree analysis, all conceivable faults (and events) are analyzed to see what could have caused the fault (or what the event might

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*In such complex systems, where analytical expressions cannot be calculated, Monte Carlo simulation techniques can be used to determine these estimates.

initiate). A backward (and a forward) time analysis is conducted of all conceivable accidental occurrences broken down by the elementary component contributions. Dependent probabilities of failures, failure rates of the components, etc., are important data parameters. Monte Carlo simulation and certain probabilistic approximations are used to estimate the probabilities of the larger events. Reliability engineers have used such an approach in the ballistic missile program, in the Apollo moon program, in the aerospace industry, and in the *Reactor Safety Study* conducted by N. C. Rasmussen.[9]

Fault tree analysis was intended by its developers to 1) compute the safety of a complex system, 2) assess the changes in system safety when elements within the system are changed, 3) retrospectively find the specific failure that leads to any actual system failure, and 4) document with evidence that a safety analysis has been performed. Experience within the aerospace industry has found that fault tree analysis is not a satisfactory tool for estimating the system reliability nor for assuring any completeness of a reliability analysis. Fault tree analysis has proven useful only in items 2 and 3, i.e., to assess the impact of changes in design and to track back to study the causes of system failure.* During design of safety systems, backup redundancy, and operating procedures, fault tree analysis can be useful in improving the system's safety. This methodology has proven to be a good relative measuring technique, but is poor at establishing the absolute numbers policy-level decisionmakers would like to have.

SYNOPSIS

Research to date is clearly insufficient to estimate the risk of LNG operations; several important avenues must be examined to see if they will provide the valuable information needed by decisionmakers for choosing sites for terminals and designing safety systems and operating procedures. The nature of the analogy between transport of LNG and other operations must be examined in more detail and implications relating them justified

*Use of the fault tree methodology for estimating system reliability has been strongly criticized. Evidence supporting this conclusion is substantial. A careful fault tree analysis is simply not a complete safety analysis. See Ref. 10.

scientifically. A fault tree study can provide a valuable means to improve the system's safety even if it cannot be used to estimate the probabilities and system reliability. Terrorism should be considered as one of the possible release causes, and estimates, however difficult, must be made and mitigating measures taken.

The important question is how to improve the quantitative risk assessment in LNG operations. What research plan could be proposed that could overcome many of the criticisms mentioned? Is some new methodology available for making risk assessments of the operation of potentially hazardous systems? We have found no easy answer. It is easy to criticize past research for omissions of critical factors, unjustifiable extrapolation of and failure to validate models, unsupported assumptions, and estimations based on inadequate data. Conducting an adequate risk assessment will not be an easy task that could be based on the application of some new methodology, but rather a redoubling of efforts, with particularly close attention paid to correcting the weaknesses criticized here.

Original research is needed in the assessment of spill probabilities. So far most of the research has been based on extrapolations of similar existing systems without proof of the validity of the procedure. Much of the research, particularly that found in the many environmental impact statements, has been only surveys of the state of the art, applying that state of the art to the local situation.

Preparation of a fault tree analysis for LNG systems such as proposed in Ref. 8 would be a valuable contribution. Design and operational improvements of the system could be made from this type of analysis even though absolute probability estimation is not justified. The insurance industry; the analogous systems of crude oil, LPG, and refined oil product importation; sabotage; etc., would each be the center of attention for studies. Critical questions, such as whether a fire will start upon a collision involving the LNG ship--now assumptions in most analyses--could be answered more definitely on the basis of experiments and models. Mitigating measures for all release types for each accident cause will inevitably be improved by these scientific approaches to risk assessment.

III. FLUID MECHANICS AND HEAT TRANSFER OF LNG SPILLS ON WATER

Once a spill has occurred, the subsequent course of events is susceptible to physical and mathematical analysis. This section and the next discuss briefly the drawbacks of the type of analysis heretofore applied to the problem and suggest an approach which treats the problem more realistically.

When a spill occurs without accidental ignition, those in charge must decide whether the total damage will be minimized by burning or not burning, a decision which can be made rationally only if there is a quantitative means of assessing the amount and distribution of the LNG vapor produced by the interaction between the LNG and the underlying surface. This information is required as an input to the atmospheric dispersion problem (treated in Section IV) and to the problem of steady combustion over a pool of LNG. In Section III the underlying surface will be assumed to be water, because for spills on land containment is easier, boil-off is more easily controlled, and more reliable experimental data exist.

Neither an exact theory nor an experimentally validated model exist for the evaporation of an LNG spill. Several models have been proposed; however, in each case experimental observations revealed serious deficiencies. For example, Fay[11] and Hoult[12] employ the analysis that Fannelop and Waldman[13] developed for oil slicks to estimate the evaporation of LNG. Their crucial assumption is that the evaporation of LNG occurs by the cooling and freezing of the water beneath the spill. Together with other approximations, they assume that a certain quantity of ice exists and that the cooling required to form the ice supplies the heat necessary for evaporation. These assumptions allow them to avoid the complicated boiling heat transfer problem in determining the evaporation rate. These models have been criticized because no significant ice formation has been observed in other than confined spills.[14,15]

Phani Raj and Kalelkar[16] also employ the analysis of Fannelop and Waldman to determine the LNG dynamics; again, however, the heat transfer problem is avoided by assuming that the evaporation rate is constant.

There is some experimental evidence to support this assumption,[15] but employing empirical relations does not allow the display of critical parameters required for scaling laws.

One major criticism of all previous theoretical models is that oil slick dynamics was directly employed in the LNG spill problem without any consideration of evaporation. Evaporation is a major influence in an LNG spill, and neglecting its influence on the flow results in a serious overestimation of evaporation time.

The following section develops the theory of the interaction of LNG with ambient water. Approximations employed in previous works are discussed and a new model proposed. Although a solution technique is discussed, a solution of the proposed model is not given.

THEORY

It is appropriate to review the physical situation before entering into the mathematical formulation of the model. At time zero a volume V of LNG is spilled on ambient water. If boiling were not to occur, the problem of interest would be purely one of hydrodynamics, i.e., the motion caused by the sudden release of LNG on an ambient water. The sudden release of LNG displaces the ambient water, which produces a buoyancy effect, which in turn produces a radial pressure gradient that drives the LNG radially outward. The mandatory conditions of continuity of pressure and normal velocity across the LNG-water interface require that the radial pressure gradient produce a corresponding motion in the ambient water. At any particular time and radial location, the thickness of the LNG layer is determined by conservation of mass, and the surface of the water adjusts to satisfy the local hydrostatic condition. The flow caused by the LNG spill can be characterized as deep water waves produced in ambient water by an initial surface disturbance. This problem in its inviscid limit does not have analytical solutions for an arbitrary range of parameters; in fact, the linearized version of the problem has yielded analytical results only in the asymptotic limit of long times and large radial distances.[17]

LNG normally boils at 111 K (-259°F). When it is placed on ambient water with a temperature of 289 K (60°F) a temperature difference of

approximately 178 K (319°F) results. This temperature difference is sufficient to produce stable film boiling; therefore, at some time after time zero, the flow scheme can be visualized as a spread of LNG that is separated from the ambient water by a film of LNG vapor.

The vapor film, which is also driven by buoyancy, acts to regulate the flow of heat from the water to the LNG by either increases or decreases in its thickness. Although much is still unknown about the film boiling process, it is generally accepted that the discharge of bubbles through the liquid layer is an orderly process that occurs at the liquid-vapor interfaces and is amenable to theoretical considerations. The magnitude and distribution of the discharged vapor are desired results from a study of LNG spills.

Crucial assumptions in the following developments are that (1) the rate of vapor discharging into the liquid layer can be calculated employing film boiling theory and (2) the flow of the LNG layer is independent of the vapor flux through it. The latter assumption implies that two-phase effects on the LNG layer are negligible.

Including viscous effects will modify the model of the LNG spread and the water both being driven radially by buoyancy effects and separated by vapor film. It will be shown later that viscous effects produce transition layers between the LNG and the vapor film and between the vapor film and the water. Early on, the transition layers are thin; however, later the transition layer between the LNG and the vapor film dominates the flow.

EQUATIONS

Assuming that the fluids have constant properties and that the flow is laminar and axisymmetric, one finds that the governing equations are

$$\frac{\partial u}{\partial x} + \frac{u}{x} + \frac{\partial w}{\partial z} = 0 \tag{3.1}$$

$$\frac{\partial u}{\partial t} + u\,\frac{\partial u}{\partial x} + w\,\frac{\partial u}{\partial z} = -\frac{1}{\rho}\,\frac{\partial p}{\partial x} + \nu\,\frac{\partial^2 u}{\partial z^2} \tag{3.2}$$

$$\frac{\partial p}{\partial z} = -\rho g \tag{3.3}$$

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + w \frac{\partial T}{\partial z} = \frac{\nu}{P_r} \frac{\partial^2 T}{\partial z^2} \tag{3.4}$$

In these equations u and w are the horizontal and vertical components of velocity, P_r is the Prandtl number, and the other symbols have their usual significance. Implicit in these equations are the thin-layer assumptions. The boundary and initial conditions are

$$\left.\begin{array}{llllll} t = 0 & z = z_e = \delta_{L,0}: & u = 0; & T = 111\ K; & \rho = \rho_L \\ & & & (-259°F) & \\ & z = 0: & u = 0; & T = 289\ K; & \rho = \rho_w \\ & & & (60°F) & \\ t > 0 & z = z_e: & u = u_L; & T = 111\ K; & \rho = \rho_L \\ & z \to -\infty: & u \to 0; & T \to 289\ K; & \rho = \rho_w \end{array}\right\} \tag{3.5}$$

The subscript e refers to the upper edge of the LNG layer, L to the LNG layer itself, w to the ambient water, and (in following equations) v to the vapor layer. The thickness of a layer is denoted by δ with a suitable subscript.

Figure 1 illustrates the coordinate system and conditions at time zero. The coordinate system is referred to the undisturbed water level. Figure 2 shows conditions at a later time if there is no boiling. Figure 3 shows conditions with boiling, a layer of vapor between the LNG and the water, and two transition layers. For the moment the transition layers will be ignored.

Employing Eq. (3.3) and the fact that the weight of the LNG plus the vapor equals that of the displaced water, one can derive the following pressure distributions:

a. LNG layer

$$p - p_e = -\rho_L g(z - z_e) \tag{3.6a}$$

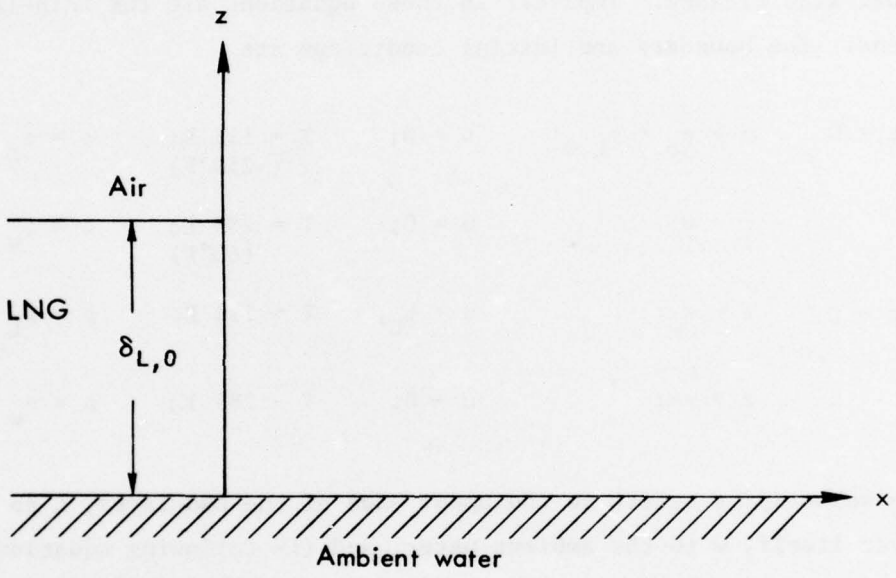

Fig. 1 — The flow at $t = 0$

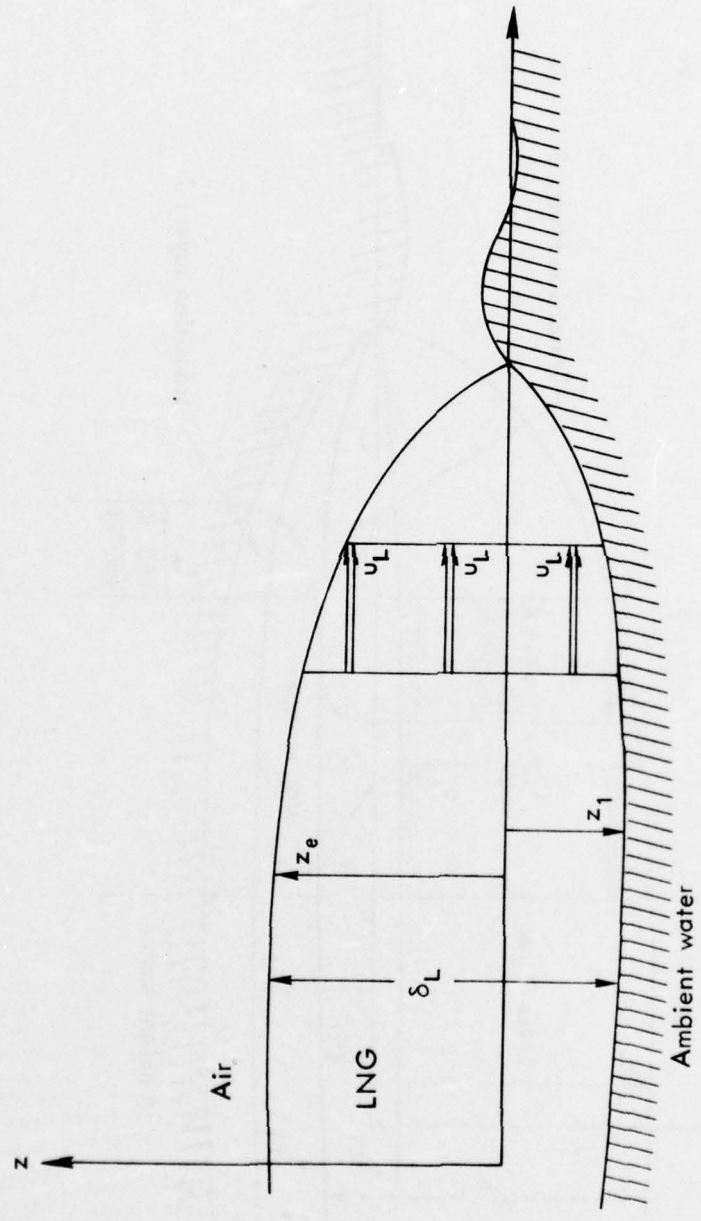

Fig. 2 — The flow without boiling or viscous effects at $t > 0$

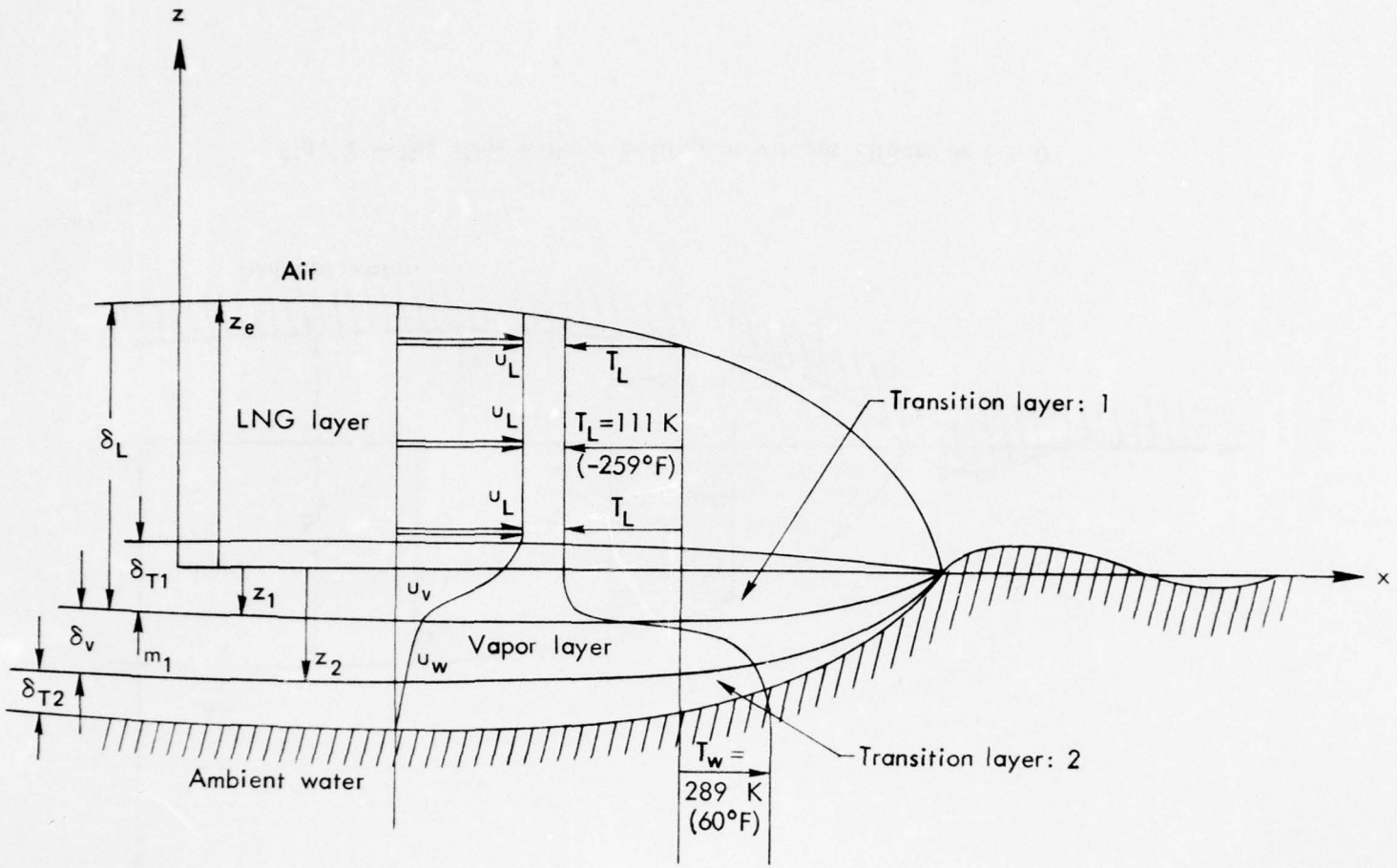

Fig. 3 — The flow with boiling and viscous effects at t > 0

$$z_e = \delta_L \, \Delta\rho \tag{3.6b}$$

where δ_L is the thickness of the liquid layer, and

$$\Delta\rho = \frac{\rho_w - \rho_L}{\rho_w}$$

$$\delta\rho = \frac{\rho_w - \rho_v}{\rho_w}$$

Note that $\rho_L >> \rho_v$ and that $\delta\rho \approx 1$.

b. vapor layer

$$p - p_e \approx \rho_L g \, \delta_L \tag{3.6c}$$

c. ambient water

$$p - p_e = \rho_L g \, \delta_L + \rho_w g(z - z_1) \tag{3.6d}$$

Equations (3.6a) through (3.6d) are valid as long as $\delta_v/\delta_L << 1$, where δ_v is the thickness of the vapor layer. They will be used to discuss the flow in the various layers.

The LNG Layer

In this section a simple dimensional argument will be used to simplify Eqs. (3.1) through (3.4) and determine the set most appropriate for the LNG layer. It will be shown that the flow in the LNG layer is mainly inviscid for early and moderate times and that viscous effects are confined to a small transition layer.

Employing Eqs. (3.2), (3.6a), and (3.6b), one can derive the following momentum equation:

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + w \frac{\partial u}{\partial z} = -\alpha \frac{\partial \delta_L}{\partial x} + \nu \frac{\partial^2 u}{\partial z^2} \tag{3.7}$$

where $\alpha = g \Delta\rho$.

This equation can be nondimensionalized using the characteristic length L_1 and characteristic time τ and the following definitions:

$$\hat{x} = \frac{x}{L_1}; \quad \hat{\delta}_L = \frac{\delta_L}{\delta_{L,0}}; \quad \hat{u} = \frac{u}{u_{L,0}} = \frac{u\tau}{L_1} \tag{3.8}$$

It will be assumed that this has been done, so the carets can be dropped. The volume of the LNG spill is denoted by V, and initially $V = \delta_{L,0} L_1^2$.

If one integrates Eq. (3.1) across the LNG layer, then one will find that the order of magnitude for the normal velocity is

$$w = 0\left(\frac{u_{L,0}\ \delta_{L,0}}{L_1}\right) \tag{3.9a}$$

In addition, if one assumes that the viscous effects in Eq. (3.7) have the length scale $\sqrt{\nu\tau}$, which is the characteristic scale for an unsteady boundary layer, the order of magnitude of the viscous effect is

$$\nu \frac{\partial u}{\partial z} = 0\left(\frac{\nu u_{L,0}}{\sqrt{\nu\tau}}\right) \tag{3.9b}$$

The order of magnitude of the ratio of buoyancy to inertial terms is $\alpha\delta_{L,0}\tau^2/L_1^2$, and the ratio of inertial terms to viscous terms is $(\nu\tau)^{1/2}/\delta_{L,0}$ or $(\nu\tau)^{1/2}L_1^2/V$. Thus the viscous terms can be neglected in comparison to the buoyancy in the small time regime except for a viscous layer (transition layer) near the interface with thickness $0(\sqrt{\nu\tau})$. This transition layer will be ignored for the present but will be discussed

later. The same order of magnitude argument is presented in more detail in Ref. 13; however, the interpretation of the transition layer is unique to the present discussion.

Employing the inviscid approximation and the assumption that u is independent of z,[18] an integration of the continuity equation results in

$$w_e - w_1 = -\frac{\delta_L}{x}\frac{\partial}{\partial x}(ux) \tag{3.10}$$

where the subscript 1 represents the lower surface of the LNG layer. The mass of LNG evaporated at the interface ($z = z_1$) is

$$m_1 = -\rho_L w_1 + \left(\rho_L \frac{\partial z_1}{\partial t}\right) + \rho_L u_L \frac{\partial z_1}{\partial x} \tag{3.11}$$

Since z_e is a streamline, which implies that

$$w_e = \frac{\partial z_e}{\partial t} + u_L \frac{\partial z_e}{\partial x}$$

Eqs. (3.10) and (3.11) can be combined to give

$$\frac{\partial \delta_L}{\partial t} + u\frac{\partial \delta_L}{\partial x} + \frac{\delta_L}{x}\frac{\partial}{\partial x}(ux) = -\frac{m_1}{\rho_L} \tag{3.12}$$

Consistent with the assumptions made, the reduced momentum equation is

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = -\alpha\left\{\frac{\partial \delta_L}{\partial x} + \frac{\delta\rho}{\Delta\rho}\frac{\partial \delta_v}{\partial x}\right\} \tag{3.13}$$

Equations (3.12) and (3.13) are the governing equations for the LNG layer. Employing the above equations, and pursuing an analysis similar to

that of Ref. 13, one finds that the effects of mass transfer m_1 on the LNG flow influence the propagation velocity throughout the layer except at the leading edge. Early on, when evaporation is small, the effect of m_1 on the LNG flow is negligible, though it is very significant for later times.

Except for the sink term, $- m_1/\rho_L$, in Eq. (3.12), the above equations are identical to those of Ref. 13. Because of the evaporation and the subsequent mass transfer from the LNG layer, however, they must be interpreted differently.

The Transition Layer: 1

The transition layer between the LNG layer and the LNG vapor layer is of importance to the present model because it provides a means of transferring momentum from the former to the latter. Initially, this layer is very thin in comparison to the LNG layer and is essentially a boundary layer between the LNG and the vapor layer. But at some later time when the LNG layer has spread out and lost mass through evaporation, the transition layer may be a large fraction of the LNG layer. Eventually, there is no distinction between the transition layer and the LNG layer. The equations that govern this layer are the full equations (3.1), (3.2), and (3.3). At some later time when the entire LNG flow is dominated by viscous effects, these equations may be modified similarly to those reported in Ref. 13.

The boundary conditions are

$$\begin{aligned} z = \delta_L: &\quad u = u_L \\ z = z_1: &\quad u = u_v \qquad m = m_1 \end{aligned} \tag{3.14}$$

where both u_v and m_1 are unknowns to be determined by solution of the complete problem.

The Vapor Layer

The vapor layer is being driven by two effects: a pressure gradient produced by gravity and the net shear force impressed by the two transitional layers. Intuitively, one would think that the vapor layer moves as

a viscous-dominated flow in which convection of energy is small unless the evaporation becomes exceedingly large.

To test this assertion, one can deduce from Eq. (3.2) that the inertial terms in the vapor layer are at most $O(\rho_v u_L^2/L)$, and since the pressure is impressed by the LNG layer, the pressure force is $O(\rho_L u_L^2/L)$. The viscous force in the layer is nearly the same force that exists in the Transition Layer: 1; there the viscous effect is $O(\tau_L/\delta_v)$. In comparing these three effects and assuming that $\tau_v = O(\rho_L u_L^2 \delta_v/L)$, which is required to balance the pressure gradient and shear terms, one finds that the dominant effect is a balance between pressure gradient and shear gradient.

When a similar argument is applied to the energy equation, one finds that the heat conduction term dominates. Therefore, the equations for the vapor layer are

$$0 = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu \frac{\partial^2 u}{\partial z^2} \tag{3.15}$$

$$0 = \frac{\partial^2 T}{\partial z^2} \tag{3.16}$$

and the boundary conditions are

$$\begin{aligned} &z = z_1: \quad u = u_v; \qquad -m_1 h_{fg} = -\kappa_v \frac{\partial T}{\partial z}; \qquad \mu_L \frac{\partial u}{\partial z} = \mu_v \frac{\partial u}{\partial z} \\ &z = z_2: \quad u = u_{w,T}; \qquad Q = -\kappa_v \frac{\partial T}{\partial z_1}; \qquad \mu_v \frac{\partial u}{\partial z} = \mu_w \frac{\partial u}{\partial z} \end{aligned} \tag{3.17}$$

The subscript 2 refers to the bottom edge of the vapor layer, h_{fg} is the heat of vaporization, κ is conductivity, μ is viscosity, and Q is the energy input from the water. The boundary conditions at $z = z_2$ are a consequence of the momentum and energy transfer from ambient water through the second transition layer.

An additional effect on the motion of the vapor layer, which enters through the boundary conditions at $z = z_1$, is due to film boiling. The

present theory of film boiling assumes that vapor is continuously generated at the liquid-vapor interface, and the thickness of the vapor continues to grow. At a certain critical thickness, hydrodynamic instabilities occur, producing a periodic disturbance at the interface. It has been observed that the interface will break up at regular intervals, producing the vapor bubbles which flow through the liquid layer. This is the crucial element of the model in that the discharge vapor (m_2) is the required result. The status of film boiling theory as reported by Berenson[19] is not very cogent for horizontal heating surfaces in a flow field. It is anticipated that theories reported in Refs. 19, 20, and 21 will have to be modified before they can be employed in the proposed model.

The Transition Layer: 2

This layer provides a transfer of energy from the ambient water to the vapor layer. Since this is also a boundary layer, the equations that govern this layer are Eqs. (3.1), (3.2), and (3.4), with the pressure given by Eqs. (3.6b) and (3.6d), and the boundary conditions are

$$z = z_2: \quad u = u_{w,T}; \quad -\kappa_v \frac{\partial T}{\partial z} = Q; \quad \mu_v \frac{\partial u}{\partial z} = \mu_w \frac{\partial u}{\partial z}$$

$$z \to -\infty: \quad u \to 0; \qquad T \to T_w \tag{3.18}$$

The model we propose is one in which the LNG layer is separated from the water by a viscous-dominated LNG-vapor layer, which in turn is separated on top from the LNG by a viscous transition layer and on the bottom from the water by another viscous transition layer (see Fig. 3). Therefore, this is a multilayer model with well-understood fluid dynamics. The interesting aspect of this model is that momentum is transferred from the LNG layer through the transition layers to the ambient water. On the other hand, energy is transferred from the ambient water through the transition layers to the LNG layer. Film boiling theory is required to estimate the fraction of the LNG evaporated at the LNG-vapor interface that forms the bubbles that flow through the LNG layer. We anticipate that the

interface instability theory of Refs. 19, 20, and 21 could be useful in determining the amount of vapor that flows through the LNG.

METHOD OF SOLUTION

The first step is to determine either analytically or numerically the inviscid flow of the LNG layer and the ambient water without the effects of boiling. To obtain approximate numerical results, one can employ techniques developed in Refs. 22, 23, and 24. These results can be employed in the proposed model to study the small and moderate time regimes.

The second step would be to modify these flows by considering the vapor and transition layers. Except for large times, these two steps can be treated separately.

At large times, the effects of viscosity and evaporation are very pronounced on the flow at the LNG layer. Therefore, the LNG layer, the transition layers, and the vapor layer cannot be treated separately; instead, the full flow problem must be studied.

Approximate solutions are appropriate in view of the uncertainty in the physics of the film boiling. One could employ integral methods for solution of the flows in the transitional and vapor layers. A second method would be to ignore the momentum transfer to the ambient water and consider the ambient water as a hot stationary surface. This simplification reduces the LNG problem to flow over such a surface with evaporation. These simplifications would certainly give the order of magnitude and the correct parameters.

SYNOPSIS

A model for the interaction between LNG and the ambient water has been proposed which is physically more realistic than its predecessors. This multilayer model is necessarily more complex than other models, but numerical solutions can be achieved by means of modern computing techniques. Further study of the model may reveal additional simplifications that could be employed to obtain either simpler numerical or approximate analytical solutions.

The weakest link in the model is the status of film boiling theory, which is not well developed; therefore the simplified versions of the proposed model might be sufficient. It is still not known whether or not current theories can be employed in a flow as complicated as the one proposed. However, this weakness would occur in any model.

IV. ATMOSPHERIC DISPERSION OF A VAPOR CLOUD

Once a spill of LNG occurs and a vapor cloud forms through evaporation, the vapor cloud will mix with the atmosphere and be transported, perhaps to considerable distances, by the winds. The high density of the cold vapor cloud will inhibit its mixing, but inevitably some portion of the cloud will reach the degree of mixture (between 5 percent and 14 percent at normal temperature) at which it is flammable. Then, any spark or open flame will ignite the flammable mixture, and, since continued mixing occurs at the edge of the methane cloud, the fire can easily be sustained and propagate. There is also danger that the methane cloud, or some portion of it, might reach just the proper degree of mixing with air and receive just the proper impulse to cause it to detonate.

The atmospheric dispersion problem, then, is to predict the size, temperature, concentration, and motion of the cloud from the time and place of its origin until it is so completely mixed with the air that no more flammable pockets exist. The basic datum, of course, is the rate of production of the gas--i.e., the rate of evaporation--which can be determined from a model such as that described in Section III. The evolution of the cloud thereafter will depend on the ambient wind, temperature, and humidity; the variations of these quantities in the horizontal, in the vertical, and with time; the nature of the local terrain; the composition and temperature of the vapor cloud; and perhaps other lesser factors. If one could make an accurate forecast of the motion, size, and properties of the cloud, one could make intelligent decisions as to whether or not to burn it, what evacuations to order, etc.

PLUME MODELS

The approach that has been almost universally taken is to adapt to the LNG problem the procedures developed over the years to describe and predict the atmospheric dispersion of effluents from industrial smokestacks and of radioactive particles from explosions or inadvertent releases from nuclear plants. Because of the latter concern, the Atomic Energy Commission has been a leader in the field, and one of the most valuable reference sources

is their publication *Meteorology and Atomic Energy*.[25] Since the dispersion of the vapor cloud associated with a pool of LNG offers in some particulars a similar problem, it is not surprising that workers in the field turned to this body of completed research.

The basic tool used in most of the studies derives from an equation proposed by Sutton[26,27] for a plume from a continuous, elevated point source with Gaussian diffusion. In Ref. 25 it is shown that for an instantaneous point source the Gaussian formula is

$$\chi = \frac{Q}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left\{-\left[\frac{(x - \bar{u}t)^2}{2\sigma_x^2} + \frac{y^2}{2\sigma_y^2} + \frac{z^2}{2\sigma_z^2}\right]\right\} \qquad (4.1)$$

where χ is the concentration, Q the source strength, $\bar{u}$ the wind speed, t the time time of travel of the cloud, x the downwind distance, y the crosswind distance, z the distance above ground, and σ_x^2, σ_y^2, and σ_z^2 the variance of distribution in the three directions. This equation assumes Fickian diffusion under homogeneous, stationary conditions. By the method of superposition, Eq. (4.1) can be integrated to get an expression for a continuous point source:

$$\chi = \frac{Q}{2\pi\bar{u}\sigma_y\sigma_z} \exp\left\{-\left(\frac{y^2}{2\sigma_y^2} + \frac{z^2}{2\sigma_z^2}\right)\right\} \qquad (4.2)$$

The symbols in Eq. (4.2) have the same meaning as in Eq. (4.1) except that Q is now the emission rate. In deriving Eq. (4.2), the diffusion along the x-axis has been neglected by comparison with the gross transport. It should be noted that σ_x, σ_y, and σ_z are all functions of x.

One additional modification to Eq. (4.2) is necessary because of the presence of the ground surface, which reflects the effluent back up. This is handled by assuming a virtual source at the same distance below the ground as the actual source is above it (this distance being designated h) and adding the two solutions, whereupon Eq. (4.2) becomes

$$\chi = \frac{Q}{2\pi \bar{u} \sigma_y \sigma_z} \exp\left\{-\frac{y^2}{2\sigma_y^2}\right\}\left[\exp\left\{-\frac{(z-h)^2}{2\sigma_z^2}\right\} + \exp\left\{-\frac{(z+h)^2}{2\sigma_z^2}\right\}\right] \quad (4.3)$$

This is the form used by Barad and Haugen[28] in a paper that uses experimental data to show that the assumption of Gaussian diffusion is justifiable for a wide range of atmospheric applications.

If the source is at ground level, which is the usual case for an LNG spill, h = 0, and Eq. (4.3) becomes

$$\chi = \frac{Q}{\pi \bar{u} \sigma_y \sigma_z} \exp\left\{-\left[\frac{y^2}{2\sigma_y^2} + \frac{z^2}{2\sigma_z^2}\right]\right\} \quad (4.4)$$

These equations, generally referred to either as the Sutton or Pasquill equations,[29,30] or some variation on them, are the most frequently used tools for studying the dispersion in the atmosphere of vapor from LNG spills (see, for example, Refs. 31-35).

If Gaussian dispersion is not assumed, Sutton[36] shows that in place of Eq. (4.3) one has

$$\chi = \frac{Q}{\pi C_y C_z \bar{u} x^{2-n}} \exp\left\{-\frac{y^2}{C_y^2 x^{2-n}}\right\}\left[\exp\left\{-\frac{(z-h)^2}{C_z^2 x^{2-n}}\right\} + \exp\left\{-\frac{(z+h)^2}{C_z^2 x^{2-n}}\right\}\right] \quad (4.5)$$

where C_y and C_z are lateral and vertical diffusion coefficients (independent of x) and n is a parameter related to the diffusing power of the turbulence. Obviously, Eq. (4.5) is somewhat more general than Eq. (4.3), and at least one LNG study[37] has made use of it. Actually, in the latter paper a still more general form of Eq. (4.5) was used, for in place of the single parameter n, two parameters, n_y and n_z, were used. Thus, four parameters, C_y, C_z, n_y, and n_z, must be determined from field experimentation. Values of these parameters appropriate to a variety of circumstances have been given

by Haugen, Barad, and Antanaitis.[38] Barad and Haugen[28] point out that if the crosswind and vertical concentration distributions in the absence of reflection are Gaussian, i.e.,

$$\left.\begin{aligned} \chi(y) &= \chi(0)\ \exp\left\{-\frac{y^2}{2\sigma_y^2}\right\} \\ \chi(z) &= \chi(0)\ \exp\left\{-\frac{z^2}{2\sigma_z^2}\right\} \end{aligned}\right\} \tag{4.6}$$

then

$$\left.\begin{aligned} C_y^2 x^{2-n} &= 2\sigma_y^2 \\ C_z^2 x^{2-n} &= 2\sigma_z^2 \end{aligned}\right\} \tag{4.7}$$

Substituting Eq. (4.7) into Eq. (4.5) yields Eq. (4.3).

There are many arguments in favor of using the non-Gaussian equations, but experience with stack effluents has shown that, by and large, the simpler Gaussian equation gives reasonably good results, so it is favored by most investigators. Even so, the Gaussian equation requires that two parameters, σ_y and σ_z, be determined empirically.

One of the most widely used methods for choosing appropriate values of σ_y and σ_z was developed by Pasquill.[29-30] Since these parameters depend on wind speed and on atmospheric stability, which in turn is correlated with radiation balance in the lower atmosphere, the first step is to use these variables to determine which of several turbulence categories is applicable to the situation at hand. Pasquill's suggested classifications are shown in Table 1, which is taken from Ref. 25. The second step takes into account the dependence of σ_y and σ_z on distance from the source. Figures 4 and 5, also reproduced from that publication, show this dependence for families of curves corresponding to the turbulence categories of Table 1.

Table 1

RELATION OF TURBULENCE TYPES TO WEATHER CONDITIONS

A--Extremely unstable conditions
B--Moderately unstable conditions
C--Slightly unstable conditions
D--Neutral conditions[a]
E--Slightly stable conditions
F--Moderately stable conditions

Surface Wind Speed (m/sec)	Daytime Insolation			Nighttime Conditions	
	Strong	Moderate	Slight	Thin Overcast or ≥ 4/8 Cloudiness[b]	≤ 3/8 Cloudiness
<2	A	A-B	B		
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

SOURCE: Ref. 25.

[a]Applicable to heavy overcast, day or night.

[b]The degree of cloudiness is defined as that fraction of the sky above the local apparent horizon which is covered by clouds.

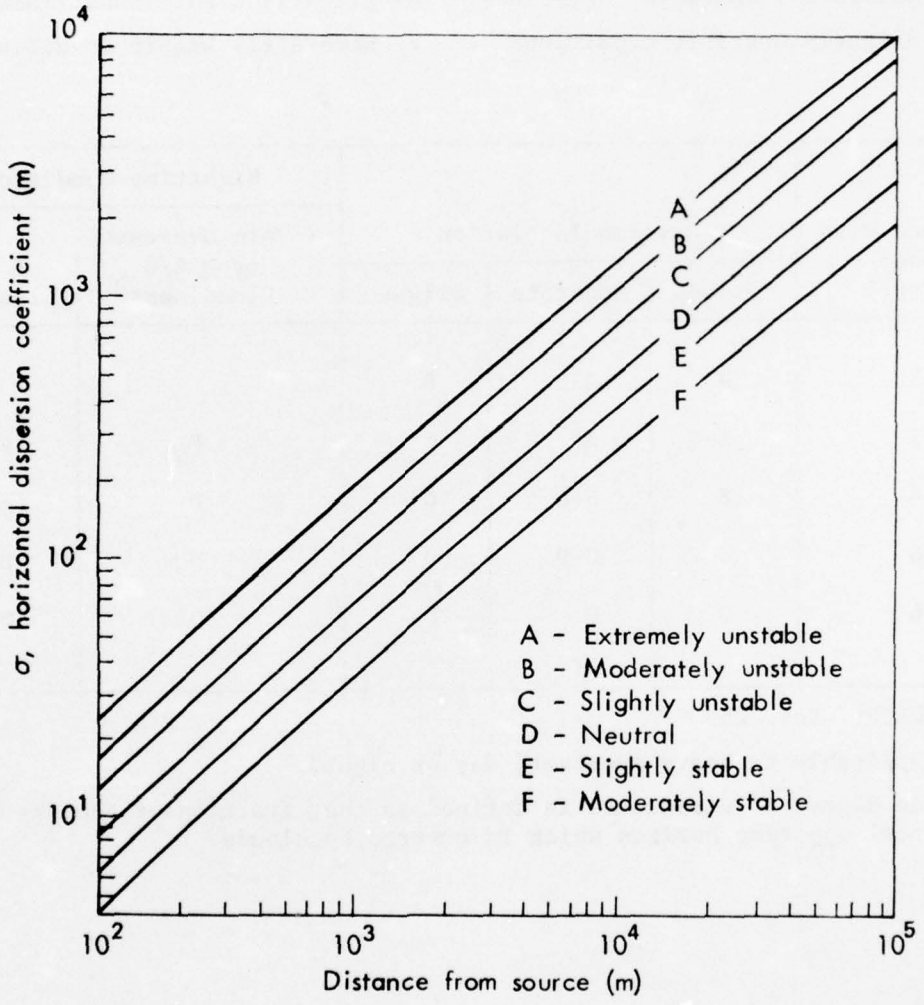

Fig. 4—Lateral diffusion, σ_y, versus downwind distance from source for Pasquill's turbulence types (Source: Ref. 25)

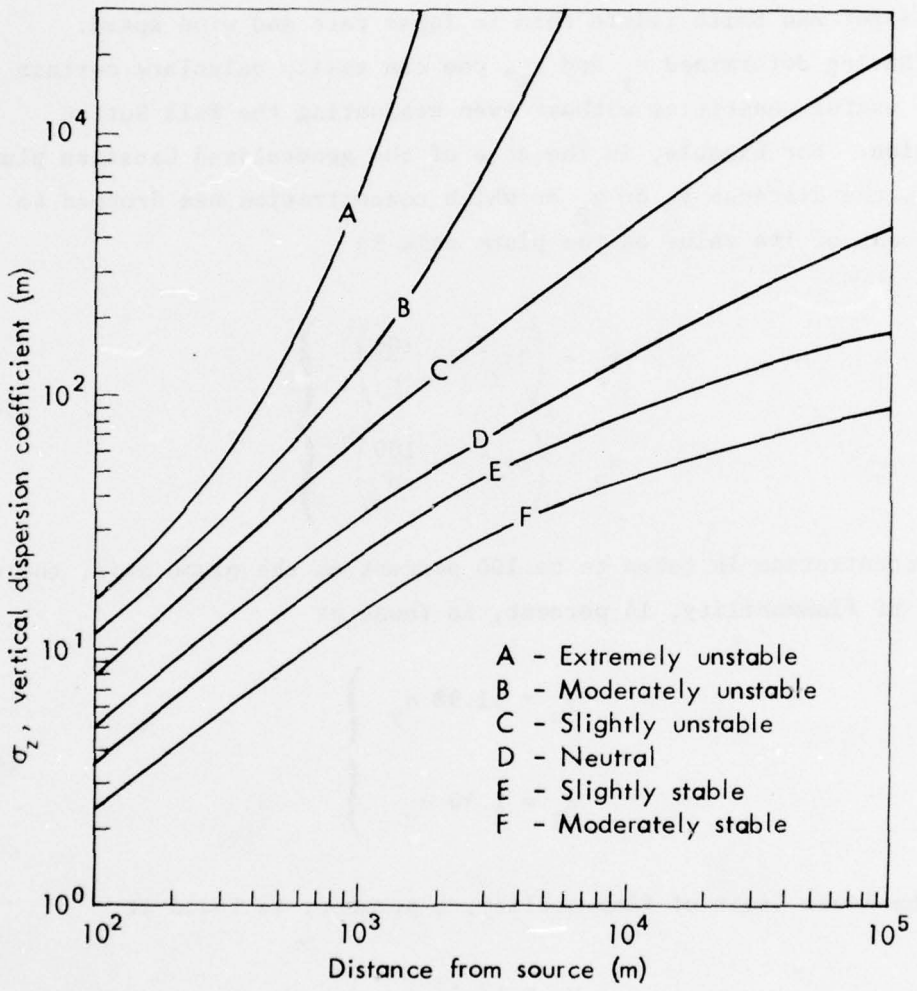

Fig. 5 — Vertical diffusion, σ_z, versus downwind distance from source for Pasquill's turbulence types (Source: Ref. 25)

The turbulence categories of Pasquill are not universally used. Some papers, for example, refer to a classification by Singer and Smith,[39] generally known as the Brookhaven gustiness classes, that enable one to choose values of n for use with Eq. (4.5). These categories are defined mainly in terms of fluctuation of wind direction, but Singer and Smith relate them to lapse rate and wind speed.

Having determined σ_y and σ_z, one can easily calculate certain other useful quantities without even evaluating the full Sutton equation. For example, in the case of the generalized Gaussian plume model, the distance y_p or z_p at which concentration has dropped to p percent of its value on the plume axis is

$$\left.\begin{aligned} y_p &= \left(2\sigma_y^{\,2}\ ln\ \frac{100}{p}\right)^{\frac{1}{2}} \\ z_p &= \left(2\sigma_y^{\,2}\ ln\ \frac{100}{p}\right)^{\frac{1}{2}} \end{aligned}\right\} \tag{4.8}$$

If concentration is taken to be 100 percent on the plume axis, the upper limit of flammability, 14 percent, is found at

$$\left.\begin{aligned} y_u &= \pm 1.98\ \sigma_y \\ z_u &= 1.98\ \sigma_y \end{aligned}\right\} \tag{4.9}$$

and the lower limit of flammability, 5 percent, is found at

$$\left.\begin{aligned} y_L &= \pm 2.45\ \sigma_y \\ z_L &= 2.45\ \sigma_z \end{aligned}\right\} \tag{4.10}$$

Care should be taken in using Eqs. (4.9) and (4.10), for it is amply demonstrated by observation that short-term fluctuations within the plume

create pockets of much higher or much lower concentration than the time average value suggested by the model.

One serious deficiency of the Sutton equations as shown above is that they apply to a point source, whereas a spill of LNG is more properly considered as an area source. Integration of Eqs. (4.5) and (4.3) across the plume axis from $-y_0$ to y_0 yields formulas for a continuous cross-wind line source of width $2y_0$:[34,35]

$$\chi = \frac{Q}{\sqrt{\pi}\ \bar{u}\ C_z x^{1-n/2}} \left[\exp\left\{\frac{-(z-h)^2}{C_z^2 x^{2-n}}\right\} + \exp\left\{\frac{-(z+h)^2}{C_z^2 x^{2-n}}\right\}\right]$$

$$\times \left[\operatorname{erf}\left\{\frac{y_0 - y}{C_y x^{1-n/2}}\right\} + \operatorname{erf}\left\{\frac{y_0 + y}{C_y x^{1-n/2}}\right\}\right] \qquad (4.11)$$

and

$$\chi = \frac{Q}{\sqrt{2\pi}\ \bar{u}\ \sigma_z} \left[\exp\left\{\frac{-(z-h)^2}{2\sigma_z^2}\right\} + \exp\left\{\frac{-(z+h)^2}{2\sigma_z^2}\right\}\right]$$

$$\times \left[\operatorname{erf}\left\{\frac{y_0 - y}{\sqrt{2}\ \sigma_y}\right\} + \operatorname{erf}\left\{\frac{y_0 + y}{\sqrt{2}\ \sigma_y}\right\}\right] \qquad (4.12)$$

In Eqs. (4.11) and (4.12) the symbol erf refers to the error function, which is tabulated in standard sources, for example, Ref. 40.

An area source can be treated by summing Eq. (4.11) or (4.12) over a range of x.

SOME PROBLEMS WITH PLUME MODELS

Even when these improvements are included, many deficiencies remain in this diffusion-equation approach. One problem is that the equations shown here represent a steady state. Initially the vapor cloud will exist only directly above the spill, which itself is changing in area unless it is confined by a dike. It will immediately start to spread downwind, but

the wind itself is seldom steady. It has already been shown that the rate of production of vapor varies. Some nonsteady aspects of the problem can be treated by repeated use of the steady-state equations. Welker, Wesson, and Sliepcevich[37] point out that the leading edge of the plume travels downwind at the rate of the wind speed, so that a point at a distance x from the spill is not affected until time $t = x/\bar{u}$ (provided $\bar{u}$ is constant). Furthermore, the rate of evaporation might not be constant, so the concentration at distance x and time τ is a function of the evaporation rate at time $\tau - x/\bar{u}$; that is, the gas that evaporated at time $\tau - x/\bar{u}$ reaches point x at the time τ. Use of the steady-state equations in this way is clumsy. A theory incorporating time dependence would be preferable.

Another problem is that of the buoyancy of the gas. Plume theory, having been developed for effluents from industrial stacks, is based on the assumption of a plume of neutral or positive buoyancy. The vapor from a spill of LNG, on the other hand, is strongly negatively buoyant. Presumably, the great negative buoyancy of the cold plume inhibits mixing, and so the eddy diffusion coefficients determined empirically for smoke plumes and stack effluents are not necessarily valid. Hoult[12] considers the problem and shows that ignoring the negative buoyancy gives ground concentrations that are too low. He does not, however, proceed to show how the Sutton model could be modified to take this into account.

Buoyancy is a function of density. The density of a perfect gas is determined by the equation of state

$$\rho = \frac{pm}{RT} \tag{4.13}$$

to be a function of pressure p, molecular weight m, and temperature T. R is the universal gas constant. It is readily shown by means of Eq. (4.13) that the negative buoyancy of a cloud newly evaporated from an LNG spill is not overcome until the vapor cloud has warmed (depending on the ambient temperature) some 50 K(90°F). This warming can come about through conduction, radiation, and mixing. The first two processes are rather inefficient in this context, and unless the ambient atmosphere is very turbulent, the high density of the vapor cloud makes mixing inefficient as

well. Thus there is a possibility that a large vapor cloud might be long-lived.

Even when mixing occurs, pockets of a flammable mixture having a temperature somewhere between that of the newly formed methane cloud and that of the ambient air will tend to stay near the ground.

Suppose in some limited region methane with a temperature of T_M mixes completely with air with a temperature of T_A in the proportions of χ parts of methane to $1 - \chi$ parts of air. In coming to a common temperature $\bar{T}$, the air gives off heat to the methane in the amount $(1 - \chi)c_{pA}(T_A - \bar{T})$, the methane takes up heat from the air in the amount $\chi c_{pM}(\bar{T} - T_M)$, and these two quantities must be equal:

$$(1 - \chi)c_{pA}(T_A - \bar{T}) = \chi\, c_{pM}(\bar{T} - T_M) \tag{4.14}$$

In Eq. (4.14) c_{pA} is the specific heat of air and c_{pM} is the specific heat of methane, both for processes at constant pressure. Rearranging Eq. (4.14),

$$\bar{T} = \frac{\alpha T_M + \beta T_A}{\alpha + \beta} \tag{4.15}$$

where

$$\alpha = \frac{c_{pM}}{c_{pA}} \approx \frac{0.50}{0.24} = 2.08 \tag{4.16}$$

and

$$\beta = \frac{1 - \chi}{\chi} \tag{4.17}$$

In accordance with Eq. (4.13), the density of the ambient air is

$$\rho_A = \frac{p}{R}\frac{m_A}{T_A}$$

and that of the air-methane mixture is

$$\bar{\rho} = \frac{p}{R} \frac{[\chi m_M + (1 - \chi) m_A]}{\bar{T}} \tag{4.18}$$

The ratio of the densities is

$$\frac{\bar{\rho}}{\rho_A} = \frac{\chi m_M + (1 - \chi) m_A}{m_A} \frac{T_A}{\bar{T}}$$

or

$$\frac{\bar{\rho}}{\rho_A} = \chi(\gamma + \beta) \frac{T_A}{\bar{T}} \tag{4.19}$$

where

$$\gamma = \frac{m_M}{m_A} = \frac{16.04}{28.966} = 0.554 \tag{4.20}$$

Combining Eqs. (4.15) and (4.19) and inserting numerical values from Eqs. (4.16) and (4.20),

$$\frac{\bar{\rho}}{\rho_A} = \frac{\chi(\alpha + \beta)(\gamma + \beta)}{\alpha \frac{T_M}{T_A} + \beta}$$

or

$$\frac{\bar{\rho}}{\rho_A} = \frac{(1 + 1.08\chi)(1 - 0.446\chi)}{1 + \left(2.08 \frac{T_M}{T_A} - 1\right)\chi} \tag{4.21}$$

The mixed pocket is positively or negatively buoyant according to whether $\bar{\rho}/\rho_A < 1$ or $\bar{\rho}/\rho_A > 1$. The unmixed methane is likely to be near its

boiling temperature or T_M = 111 K. For the upper limit of flammability χ = 0.14, so for neutral buoyancy

$$1 = \frac{(1 + 0.1512)(1 - 0.06244)}{1 + 0.14\ [2.08(111/T_A) - 1]}$$

or

$$T_A = 147\ K\ (-194°F)$$

For the lower limit of flammability and neutral buoyancy, T_A is still smaller. These temperatures are far colder than any which might be observed in the atmosphere, and Eq. (4.21) shows that a still smaller value of T_A would be necessary for the mixed parcel to be positively buoyant. Hence, the flammable parts of the vapor cloud will tend to hug the ground unless there is a significant source of heat other than mixing with ambient air. The analysis above is based on idealized assumptions about a parcel, which is presumably much smaller than the entire vapor cloud, but it illustrates the order of magnitude of the temperatures and buoyancy in a real situation.

Some question has arisen as to whether a cloud of vapor might detonate rather than burn. Burgess, Biordi, and Murphy[31] have investigated this problem and have concluded that a vapor cloud in the free air would have to be very large or the impulse very strong before detonation would occur. If, however, the cloud drifts over a building, there might be a time when the mixture within the enclosure is just right to detonate from a small impulse. If such a situation could be foreseen, one might well elect to accept the damage resulting from igniting the gas earlier rather than risking the greater damage from an explosion.

All these computations are for dry air. At the same temperature, moist air is less dense. The effect of moisture can be taken into account by using the virtual temperature T^*_A in place of the actual temperature in Eq. (4.13). It can then readily be shown that neutral buoyancy exists when

$$T_M = \gamma T^*_A = 0.554\ T^*_A \qquad (4.22)$$

The virtual temperature is defined as

$$T^*_A = (1 + 0.61q)T_A \qquad (4.23)$$

where q is the mixing ratio, or mass of water vapor per unit mass of dry air. Under warm, moist conditions, such as might exist at a southeastern U.S. seaport in summer, the virtual temperature might be as much as 3°C higher than the actual temperature.

Another effect of moisture in the air is that as the air mixes with the cold gas it will be cooled below its dewpoint, and the latent heat of condensation that will subsequently be released will increase the temperature of the gas-air mixture. This will have the opposite effect of the other processes, increasing the buoyancy. If 10 g of water were condensed from a 1-kg parcel of air, the increase in temperature would be 25°C. If that water were then frozen, another 3°C increase would occur.

Still another complication that is seldom taken into account is that LNG is not pure methane. According to Drake, Geist, and Smith,[41] the methane content varies from 95 percent in pipeline gas in the Northeastern United States to 65 percent in Libyan LNG. In the latter case, there might be 25 percent ethane and 10 percent propane. Ethane has a molecular weight comparable to that of air, and propane has a still higher molecular weight. To the extent that these constituents are present, the vapor cloud is less buoyant. Fractional distillation results in a vapor cloud rich in lighter constituents (e.g., methane) immediately after the spill, but with proportionately more of the heavier constituents as time goes on. Apparently no existing model for atmospheric dispersion takes this into account.

TOWARD A MORE COMPREHENSIVE MODEL

It appears that the Sutton model, adapted from the study of stack effluents and releases of radioactive particles (and most widely used in studies of LNG spills), has a number of disabilities--especially for large spills--that can be somewhat ameliorated, but not eliminated. Hence there is a need for a different model having some or all of the following characteristics:

1. It is time-dependent, which includes the capability of accepting new values of atmospheric parameters such as wind and temperature as they are observed during the course of a computation.

2. It considers explicitly the presence of two or more gases of different molecular weight and temperature and the ways in which they mix and approach a common temperature. This would include the thermodynamic effects of cooling moist air to its dewpoint, followed by release of latent heat of condensation.

3. It is three-dimensional, allowing for variations in atmospheric parameters in all directions in the horizontal and in the vertical. It specifically takes into account the stability of the air through the lapse rate.

4. It takes account of the underlying terrain both thermally and geometrically, including the heat capacity of the underlying land or water at any given point and the presence of buildings or hills that might deflect the flow.

5. In view of the ground-hugging nature of the cold, dense gas cloud, it takes account of the different flows in the boundary layer and in the free atmosphere.

6. It minimizes dependence on empirical parameters whose values are not well known. Some empirical parameters, such as eddy diffusion coefficients, are needed, but their values should not dominate the results.

7. It is capable of being run in real time on available computers, so as to provide timely information on which to base decisions, such as the ordering of burning or evacuation. A sophisticated model such as is being described could not run on a computer of the size that might be found at an installation handling LNG or aboard a tanker, but fast communications to a centralized computer are quite feasible.

This would appear to be a rather elaborate solution to a problem that has heretofore been treated much more simply, but LNG has not heretofore been handled on as large a scale as is now envisioned. The possibility of much larger spills carries with it the possibility of much greater hazard, together with diminished capability of the old models to handle the situation. Even for the 25-year-old problem of atmospheric

dispersion of radioactive contaminants, treated until now almost exclusively by Sutton's approach, there is now a tendency toward a more sophisticated model.[42] A model tailored specifically to the problem of radioactive particles is not applicable to the LNG problem, but in several respects the general approach is pertinent.

A sophisticated model for LNG might well take as its point of departure one of the existing models of cloud dynamics which solve the hydrodynamic and thermodynamic equations numerically on a finite grid. The Rand cloud model[43] is one of these. This model is time-dependent, but only quasi-three-dimensional; even so, it represents a vast advance over the steady-state, one-dimensional Sutton model. Expansion to a full three dimensions would be straightforward, although a complete three-dimensional model would tax the facilities of even a very large computer. Some compromises are possible, however, to achieve computational tractability.

An advantage of a cloud model as the foundation on which to build a model for LNG vapor is that such models already incorporate techniques for treating mixtures of gases (e.g., air and water vapor), condensation and freezing, heat transfer, differential buoyancy, effects of irregular terrain, and other complex physical processes. Progress is being made in fuller treatment of the boundary layer and of sub-grid-scale phenomena. In short, although no single existing cloud model fully incorporates all of the characteristics listed above as desirable for an LNG model, each of the characteristics is contained in one or another of the models. The techniques are available for bringing them all together along with modifications to suit the unique requirements of an LNG model.

A model of this type would give the concentration of LNG vapor at any given point in three-dimensional space and at any given time from the occurrence of the spill until the vapor cloud was completely dissipated. It would take full account of the changing rate of production of vapor at the source, the topography of the surroundings, and the detailed variation of meteorological conditions with space and time. Such values of concentration would be means over a volume defined by one mesh length and over the duration of one time step, both of which can be made arbitrarily small, depending on the economics of computation. In practice the mesh length

might be of the order of 100 m and the time step of the order of 10 s, at least at the beginning. If a large cloud expands and drifts a considerable distance, both of these values can be increased. In any case, there are techniques for inferring the sub-grid variations about the mean, thus determining the probability of occurrence of flammable pockets at given times and places. With such information available there is sound basis for making such decisions as to whether to burn or to evacuate.

The ramifications of such decisionmaking processes are endless, but the options are available only if one has a model yielding much more and better information than current models. If handling of LNG increases as much as has been suggested, the potential hazards will easily justify a large and intensive effort directed toward developing a model of atmospheric dispersion that represents a great advance over those currently available.*

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*After this report was completed, a study by Science Applications, Inc.[44] appeared that confirms the doubts expressed herein about the validity of the plume models as applied to the LNG problem. SAI has developed a model called SIGMET that has many of the desirable characteristics listed above. Unfortunately, to date it has been possible to test it only against a rather small spill, but in that test SAI reports good verification. This appears to be an important step forward, but probably not the final answer.

V. REVIEW AND CONCLUSIONS

Accidental spillage of LNG presents a number of safety hazards. The operational risk of large-scale importation facilities must be estimated on the basis of the various possible accident scenarios and estimates of the probabilities of each. The spillage of LNG on water in a harbor, with subsequent boil-off and atmospheric dispersion, is one of the more hazardous scenarios. The adequacy of scientific models and the experimental validation used to predict the extent of this hazard have been points of contention among engineers and scientists.

The second major aspect of research discussed herein concerns the production of a vapor cloud from spilled LNG, and the third concerns the dispersion of that cloud in the atmosphere. The physics of LNG spillage on water is that of a complex boiling fluid, with a vapor film between the water and the LNG acting to regulate the flow of heat. Although small-scale spill tests have been conducted, no tests of large spills have been made. Some large experiments are needed to verify theoretical models and to establish similitude between small-scale and large-scale spills.

The rate of vaporization and characteristics of the vaporized LNG are important inputs in determining the nature of the atmospheric dispersion of LNG vapor. Dispersion models have been used to predict the size, temperature, concentration, and motion of the cloud from the time and place of origin until it is so completely mixed that no hazard exists, but research conducted in this area has led to estimates of the distance the hazardous region extends from the source that differ by orders of magnitude.

As an example of the disagreement existing concerning the range of the hazard we find that Feldbauer[45] estimates that in a stable atmosphere with a constant wind of 5 mph the distance to the limit of the flammability is 21,000 ft for a 4000-m^3 spill. Professor James A. Fay from Massachusetts Institute of Technology[46] predicted a distance similar to Feldbauer with the same spill and over 20 mi for a 25,000-m^3 spill. Under similar conditions, a 17,000-ft limit is predicted for a spill of 100,000 m^3 in the EIS

prepared for the Distrigas and Eascogas LNG terminal in New York.[2] The U.S. Coast Guard[47] feels that 15 mi is a better estimate for a spill of 100,000 m^3, and possibly even farther if consideration is given to local concentration. D. S. Burgess[48] summarizes the controversy; see Table 2.

For the same spill of 100,000 m^3, the predictions of the limits of flammability range from 17,000 ft to 670,000 ft. Burgess concludes that "Obviously, there has to be something quite wrong with somebody's calculations."

At issue is whether the vapor cloud formed by the boil-off gains any positive buoyancy during its contact with the water, whether it rises just enough to lose conductive contact with its heat source while remaining negatively buoyant, or whether it remains negatively buoyant and spreads out to a large area. Furthermore, the limits of flammability argument centers on the natural variability of gas concentration. Although the average (time or geometrical) concentration may be less than the 5 percent for a flammable mixture, natural randomness results in the existence of flammable regions.

The third major research area in assessment of the risks of LNG is the impact of the cloud of vapor on property and people in the vicinity of the LNG importation terminal. Evacuation plans are usually part of such an analysis, yet none has been examined directly in the LNG context. Such plans have been used to reduce the population under risk in studies to site nuclear reactors. Criticism of disaster planning has been made on the basis of the failure to conduct actual tests and because proper instructions were not given to those in the evacuation zones. Thus evacuation as a means of reducing risk seems too optimistic.

It seems apparent that importation of LNG in substantially increased quantities will create hazards that cannot properly be evaluated by existing techniques. The large differences in the estimates quoted by Burgess indicate clearly that the models in use to predict the rate of evaporation and the atmospheric dispersion are woefully inadequate.

In both instances the models have been taken over from existing technologies with a minimum of changes to allow for the unique characteristics of the LNG problem. While this procedure is not in itself bad, in some ways

Table 2

DISTANCES TO END OF FLAMMABLE ZONE FOR VARIOUS SPILL SIZES UNDER STABLE ATMOSPHERE

(in feet)

Spill Size (m^3)	MIT[a]	BuMines[b]	API[c]	FEIS[d]
100,000	670,000	>400,000	(74,000)	17,000
25,000	300,000	>200,000	37,000	--
5,000	120,000	>90,000	(17,000)	4,500
1,000	53,000	>40,000	(7,400)	--
100	13,000	2,600	(2,300)	--
10	3,000	>4,000	--	--

[a]Ref. 48.

[b]Ref. 31.

[c]Ref. 50. The figures in parentheses are crude extrapolations made by Burgess of their estimate for a spill of 25,000 m^3.

[d]Ref. 2.

the models were already beginning to outlive their usefulness in the old technologies and in other ways were not properly adaptable to the new conditions.

With different physical models and insufficient historical records for proper statistical treatment, it is not surprising that there is a lack of consensus on the degree of expected hazard. One path toward the development of better physical models has been set forth in this report. There are, perhaps, other equally valid paths, but any of them will lead to much more complex models than those now in use. Formulating such sophisticated models is not a trivial undertaking, so there should be no delay in their development.

As to the statistical part of the assessment of hazards, there is no substitute for experience. The cautionary note is that while we are gaining that experience we must make extraordinary efforts to foresee and avoid

hazardous conditions. With the potential for large-scale damage so great and our knowledge of the probabilities and our ability to model the physical processes so small, we must exercise a special degree of caution in planning for new facilities and increased shipping.

It is clear that the systems safety research necessary before LNG terminals proliferate is just beginning. Such a safety analysis must include a composite of most of the probability estimation approaches mentioned here. The place for fault tree analysis in the prospective safety study of LNG operations is unclear. While catastrophic accidents can occur, they seem only to require remote siting to virtually eliminate any hazard to innocent property and people. Unconventional events, such as sabotage, can be minimized at remote sites. Once adequate safety analyses are available and more operating experience has been obtained, then the question of siting in inhabited areas such as in conventional harbors can again be addressed.

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