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Liquefied Gaseous Fuels Safety and Environmental Control Assessment Program: Second Status Report

October 1980

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U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Environment
Environmental and Safety Engineering Division

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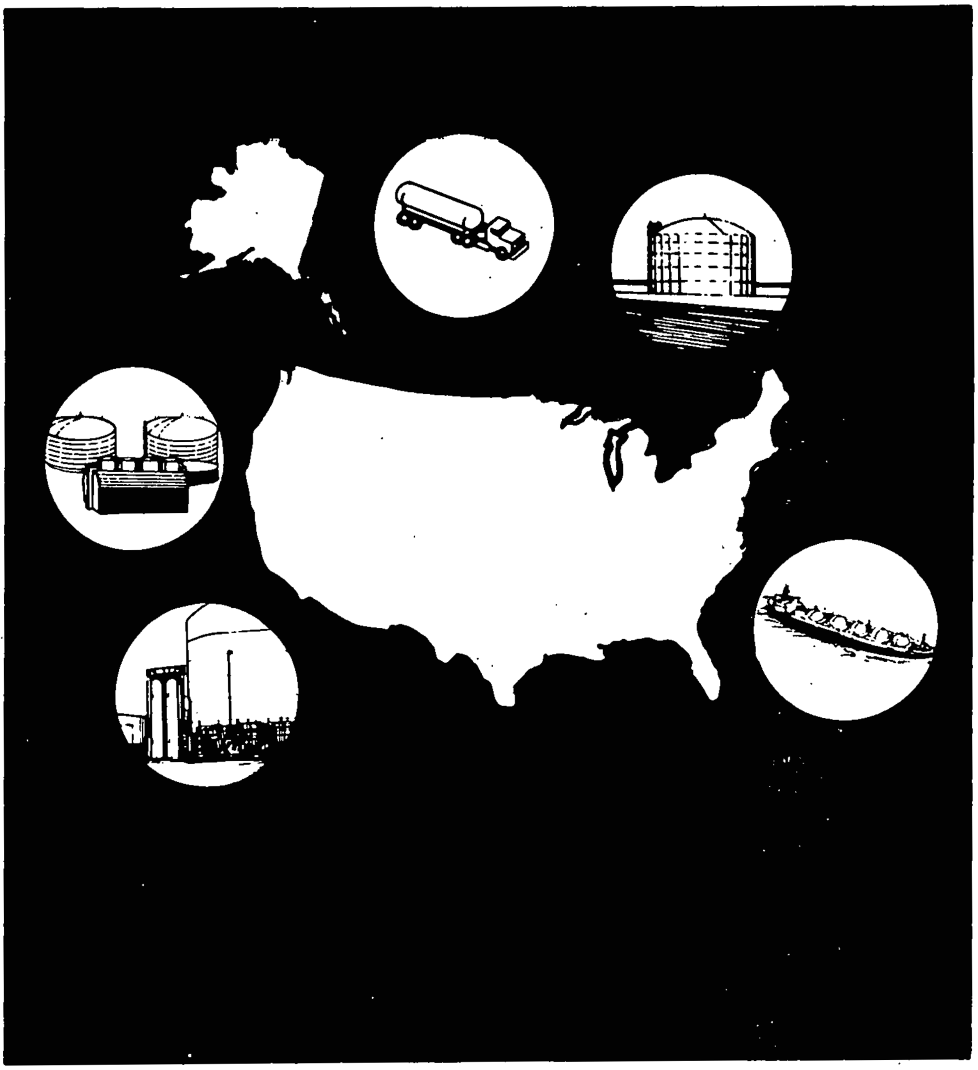

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VOLUME 3

LPG, AMMONIA, HYDROGEN REPORTS

The Reports contained in this document were prepared for the government under a variety of contracts:

Aeroject Energy Conversion Company	DE-AC-03-78EV02057
Applied Technology Corporation	DE-AC-05-78EV06020
Arthur D. Little, Inc.	DE-AC-02-78EV04734
Jet Propulsion Laboratory	NAS-7-100
Lawrence Livermore Laboratory	W-7405-ENG-48
Los Alamos Scientific Laboratory	W-7405-ENG-36
Massachusetts Institute of Technology	DE-AC-02-77EV04204 DE-AC-02-79EV04548
Naval Weapons Center	DE-AI-01-79EV10072 MIPR Z-70099-8-816817A
Pacific Northwest Laboratory	DE-AC-06-76RLO 1830

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Microfiche: $3.00

ACKNOWLEDGMENT

The Liquefied Gaseous Fuels Safety and Environmental Control Assessment Program originated in the Environmental and Safety Engineering Division, Office of the Assistant Secretary for Environment, U.S. Department of Energy. The Program is coordinated among the following:

- U.S. Department of Commerce
  - Maritime Administration
  - National Bureau of Standards

- U.S. Department of Transportation
  - Coast Guard
  - Federal Railroad Administration
  - Office of Pipeline Safety Regulations

- National Aeronautics and Space Administration
- National Science Foundation
- The Fertilizer Institute
- The Gas Research Institute

This document was compiled by Pacific Northwest Laboratory, operated by Battelle Memorial Institute, who is assisting the Environmental and Safety Engineering Division in the development and planning of this program.

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FOREWORD

The Assistant Secretary for Environment has responsibility for identifying, characterizing, and ameliorating the environmental, health, and safety issues and public concerns associated with commercial operation of specific energy systems. The need for developing a safety and environmental control assessment for liquefied gaseous fuels was identified by the Environmental and Safety Engineering Division(a) as a result of discussions with various governmental, industry, and academic persons having expertise with respect to the particular materials involved: liquefied natural gas, liquefied petroleum gas, hydrogen, and anhydrous ammonia.

This document is arranged in three volumes and reports on progress in the Liquefied Gaseous Fuels (LGF) Safety and Environmental Control Assessment Program made in Fiscal Year (FY)-1979 and early FY-1980. Volume 1 (Executive Summary) describes the background, purpose and organization of the LGF Program and contains summaries of the 25 reports presented in Volumes 2 and 3. Annotated bibliographies on Liquefied Natural Gas (LNG) Safety and Environmental Control Research and on Fire Safety and Hazards of Liquefied Petroleum Gas (LPG) are included in Volume I.

Volume 2 consists of 19 reports describing technical effort performed by Government Contractors in the area of LNG Safety and Environmental Control. Volume 3 is a similar compilation and contains 6 contractor reports on LPG, anhydrous ammonia and hydrogen energy systems.

(a) Effective June 1980, the Environmental Control Technology Division was augmented by acquiring additional functions: the new name of the organization is the Environmental and Safety Engineering Division. Throughout the text, where the old name is used, is should now refer, in all cases, to the Environmental and Safety Engineering Division, Office of the Assistant Secretary for Environment. Future publications will reflect this change completely.

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FLAME PROPAGATION

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SCALE EFFECTS EXPERIMENT

VOLUME 3 - LPG, AMMONIA AND HYDROGEN REPORTS

LIQUEFIED PETROLEUM GAS

AMMONIA

HYDROGEN

REPORT T

Simultaneous Boiling and Spreading of Liquefied Petroleum Gas (LPG) on Water

R. C. Reid
K. A. Smith
H. Chang

Prepared for the
Environmental and Safety Engineering
Division
U.S. Department of Energy
under Contract DE-AC-02-79EV04548

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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FIGURES

SUMMARY

The objectives of this project are to measure the rates of boiling and spreading of liquefied petroleum gas (LPG) on a water surface and to develop an analytical model to describe the phenomena involved. The past year has been devoted primarily to the design, fabrication, testing and modification of various spill apparatus components.

The apparatus is designed for one-dimensional studies. A long, narrow, water-filled channel has been constructed for measuring the boiling and spreading rates of liquefied petroleum gas (LPG) spilled on water. Vapor concentrations and temperatures of vapor and liquid will be used to quantify the results.

Spills of pentane and liquid nitrogen on water were conducted, and the spreading rates were measured as a function of time. The quantities spilled varied from 0.5 to 3.0 liters. Experimental results with pentane agree well with a theoretical model proposed by Fannelop and Waldman. Several liquid nitrogen runs were also made; however, the experimental data could not be correlated satisfactorily by an analytical model. Future work will emphasize LPG spilled with simultaneous boiling and spreading.

INTRODUCTION

The objectives of this project are to measure experimentally the rates of boiling and spreading of liquefied petroleum gas (LPG) on a water surface and to develop an analytical model to describe the phenomena involved. Our principal effort has been to complete the construction of the apparatus and conduct preliminary experiments. Future experiments are anticipated to provide quantitative data on which to base the development of an analytical model for estimating potential hazards of LPG tanker accidents.

EXPERIMENTAL PROGRAM

One-dimensional boiling and spreading tests are to be conducted in a long, narrow water trough. The trough, which is made of 17.8-cm-OD, 16.5-cm-ID Plexiglas tubing and is approximately 4 m long, is half filled with water. Liquefied Petroleum Gas (LPG) or a simulant liquid is spilled at one end, and the evolved hydrocarbon vapors are ducted to the hood. Figure 1 shows a schematic representation and Figure 2 shows an actual photograph of the apparatus.

Simply spilling the cryogen from the opening of the trough would cause severe disruption of the water surface and the momentum impact would cause undesirable wave motion in the tube with back-reflections from the far end. A cryogen distributor has been designed to minimize the disturbance of water, and a packing of stainless steel wool is placed at the end of the apparatus to prevent the back-wave motion. A transverse view of the cryogen distribution is shown in Figure 3.

The distributor employs a spring-loaded piston which, upon release, opens a side port through which the cryogen flows onto the water surface. This design provides for rapid delivery of LPG without severe disruption of the water surface. The piston cylinder, with an outside diameter of 17.8 cm and a height of ∿60 cm, is fabricated from Lexan polycarbonate resin to permit observation of the cryogen liquid level. The maximum liquid capacity of the cryogen distributor is ∿3 liters. Upon full downward displacement of the piston, the effective cross-sectional flow area through the side port is ∿65 cm^2.

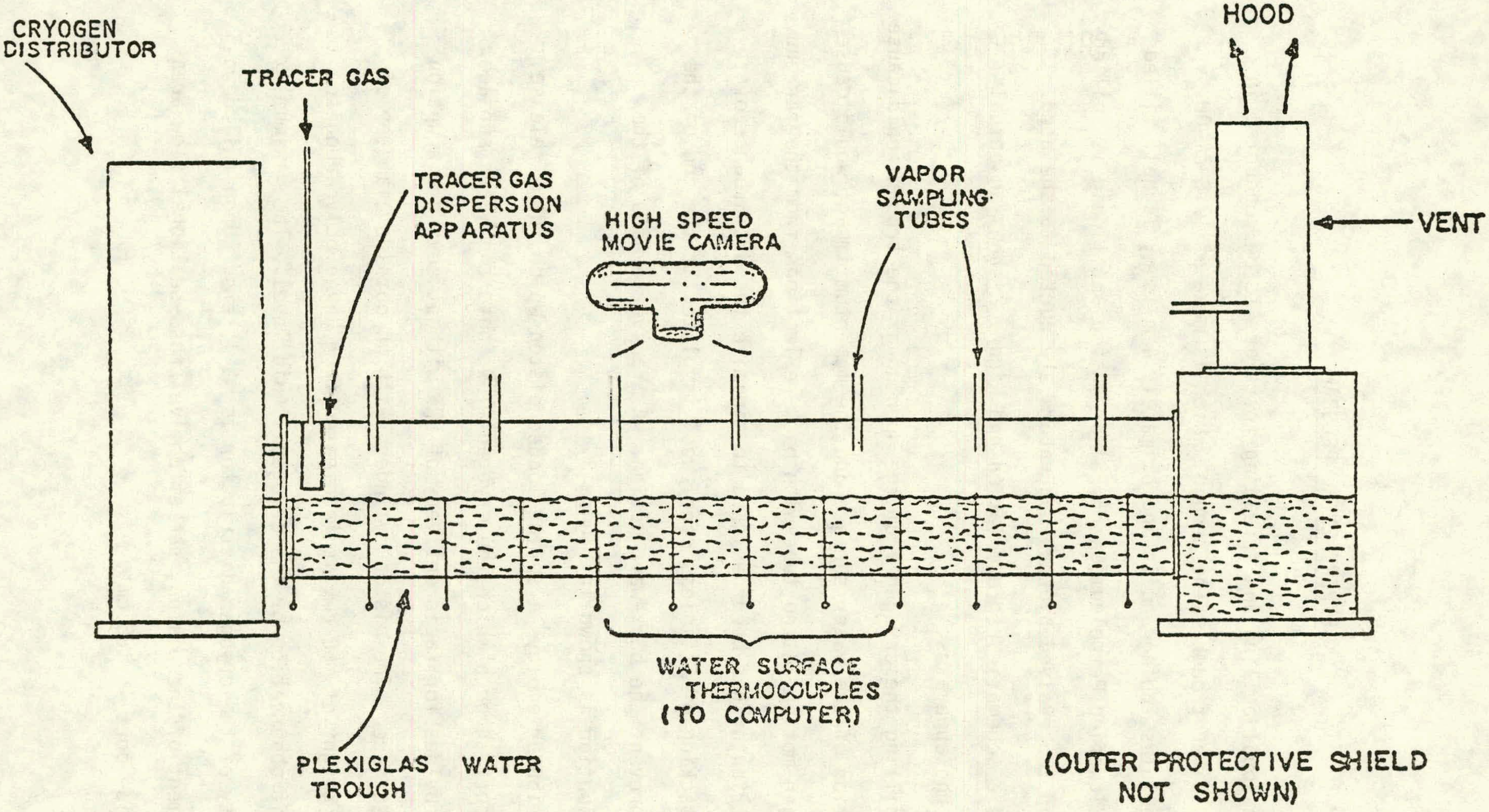


FIGURE 1: Schematic of Spill/Spread/Boil Apparatus

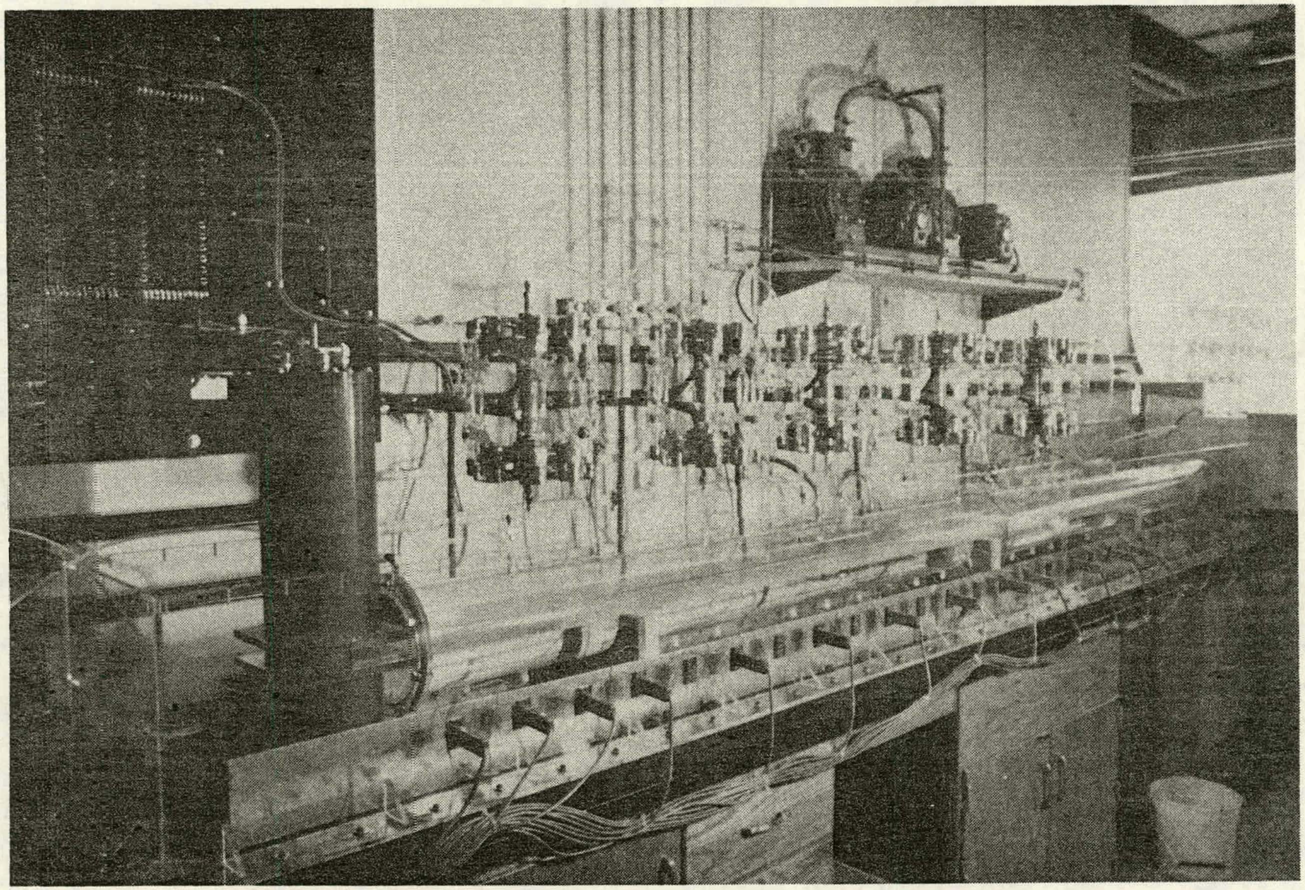


FIGURE 2: A PHOTOGRAPH OF THE SPILL/SPREAD/BOIL APPARATUS

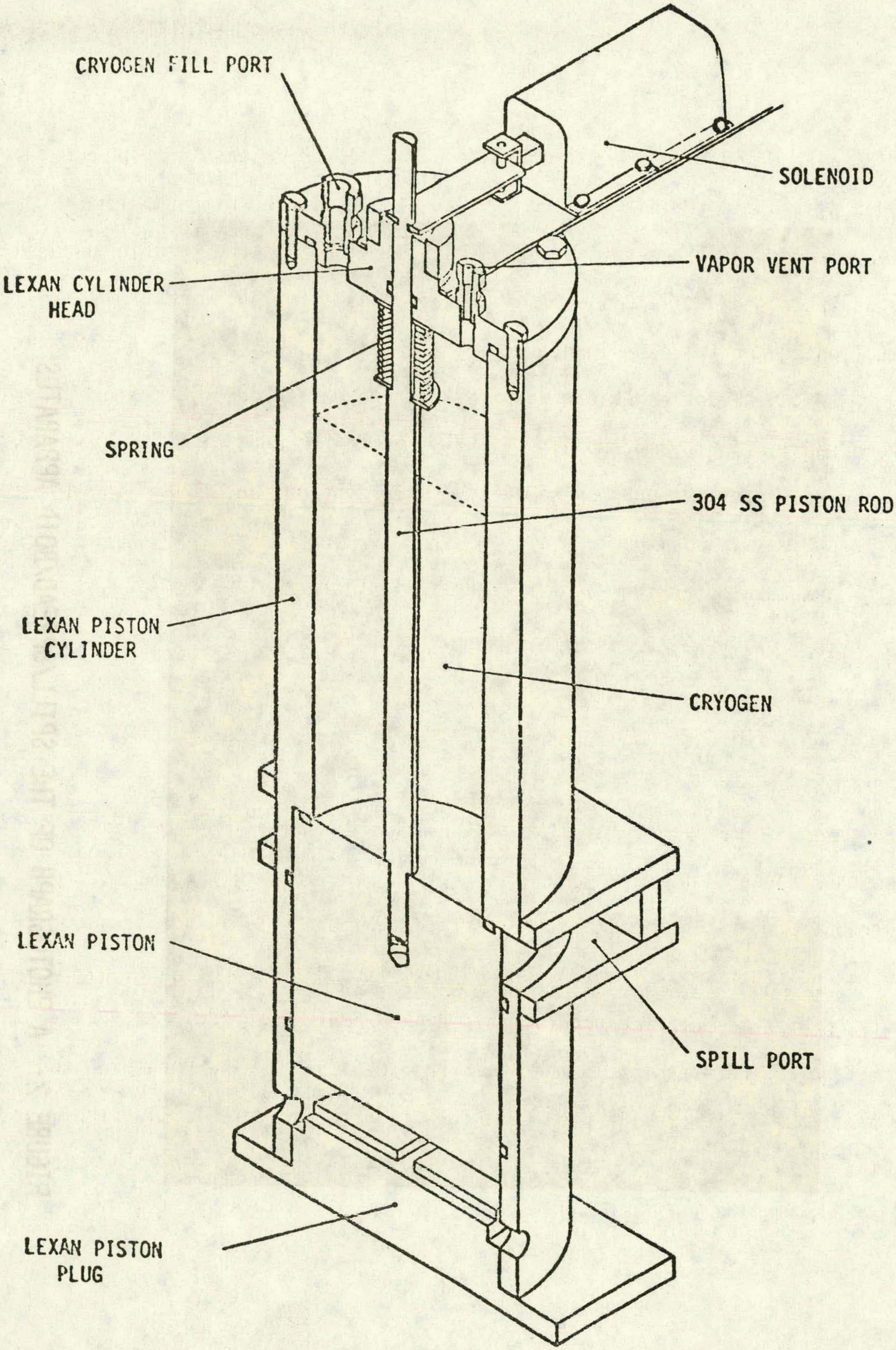


FIGURE 3: TRANSVERSE VIEW OF CRYOGEN DISTRIBUTOR

A nitrogen-driven pneumatic cylinder is used to release the spring-loaded piston and to initiate the cryogen delivery. The nitrogen flow is regulated by a three-way solenoid valve linked to a programmable sequencer (Texas Instruments 5TI-102 series), thus providing for automatic release actuation during the experiment.

Water, cryogen, and vapor temperatures are monitored by a set of chromelconstantan thermocouples. Eight vapor thermocouples, fabricated from 25-μm wire, enter through the top of the water trough, and eight liquid thermocouples, fabricated from 127-μm wire, are introduced through the bottom and located at the water surface to indicate the passage of LPG. The thermocouple outputs are fed into a NOVA-840 real time computer for storage and analysis. A high-speed camera will be used to record the movement of LPG.

The local boil-off rates of LPG on water are monitored in an indirect manner. An inert tracer gas is introduced continuously into the system through a vapor dispersion apparatus that enables the tracer gas to be distributed evenly above the water surface inside the tube. Vapor samples are taken at different locations downstream during the experiment and analyzed by a temperature-programmable gas chromatograph (currently on loan from another project in the Chem. Eng. Dept.). The temperatures and compositions of vapor will provide information needed to determine the mass boiled off as functions of time and position. The detail of data treatment is described in a subsequent section.

The temperature-programmable gas chromatograph is a Hewlett-Packard series 5734A model. The mixture samples are removed from the sampling bulb by means of a Precision Sampling-Pressure Lok gas-tight syringe and then run through two 180-cm stainless steel columns packed with 13X Molecular Sieve and Porapak-Q, respectively. The column temperature is initially set at ambient temperature. The inert tracer gas is separated from carbon dioxide by 13X Molecular Sieve, while methane, ethane, propane, and n-butane are separated by Porapak-Q column after the temperature is raised from ambient to 150°C at a rate of 16°C/min. After separation in the columns, the gases pass through a thermal conductivity detector. The output of the detector is integrated by a Hewlett-Packard series 3380 Advanced Reporting Integrator.

Eight vapor sampling stations are positioned along the spill apparatus. Figures 4 and 5 show the top view and isometric cut-away view of a sampling station. Each of these stations has the capacity to collect six vapor samples in an array of 25-cm^3 glass sampling bulbs. Each sampling bulb is initially purged and pressurized with carbon dioxide. During an experiment, when the lower solenoid valve opens just prior to sampling, the expansion of the carbon dioxide serves to purge the common inlet line of residual vapors. The upper solenoid valve, which is connected to a vacuum line, then opens and the sample is collected. Finally, the sampling stops when both solenoid valves close. Each complete sampling procedures takes ∿1 second.

The actuation of solenoid valves is controlled by the programmable sequencer. A 5TI-3200 TCAM (Time/Counter Access Module) enables easy monitoring and alteration of programmed timing operations.

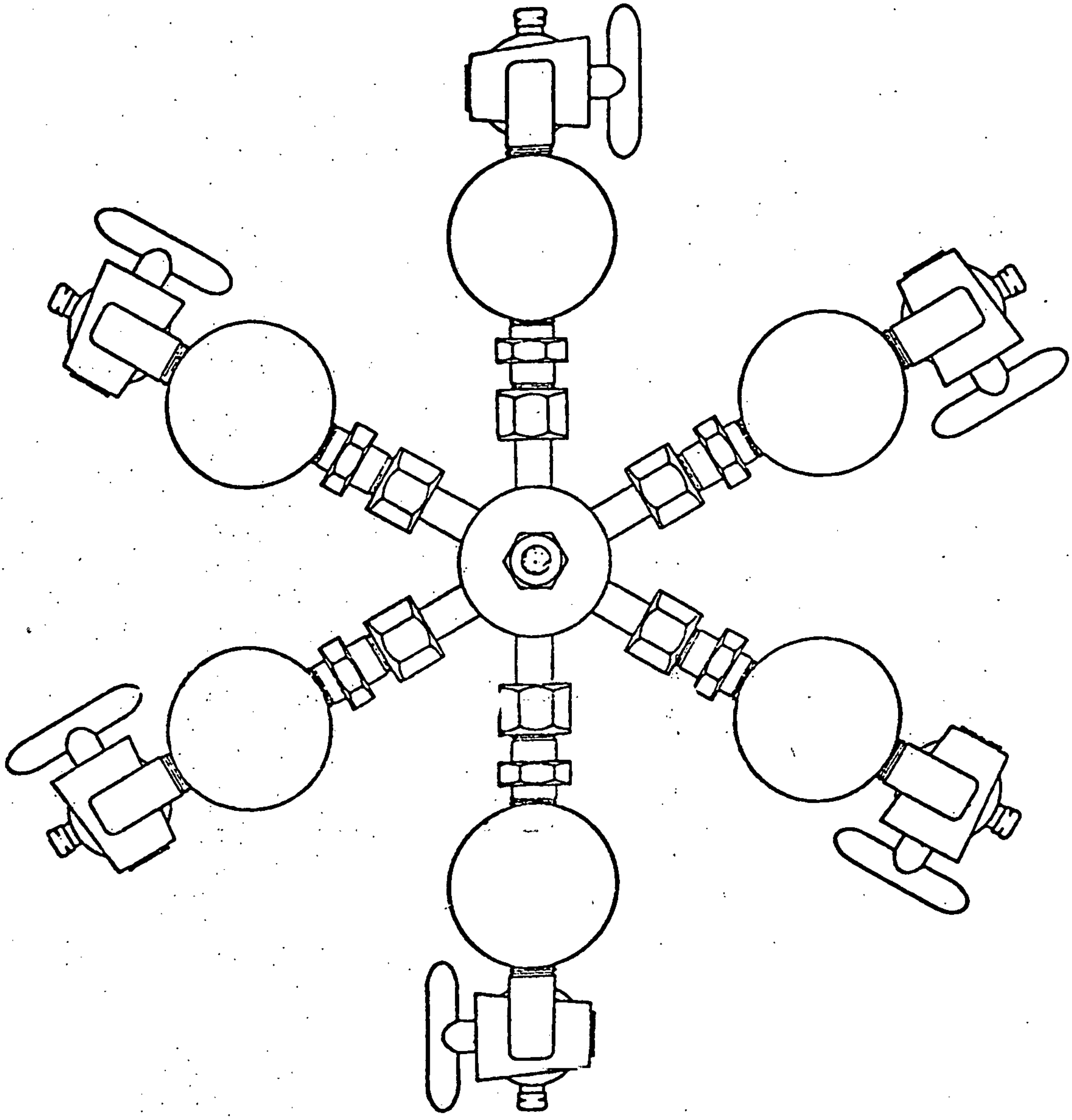


FIGURE 4

TOP VIEW OF VAPOR SAMPLING STATION

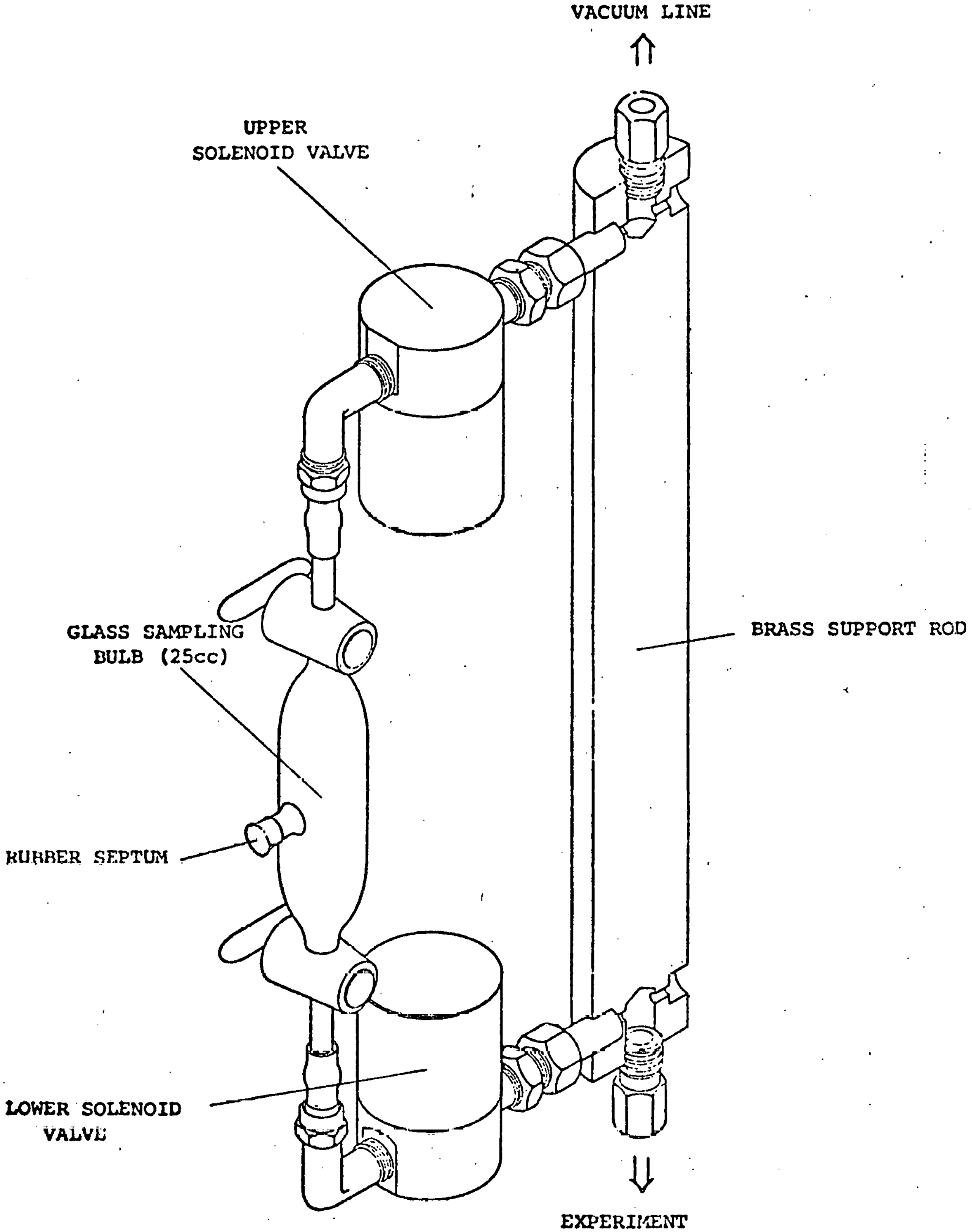
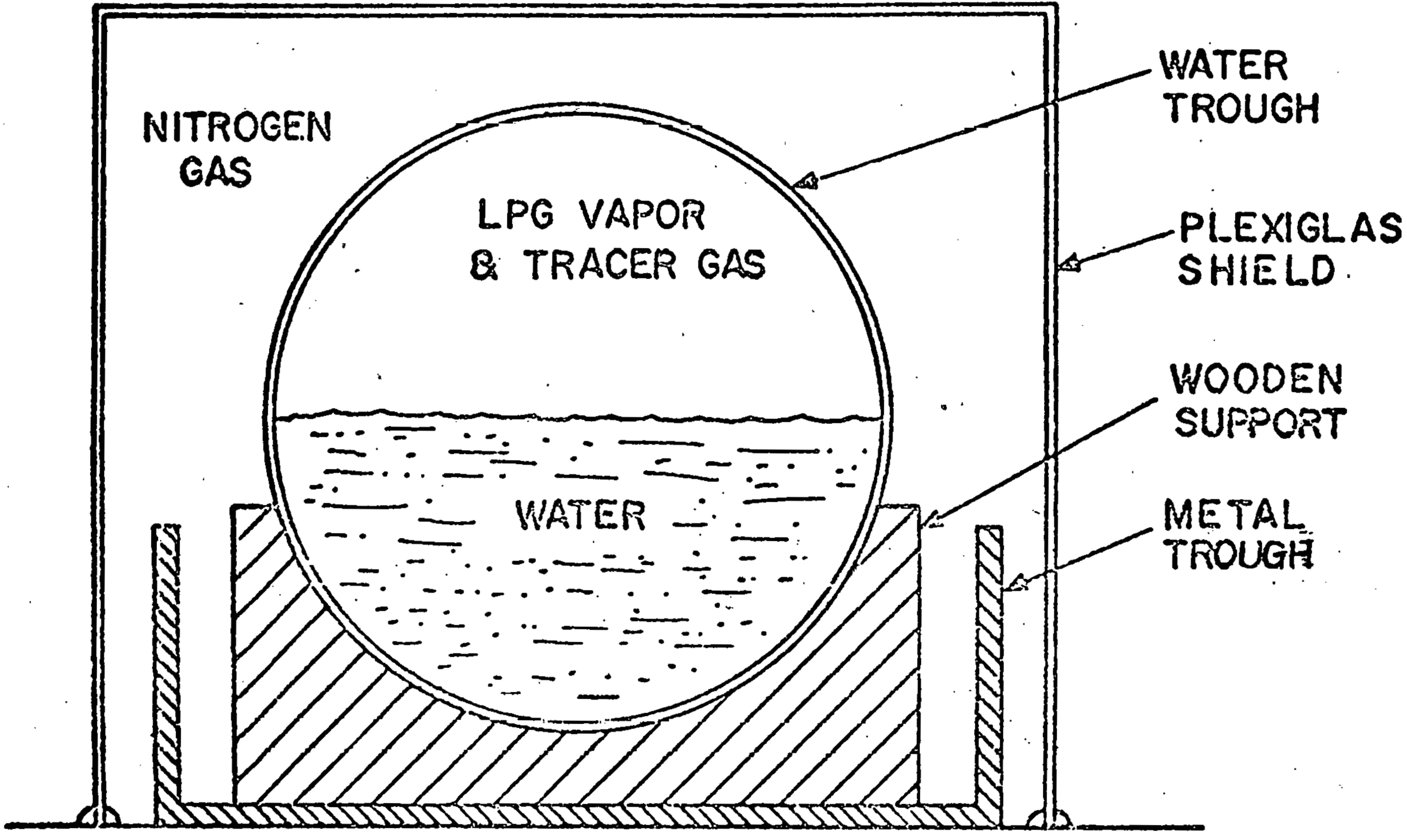


FIGURE 5

ISOMETRIC CUT-AWAY VIEW OF VAPOR SAMPLING STATION

The water trough, elevated by wooden supports, is placed within a metal U-shaped container to retain the fluid in the event of breakage. To prevent ambient air from mixing with the light hydrocarbon gases, a sealed Plexiglas box completely covers the whole apparatus, and nitrogen is introduced into the outer Plexiglas frame to purge the surrounding space of air. Figure 6 presents an end view of the safety shield.



(CROSS SECTION VIEW)

FIGURE 6: SAFETY SHIELD

DATA ANALYSIS TO DETERMINE LOCAL BOIL-OFF RATE

The tracer gas and cryogen vapor are assumed to be well mixed in the vertical direction inside the water trough. A mass balance over a differential volume element ($dV = Adx$) for the vapor phase (see Figure 7) is:

$$AVC\Big|_{x} - AVC\Big|_{x+dx} + m\,wdx = \frac{\partial}{\partial t}(CAdx) \qquad (1)$$

(mass flowing in)(mass flowing out) (evaporation source)(accumulation)

where A = cross-section are above water surface

V = vapor velocity

w = width of the channel

C = molar concentration of vapor mixture

m = local boiling rate per unit area.

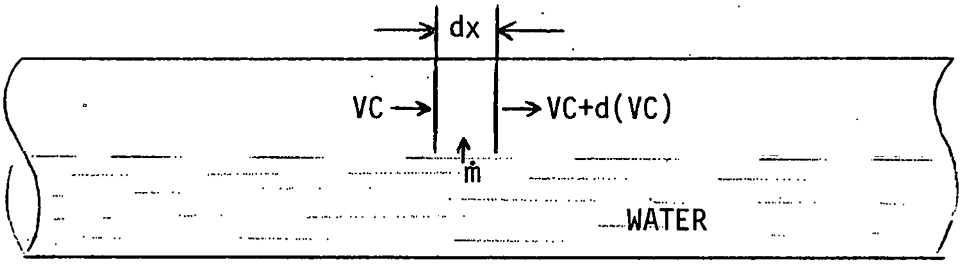


FIGURE 7: DIFFERENTIAL ELEMENT OF WATER TROUGH

Rearranging Equation 1,

$$\frac{\partial C}{\partial t} = -\frac{\partial (VC)}{\partial x} + (\frac{w}{A})m \qquad (2)$$

Similarly, the mass balance for tracer gas is:

$$\frac{\partial C^T}{\partial t} = -\frac{\partial (VC^T)}{\partial x} \qquad (3)$$

Vapor temperature measurements taken at various locations during the experiment are used to determine the molar concentration C of the vapor mixture as a function of time and position. An equation of state of the following form is used:

$$C = \frac{P}{ZRT} \qquad (4)$$

where P = pressure = 1 atm
Z = compressibility factor
R = universal gas constant
T = temperature.

The concentration of tracer gas C^T is determined by gas chromatograph analysis of the vapor samples.

$$C^T = X^T \cdot C$$

X^T is the mole fraction of tracer as obtained from sample analysis.

The local boil-off rate is determined in an indirect manner using a numerical treatment of the data. The sampled data will be fitted with an analytical expression for both independent variables, time and position. These analytical functions will be used to evaluate the local boil-off rate and gas velocity.

Writing the differential Equations 2 and 3 in finite difference form:

$$\frac{C^T_{i+1,j} - C^T_{i,j}}{\Delta t} = - \frac{V_{i+1,j+1}C^T_{i+1,j+1} - V_{i+1,j-1}C^T_{i+1,j-1}}{2\Delta x} \tag{5}$$

$$\frac{C_{i+1,j} - C_{i,j}}{\Delta t} = - \frac{V_{i+1,j+1}C_{i+1,j+1} - V_{i+1,j-1}C_{i+1,j-1}}{2\Delta x} + (\frac{W}{A})\dot{m}_{i+1,j} \tag{6}$$

where i is the ith time interval and j is the jth space interval. The analytical expressions give C^T and C at any time and position (i,j). The algorithm begins with the known velocity at j = 1 (x = 0) because the velocity there is the flow rate of pure tracer gas. Equation 5 is used to solve for the velocity at the next space interval. Substituting the two velocity values into Equation 6 allows the local boiling rate $\dot{m}$ at that particular time and position to be evaluated.

RESULTS AND DISCUSSION

The spreading of LPG on water is analogous to the spreading of an oil slick on water. The major difference between the two processes is the associated mass loss due to the evaporation of LPG.

Fay (1969, 1971) identified four basic forces that either cause or retard the spreading of oil on a water surface. The downward force of gravity causes a sidewise spreading motion of a floating oil film by creating an unbalanced pressure distribution in the pool of oil and the surrounding water. This force is proportional to the thickness and the gradient of the oil film, and the difference in density between oil and water. As the oil film spreads and becomes thinner, the gravity force diminishes.

At the front edge of the expanding slick, an imbalance exists between the surface tension at the water-air interface and the sum of surface tensions at the oil-air and oil-water interfaces. The net difference is a force which acts at the edge of the film, pulling it downwards. This spreading force does not depend upon the film thickness and will not decrease as the oil film thins out. Eventually the surface tension force will predominate as the spreading force.

These spreading forces are counterbalanced by the inertia of the oil film and of the thin boundary layer of water below it which is dragged along by friction. The inertia of an element of the oil layer decreases with its thickness as time progresses and the film spreads, but the inertia of the viscous layer of water below the oil increases with time as its thickness grows. Consequently, the viscous retardation will eventually outweigh the inertial resistance of the oil layer itself.

Fay (1969) used an order-of-magnitude analysis to recognize three principle flow regimes through which the spreading oil film passes. The first regime occurs at very short times. For a slick of sufficient size, the spreading rate is controlled by a balance of gravity and inertial forces. The second regime occurs later when the slick has become thinner. The viscous retarding force is greater than the inertial regarding force, but the gravitational force still dominates the surface-tension driving force. Therefore, the spreading rate depends on a balance of the gravity and viscous force. The third regime arises at very late times when the spreading of very thin slick is forced by surface tension and retarded by viscous forces.

Several pentane spills have been made to study the spreading of a non-volatile liquid on water. The pentane was chilled with dry ice to ∿-40°C before the spill to ensure an adequate response from the liquid-thermocouples in the water trough. Figure 8 is a photograph of the leading edge of pentane at the early time of spreading. Pentane is thicker near the spreading front and becomes thinner in the tail. This general shape is similar to Hoult's theoretical prediction for the first (gravity-inertia) regime (1972).

The experiments show that the early spreading of pentane on water agrees well with the predictions from a theoretical model of one-dimensional spreading developed by Fannelop and Waldman (1972). To be consistent with the thin layer assumption, they neglected the vertical acceleration and assumed that the oil was in hydrostatic equilibrium in the vertical direction. In the gravity-inertia regime, the gravitational force balanced the acceleration of the oil. The conservation of mass and the equation of motion are expressed as follows:

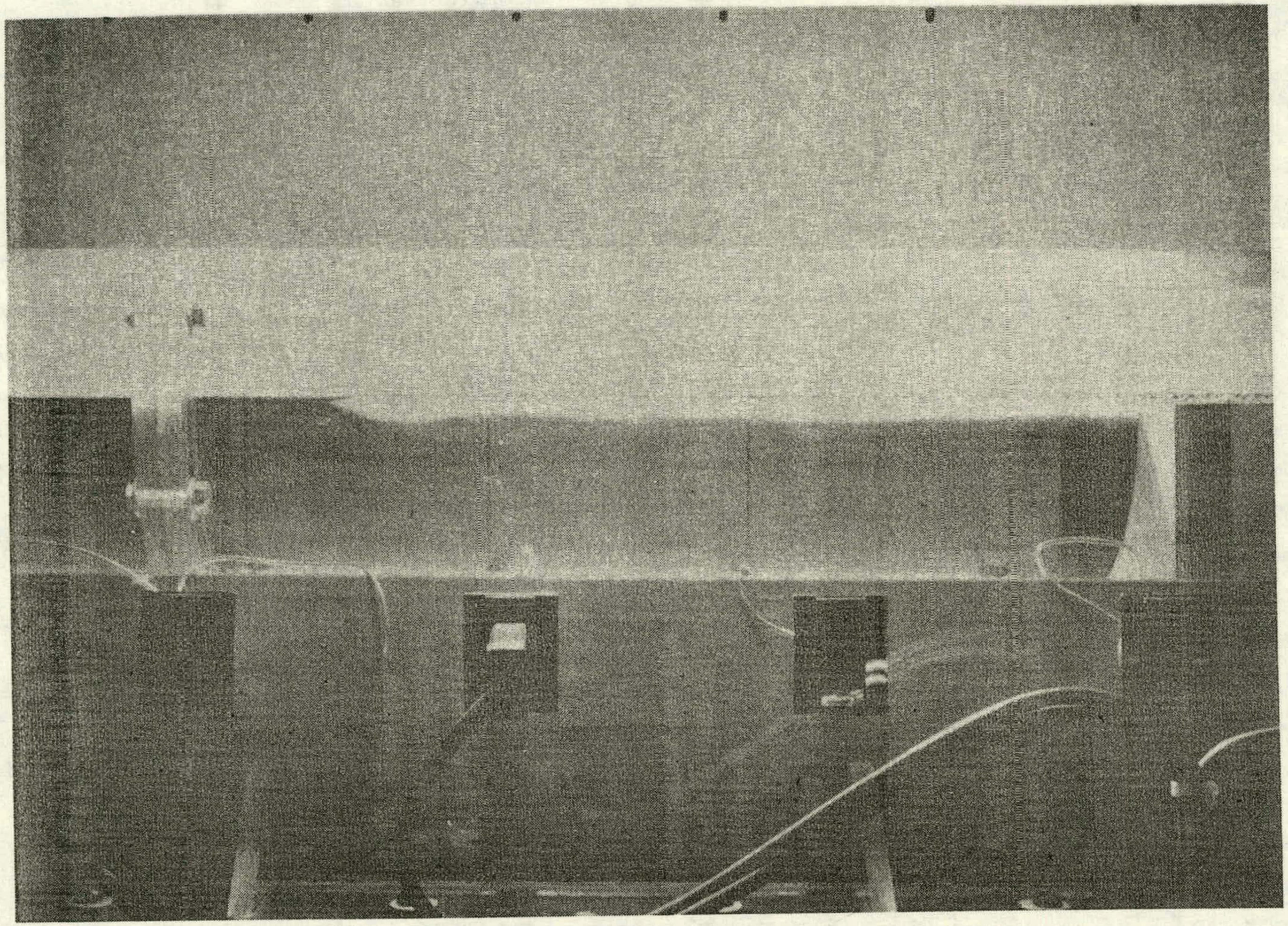


FIGURE 8: A PHOTOGRAPH OF THE SPREADING OF PENTANE ON WATER

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}(Uh) = 0 \qquad (1)$$

$$\frac{\partial U}{\partial t} + \frac{\partial U}{\partial x} = -g\Delta\frac{\partial h}{\partial x} \qquad (2)$$

where U = horizontal velocity of the oil

h = thickness of the oil

Δ = density difference between water and oil divided by density of water

g = gravitational acceleration.

The leading-edge boundary condition is used:

$$U_{LE} = (\lambda g\Delta h_{LE})^{1/2} \qquad (3)$$

where λ is experimentally determined. Fannelop and Waldman integrated Equations 1 and 2 to yield the following relation for oil slicks spreading in one-dimensional configuration. The equation gives the spreading distance as a function of time for an instantaneous spill.

$$x = \eta \left(\frac{g\Delta}{w}\right)^{1/3} V^{1/3} t^{2/3} \qquad (4)$$

where x = spreading distance from the initial spill point

V = volume of the oil

t = time after initial spill

w = width of the channel

η = experimentally determined coefficient.

Figure 9 presents the experimental results from 11 pentane spills of various volumes. The data show that the dimensionless spreading distance is proportional to the dimensionless time raised to the two-thirds power.

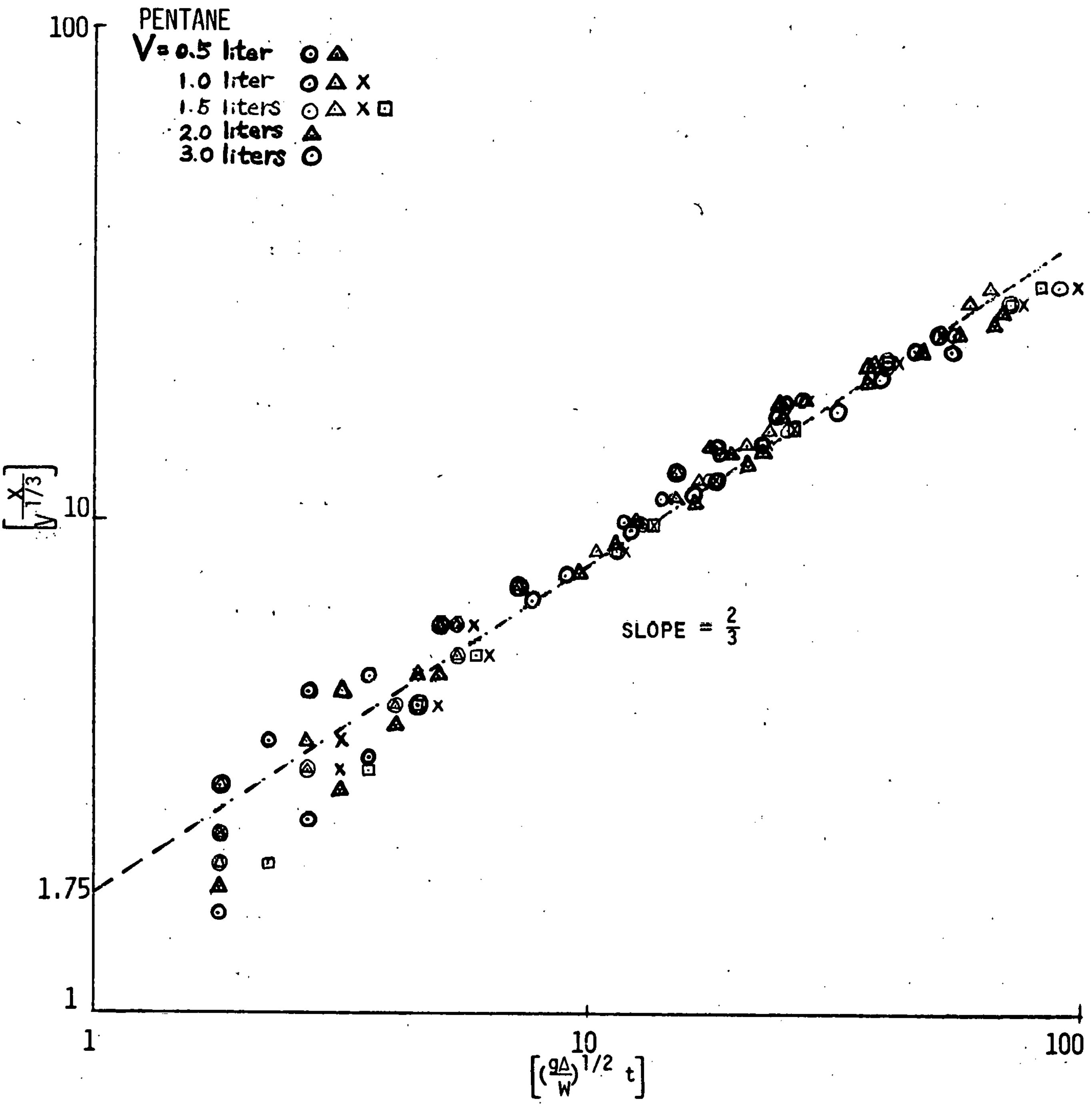


FIGURE 9: CORRELATION FOR SPREADING DISTANCE AS FUNCTION OF TIME

The intercept value is equal to 1.75 and is taken as the coefficient η. In Figure 10, experimental values and the theoretical predictions are compared. The agreement between theory and experiment is very good.

Several liquid nitrogen spills were performed to study the effect of boiling on the spreading process. Figure 11 is a photograph of the boiling and spreading of liquid nitrogen on water. Again the general shape is a thick spreading front, followed by a thinner tail, as was observed in the pentane spills. Many bubbles formed at the liquid nitrogen-water interface during spreading and caused severe agitation. A layer of ice formed on the water surface downstream of the distributor. Initially film boiling occurs because of the large temperature difference between liquid nitrogen and water. As the surface temperature of water decreases and patches of ice form and become subcooled, the ice surface initiates nucleate boiling and the rate of vaporization increases. In the vicinity of the construction cryogen distributor, however, no ice formation was observed. This may be due to the severe agitation of water near the opening of the cryogen distributor or to quick evaporation of the thin tail of the spreading cryogen. In the experiment, very soon after the spreading front has passed, the water immediately adjacent to the distributor is free of liquid nitrogen.

In Figure 12, the spreading distance-time data for liquid nitrogen and pentane spills of the same initial volume are compared. Liquid nitrogen has a higher density than pentane. When nitrogen spreads, it vaporizes, and, therefore, its volume decreases with time. Because of the density difference and the volume change with evaporation, Fannelop and Waldman's

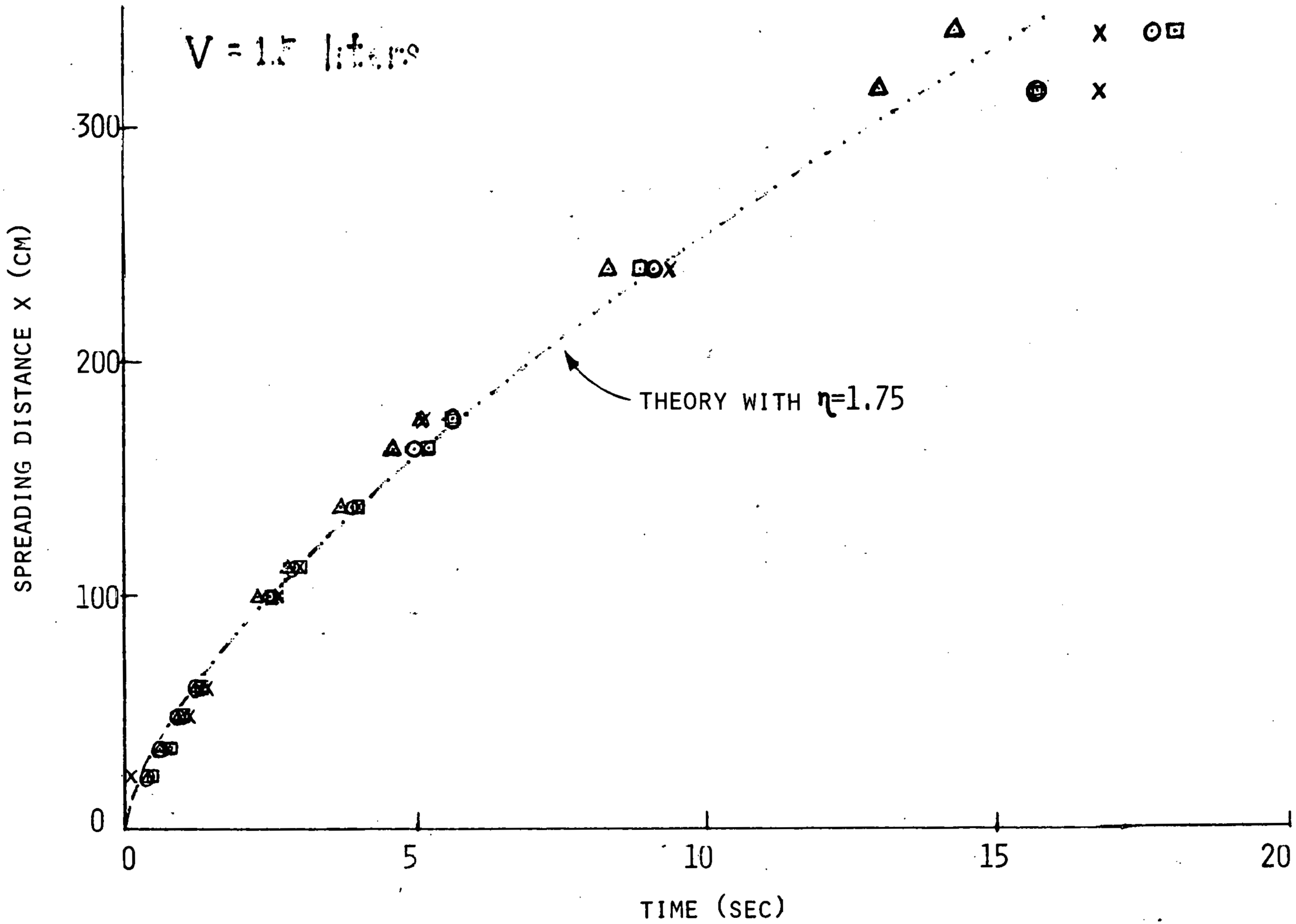


FIG.10: SPREADING DISTANCE AS FUNCTION OF TIME FOR PENTANE SPILL

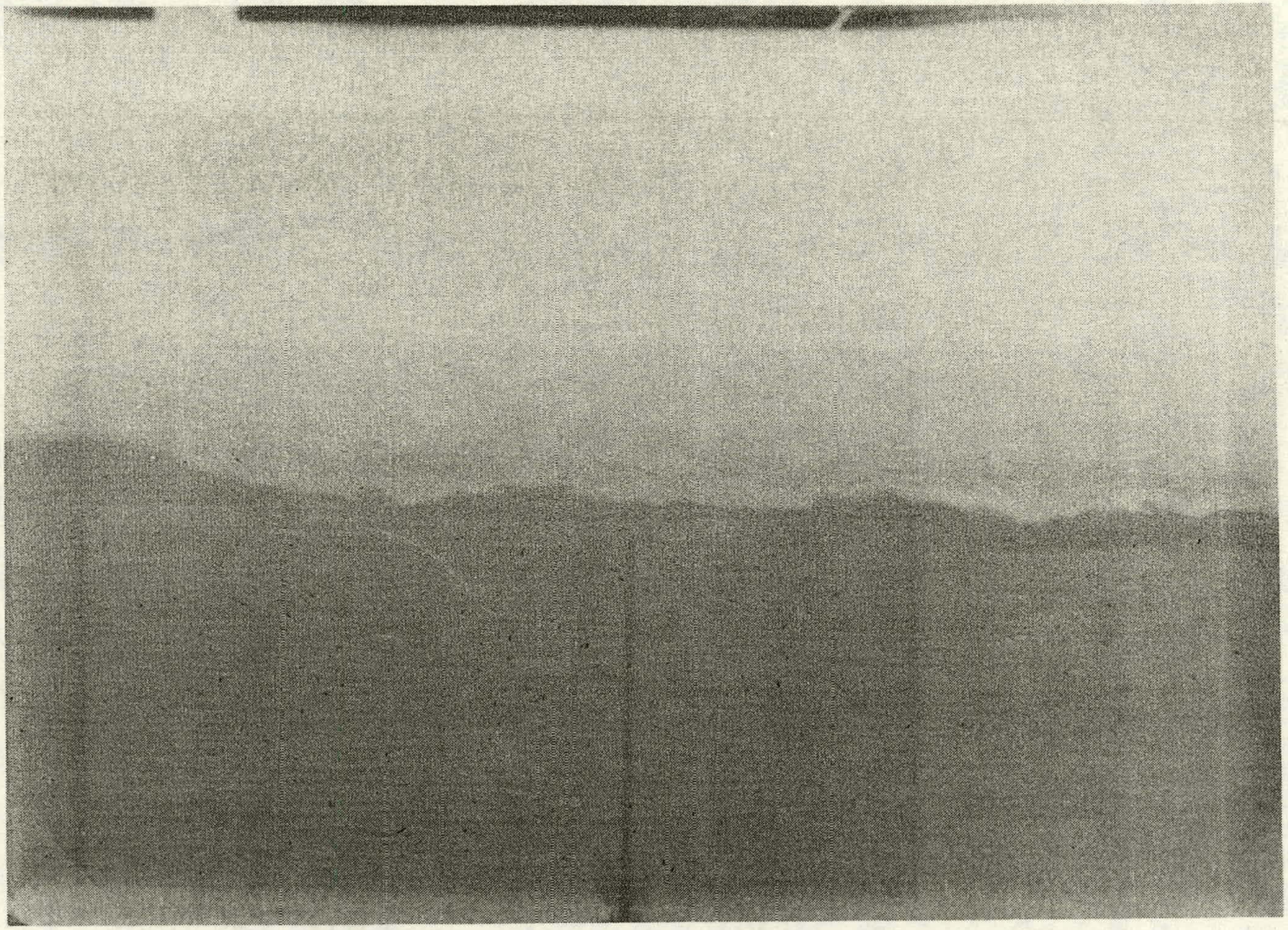


FIGURE 11: A PHOTOGRAPH OF BOILING AND SPREADING OF LIQ.N_2 ON WATER

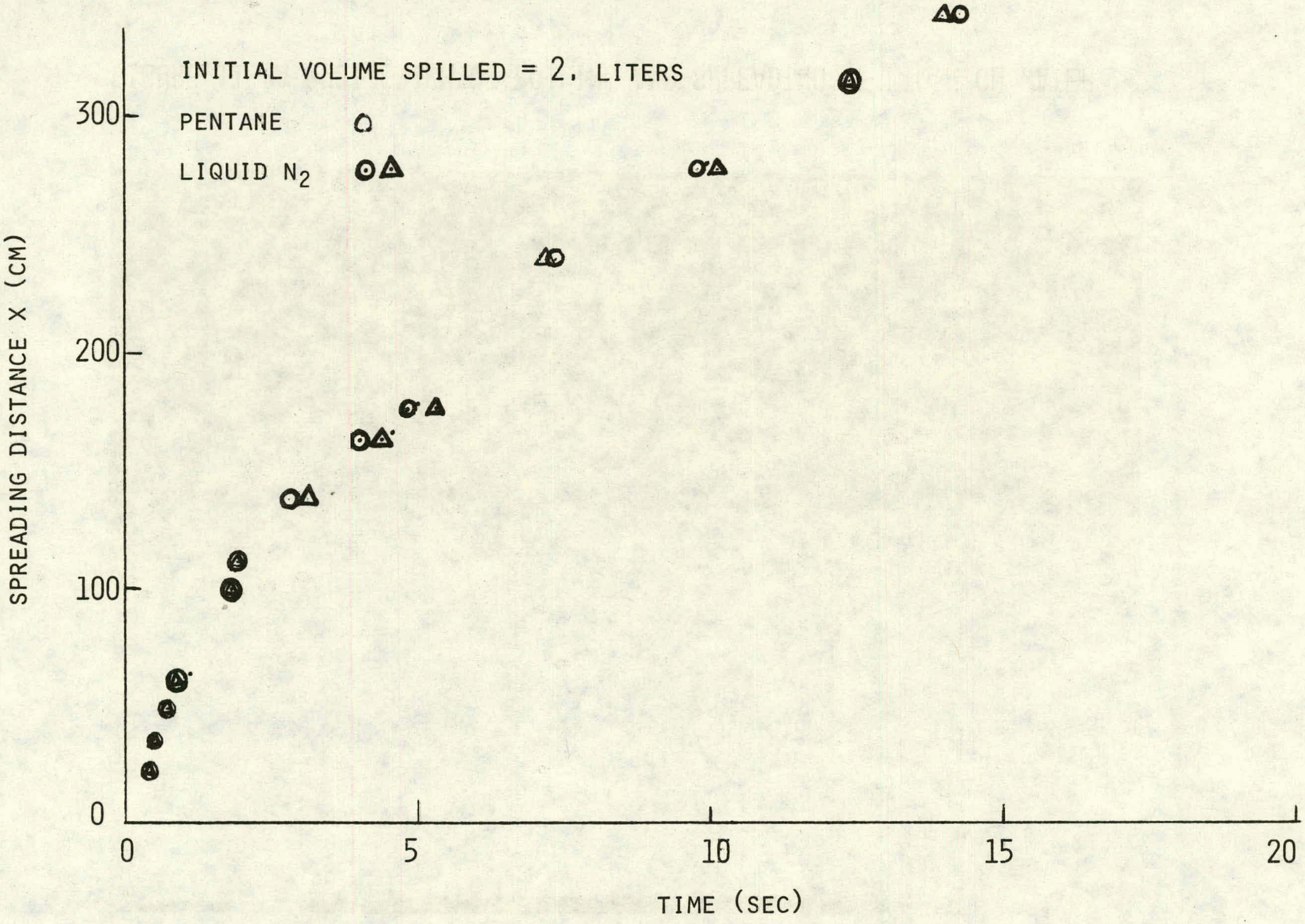


FIG.12: SPREADING DISTANCE AS FUNCTION OF TIME FOR PENTANE AND LIQUID N_2 SPILLS

theory would predict that liquid nitrogen should spread much slower than pentane. However, bubbles of evaporated nitrogen decrease the effective density of the liquid nitrogen layer and increase its volume. These facts may explain the larger-than-expected liquid nitrogen spreading rate.

Raj (1977) proposed a one-dimensional spreading model for an evaporating cryogen on a water surface. He assumed that an instantaneous spill and a "mean film thickness" could characterize the cryogen layer at any time. Assuming a constant boil-off rate per unit of interfacial area, Raj obtained an expression for the spreading rate by balancing the gravitational force with the inertial resistance force. His spreading distance as a function of time is:

$$x = 1.75\left(\frac{g\Delta}{w}\right)^{1/3} V_0^{1/3} t^{2/3} + 0.072\left(\frac{\dot{q}}{\rho\Delta Hv}\right) {\frac{(g\Delta)^2}{\frac{V_0}{w}}}^{1/3} t^{7/3} \qquad (5)$$

where x = spreading distance from the initial spill point

V_o = initial volume of cryogen spilled

$g\Delta$ = effective density = $g(\rho_{water} - \rho_{cryogen})/\rho_{water}$

w = width of the channel

$\dot{q}$ = constant heat flux

ΔHv = enthalpy of vaporization

t = time after initial spill.

In Figure 13 the experimental data from liquid nitrogen spills and the prediction of Raj's model are compared. Raj's model is limited by the assumption of constant boiling rate and, therefore, underestimates the spreading distance.

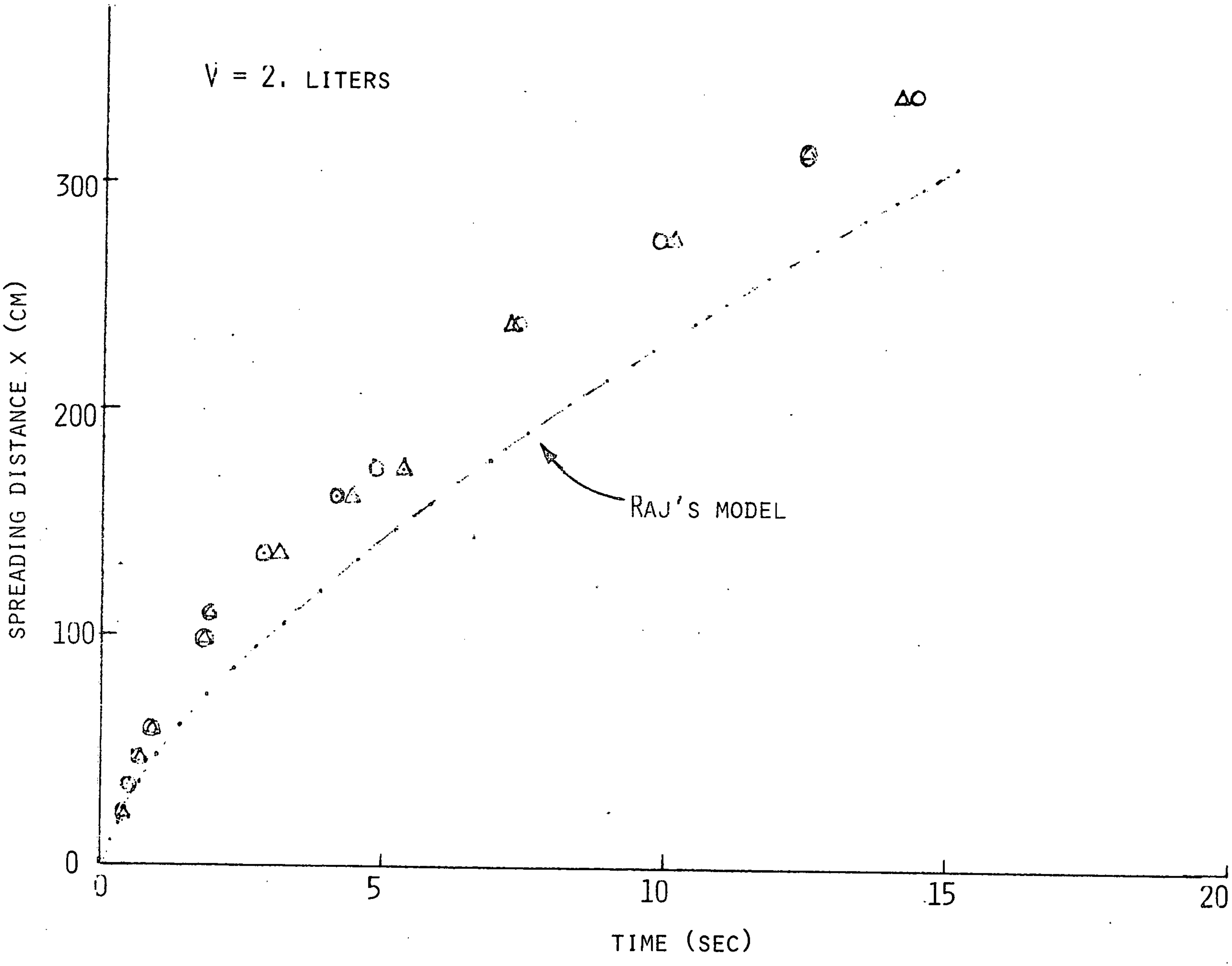


FIG.13: SPREADING DISTANCE AS FUNCTION OF TIME FOR LIQUID N_2 SPILL

A satisfactory model for describing the simultaneous boiling and spreading process has not yet been developed. Developing an adequate model is one of the project objectives.

FUTURE WORK

With the exception of the outer safety shield covering and hood connections, fabrication of the spill apparatus is nearly complete. Liquid nitrogen spills are being conducted to test thoroughly the vapor sampling system, the cryogen distributor, and the temperature monitoring system. The safety shield will be closed when the debugging tests with liquid nitrogen are satisfactorily completed.

Liquid propane and LPG spills will be carried out under the following conditions:

1. initial quantity spilled - from 0.5 to 3.0 liters
2. initial composition of LPG - propane 75-100% in volume
   ethane 0-20%
   n-butane 0-10%
3. type of spill - either instantaneous or continuous
4. agitation of water.

When the data have been obtained, an analytic model will be developed to describe the boiling/spreading process and estimate the potential hazards from real LPG accidents.

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REPORT U

LPG Safety Research

J. R. Welker
D. W. Johnson
W. E. Martinsen

Prepared for the
Environmental and Safety Engineering Division
U.S. Department of Energy
under Contract DE-AC-05-78EV06020

Applied Technology Corporation
Norman, Oklahoma 73070

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REPORT U

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FIGURES

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SUMMARY

The goal of Contract DE-AC05-78-EV06020 is to analyze the hazards of transportation of LPG and to determine fire fighting agent effectiveness for several agents, measure radiant fluxes for LPG fires, determine boiloff rates for LPG spills on solid surfaces, and measure vapor concentrations downwind of small to medium scale spills. An annotated bibliography (included in Volume 1 of this Status Report) has also been prepared covering the information found in the literature that has a bearing on the transportation hazards.

Report U covers the marine hazard analysis, the fire fighting agent effectiveness, and a few of the small scale boiloff tests. Fire radiation tests and gas dispersion tests have already been run, but the data have not been analyzed.

LPG may be transported by either barge or tank ship. The U. S. safety record has been excellent, with only one major accident with fire known to have occurred. Fault tree analysis of LPG transfer systems indicates that spills are commonplace in small quantities (< 10 gal) but should be very rare in large quantities (> 10^4 gal).

LPG fires can be extinguished with dry chemicals, but extinguishment of LPG fires is more difficult than extinguishment of LNG fires. LPG fires can be controlled with high expansion foam more easily than LNG fires, but in either case, high quality foams must be used for best effectiveness. Mobile, manual, or fixed systems can be used; the choice will depend on the location of the potential fire within a facility and the availability of personnel and support facilities.

Boiloff from LPG spills can be modeled using techniques used for modeling boiloff from LNG spills. Burning rates approach about 0.45 in./min for fires larger than about 20 ft in diameter. Radiant heating accounts for about 70 percent of the energy required for vaporizing the fuel and convective heating accounts for about 30 percent.

INTRODUCTION

Liquefied petroleum gas (LPG) is processed, transported, and stored on a routine basis in most areas of the United States. This report provides a summary of the work performed in two areas: hazards of marine transport of LPG and fire protection for LPG spills. Separate sections in this report provide details of the analytical and experimental work in these two areas. In addition, a bibliography related to LPG transportation and safety has been prepared and is included in Volume 1 of this Status Report.

The estimation of marine hazards was primarily an analytical study involving the marine transport of LPG by tanker or barge. The fire protection research was primarily an experimental program in which various sizes of LPG fires were extinguished or controlled using dry chemicals and high expansion foam as the agents. During the fire protection experiments, it was found to be possible to measure gas concentrations near the LPG pools before the pools were ignited, and radiant fluxes were measured following ignition but before fire control operations were started. The gas concentration and radiation data have not yet been analyzed and so are not included in this report.

HAZARDS OF MARINE TRANSPORT OF LPG

DESIGN OF LPG VESSELS

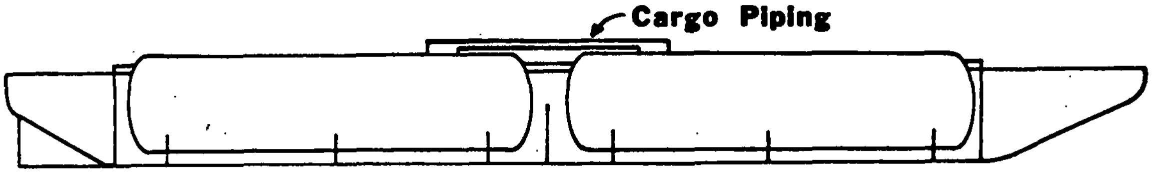
The choice of mode of transport of LPG is partly historical and partly economic. LPG (primarily propane in the United States) has traditionally been transported as a pressurized cargo at ambient temperature. The reason is apparently because most transportation and storage has been in relatively small quantities and large-scale facilities for transportation and storage of LPG have not been required. Because of the historical use pattern, marine transportation of LPG along inland waterways is also basically by pressurized tanks mounted on barges. Figure 1 shows a schematic of a typical LPG barge. The pressurized cargo containers are thick-walled pressure vessels, and the practical limit for vessel size is about 5000 m^3.

Some semi-refrigerated LPG ships are used. These ships use insulated cargo tanks with the pressure above atmospheric pressure and the temperature less than ambient temperature. The maximum cargo capacity of a semi-refrigerated LPG tanker is about 15,000 m^3. They are rarely seen in U. S. ports.

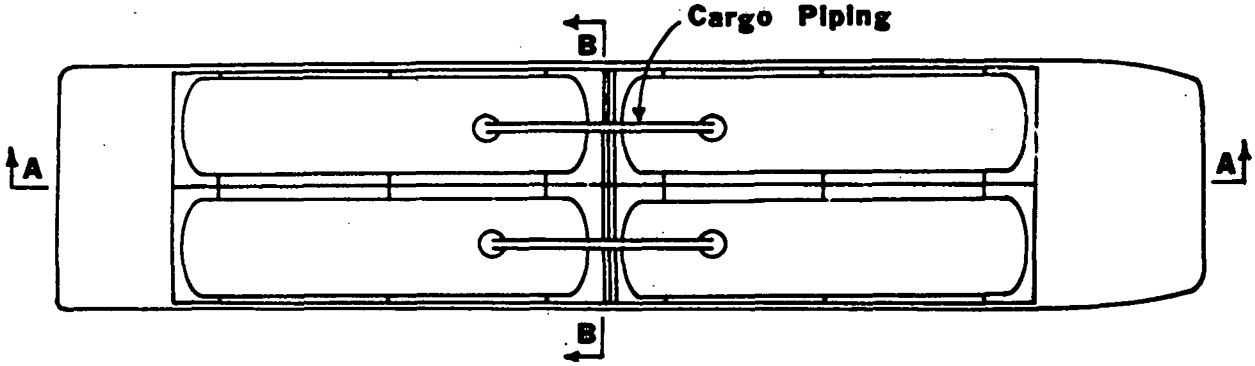
Fully refrigerated LPG vessels range in size from about 5,000 m^3 to 125,000 m^3. Those in U. S. waters are generally bringing LPG from foreign countries. Several tanker designs may be used, but in all cases the LPG is carried at a pressure only slightly above atmospheric pressure, and the cargo tanks are heavily insulated. Figure 2 is a schematic of a large refrigerated LPG tanker showing one of the possible tank configurations. In the United States the wing tanks and topside tanks cannot contain flammable liquids. Refrigeration systems are usually provided to reliquefy the boiloff gas.

OPERATIONS ON LPG VESSELS

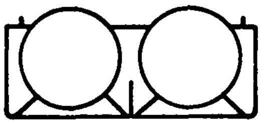
During transit, there are usually no activities carried out on a vessel that require transferring LPG (other than reliquefaction or



SECTION A-A



PLAN VIEW



SECTION B-B

Figure 1. Schematic of a Typical LPG Barge.

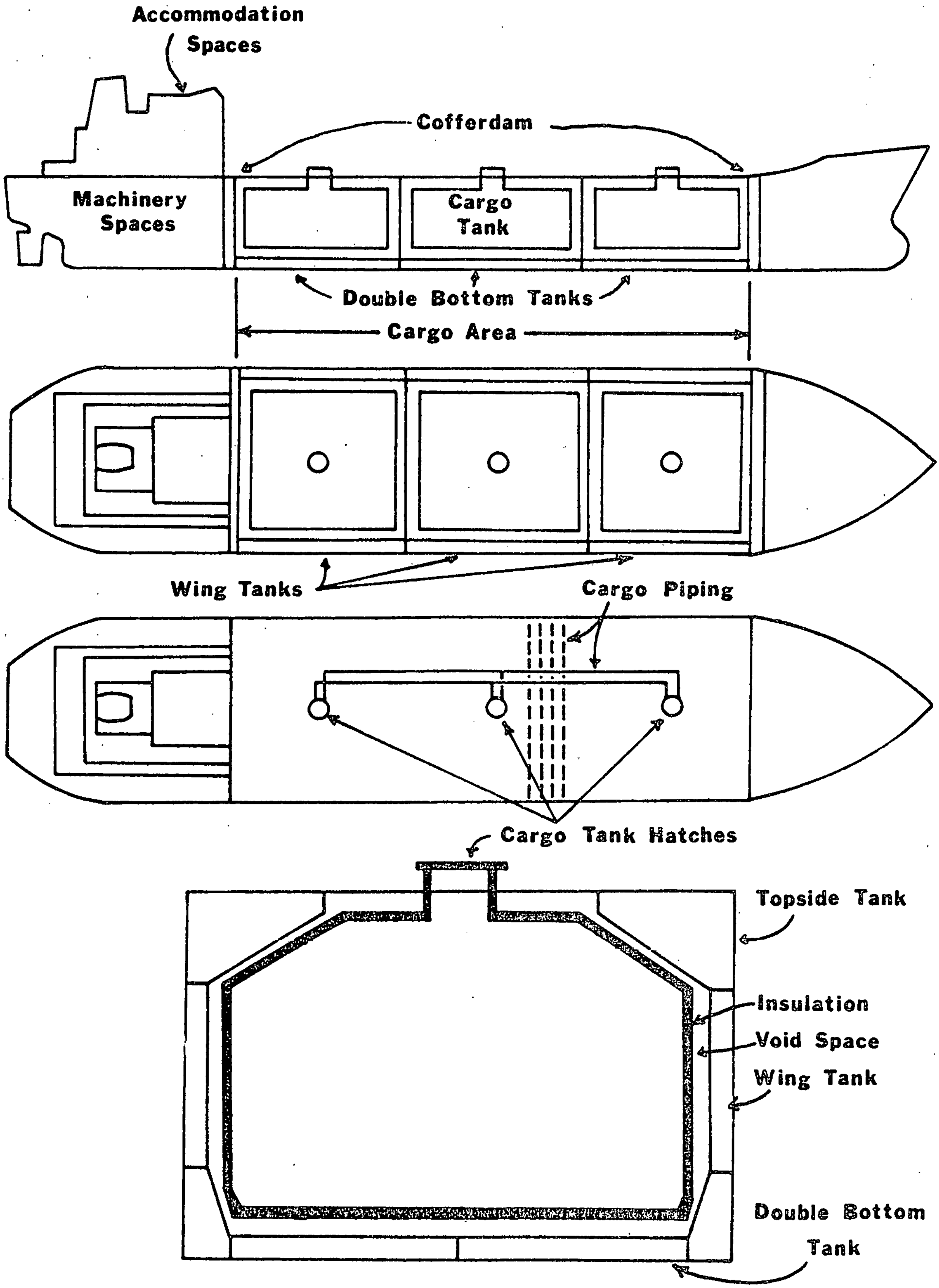


Figure 2. Schematic of a Typical LPG Tanker.

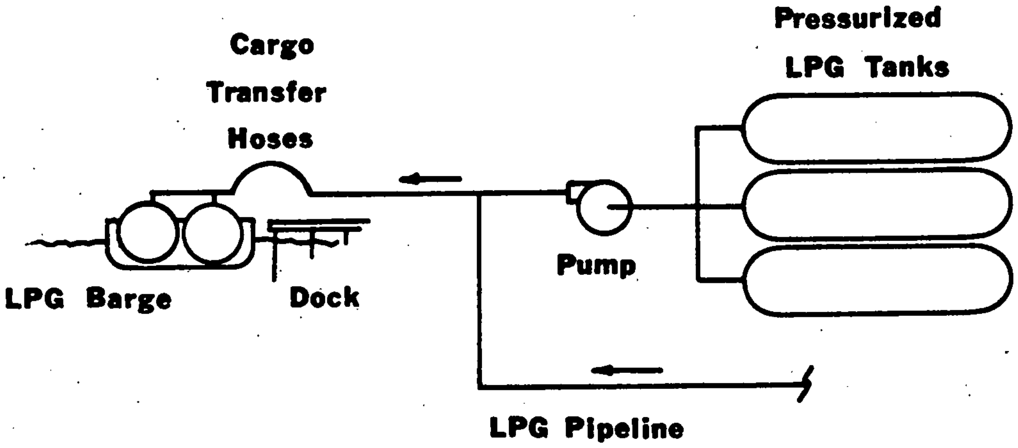
tank cooling). Once in port, the vessel may be either loaded or unloaded. If a vessel is being brought into service or taken out of service, the cargo tanks must be purged to avoid the presence of a flammable gas-air mixture.

Figure 3 shows a typical barge operation. LPG is transferred from the barge to storage tanks or a pipeline. The pipeline may later terminate at a storage tank or a storage cavern where it is held for eventual redistribution. The operations on a barge during transfer are reasonably simple. Figure 4 shows a typical arrangement of the valves on an LPG barge. Barges seldom have pumps on board, and product transfer is usually accomplished by reducing barge tank pressure and/or pumping to load and increasing tank pressure to unload.

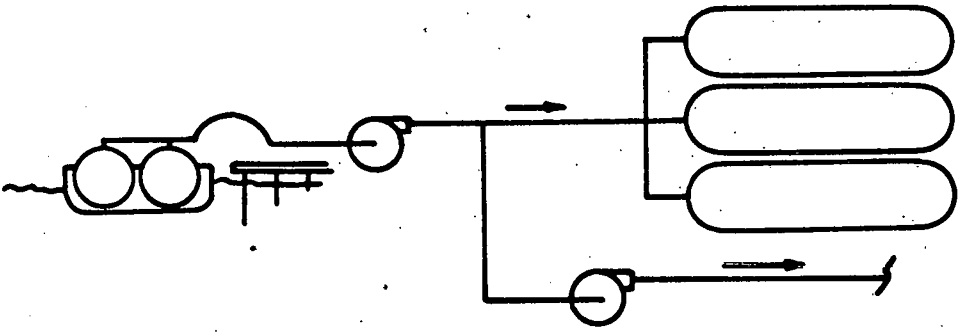
Transfer operations involving refrigerated cargoes are more complicated. Figure 5 shows the kind of piping arrangement that might be found on a large LPG tanker. Transfer of cargo from ship to shore requires both the pumping of LPG from the tank and the return of vapor to the tank. The volumetric liquid transfer rate must be closely balanced with the volumetric vapor return rate because the ship's tanks cannot tolerate large pressure changes. If vapor is not available from the land operations, it can be provided by vaporizing a small amount of LPG in the ship's vaporizer.

Refrigerated LPG is usually pumped directly from the ship to a large storage tank that is operated at about the same pressure as the ship's tank, as shown in Figure 6. In some cases, the LPG is pumped to underground storage caverns, pressurized storage tanks, or distribution pipelines. However these latter options may require the LPG to be warmed, so the transfer rates may be limited by heater capacity. Ship demurrage charges are high and operators prefer to transfer cargo rapidly to avoid high demurrage costs.

The actual sequence of operations varies in detail from one facility to another. Martinsen,et al. (1) describe in detail the types of operations that are used on typical LPG barges and tankers and the sequence of actions taken during loading and unloading. Since it is



LPG LOADING TERMINAL



LPG RECEIVING TERMINAL

Figure 3. Typical LPG Barge Transfer Operations.

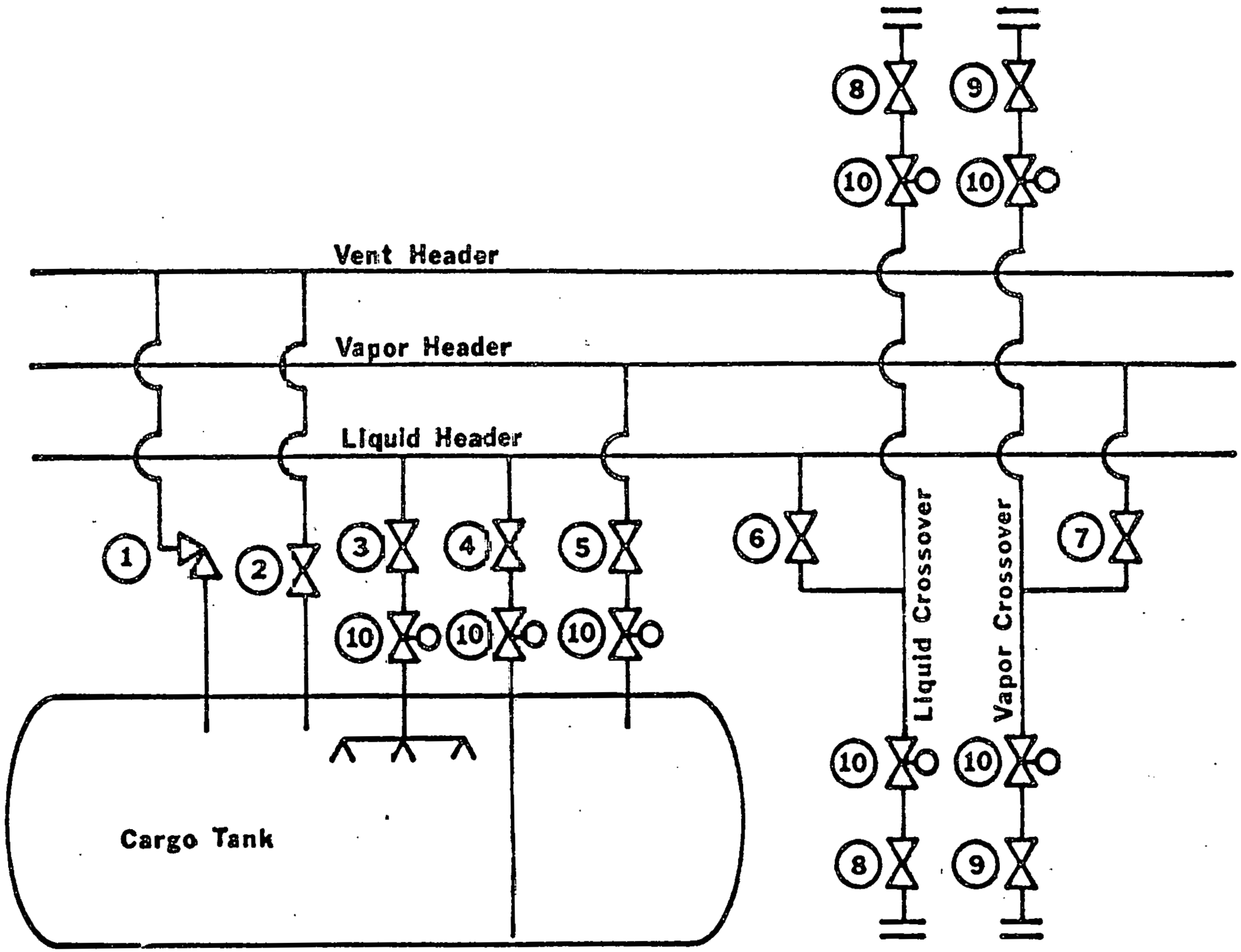


Figure 4. Typical Arrangement of Valves on an LPG Barge.

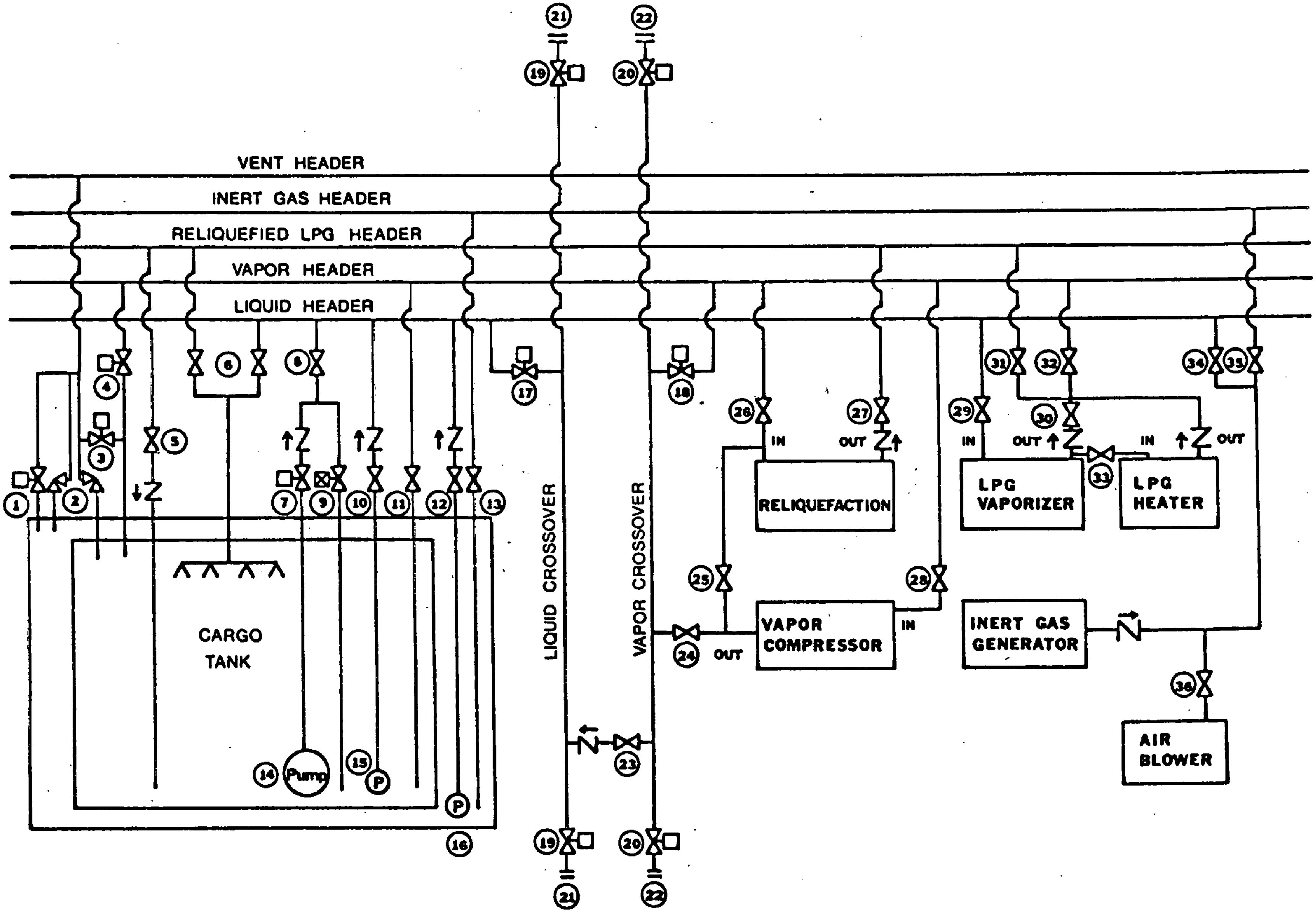


Figure 5. Piping and Control Arrangement for Composite LPG Tanker.

LPG RECEIVING TERMINAL

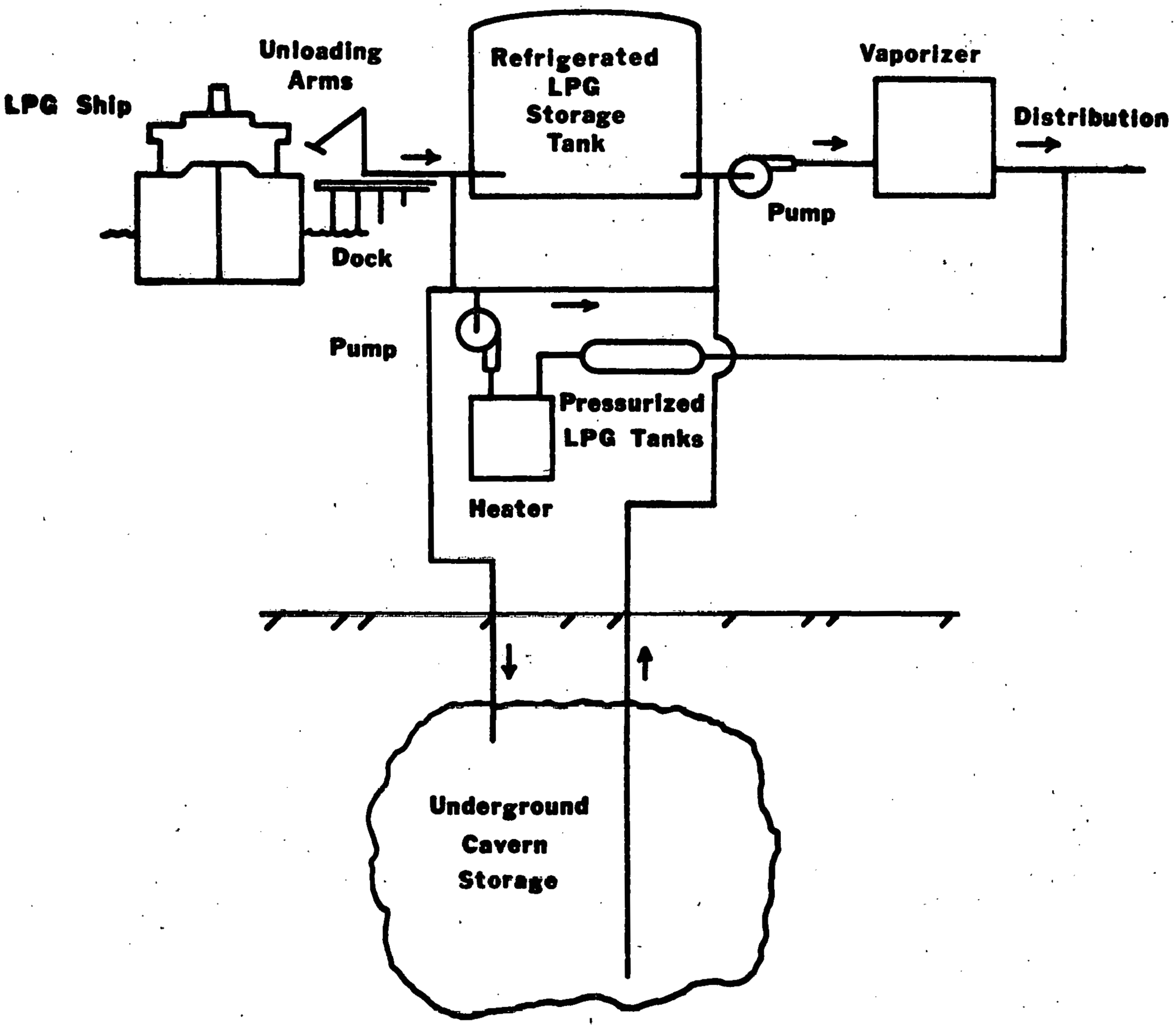


Figure 6. Possible Arrangement for Unloading LPG From Tankers.

impractical to detail the specific operations for all LPG marine practice, a composite barge and a composite tanker were used in the analysis. These composite vessels result in the designs shown in Figures 4 and 5. Few vessels would have all the piping, valves, and associated equipment shown in these two composites, but the composites incorporate all of the important equipment and operations encountered in marine transport of LPG in the United States.

In addition to the operations that are carried out while the vessel is docked, there may be special operating rules that apply to vessel movement. The large LPG tankers are usually boarded by Coast Guard personnel before they are allowed to enter U. S. ports. The Coast Guard inspection ascertains that the safety regulations are being followed before the port is entered. The inspection on the first voyage is more detailed because it also assures that the ship is constructed according to the various codes that apply. Once the inspection is complete, the vessel enters the port. Transit is usually restricted to daylight hours and a moving safety zone that prohibits other vessel traffic near the tanker may be provided. These restrictions are intended to prevent collisions during transit. Restrictions are relaxed when empty tankers leave the port.

Barge movements are not generally restricted to daylight hours. Barge traffic is required only to be towed at a safe speed and to have a tug with the barge unless the barge is tied up at the dock. The pressure vessel design for barge tanks is similar to that for railroad tanks, truck tanks, and pressurized land storage tanks, all of which have an excellent safety record. Barge transport of LPG also has a history of safe operation. Therefore, the inspection and regulation of barge traffic is not subjected to the intense effort given to tankers. Barge operations are performed on a smaller scale than tanker operations, but at much higher frequencies. The systems are generally well-engineered and have good safety records.

FIRE PROTECTION

The fire protection philosophy for LPG ships includes fire prevention, limiting fire size, fire control and extinguishment, and damage potential reduction. Fire prevention includes the design and operation of vessels in a manner such that fires do not occur. The goal is sought through release prevention, inerting, and ignition source control. The basic design of facilities is arranged so that no product is released during normal operations either in the liquid or gas phase. Inerting of tank spaces is performed before cargo is transferred to any tank, either on the vessel or on land, and if a tank must be taken out of service, it is carefully purged to remove flammable materials before maintenance or repair work is performed. Potential ignition sources are eliminated in critical areas.

If, despite the precautions taken to prevent release and subsequent ignition, a fire occurs, the vessel and transfer system are designed to limit the size (and thus the destructive potential) of the release. Fire sizes are minimized by minimizing the amount of cargo released, and, in the case of a liquid spill, limiting the area over which the cargo can spread. Rapid-acting, remote-controlled valves are usually provided so that product flow can be stopped quickly in an emergency. These valves are also designed to be fail-safe in the event of loss of control. Leak detection devices are used to monitor for leaks. Detection may include gas sensors for gas releases and low temperature detectors for liquid leaks. In addition to the sensors that are designed exclusively for emergency use, the instruments that monitor normal plant operations are watched to ensure that they are within normal operating limits. Transfer operations are under close supervision of both vessel and landside operators.

If a fire occurs, it may be extinguished, controlled, or allowed to burn out. Only small fires can be extinguished reliably, and the agent of choice for most situations is a dry chemical. Fires may be controlled using high expansion foam. Both of these fire fighting methods will be discussed further in a later section of this report. Generally, LPG fires should be extinguished only if the spill is finished and flow of product is stopped. Otherwise reignition is possible, and, if reignition occurs, the fire fighting equipment may not have enough reserve capacity for a second attempt.

The potential damage from a fire can be minimized by both passive and active systems. Passive systems are designed for high fire resistance and provide protection to personnel and critical control systems. The most common active technique for damage reduction is application of water sprays for cooling. Water is not used directly on LPG fires because it increases the fire size by increasing boiloff rates.

Various codes require that minimum fire protection capabilities be provided on LPG tankers. The IMCO code is the basic standard for international trade, and all vessels bringing LPG into U. S. ports from foreign sources must comply with it. The IMCO code specifies minimum dry chemical capacity and minimum requirements for fire water distribution and spray systems. Non-cargo spaces are also required to have minimum fire protection capability, including special equipment for machinery spaces and locations where combustible liquids are stored.

Barges have smaller cargoes, are unmanned during transit, and have little or no operating machinery on board. Therefore, they have a much less rigorous set of requirements for fire protection. They are regulated under Title 46 of the Code of Federal Regulations.

SAFETY ANALYSIS

LPG is very volatile because of its low boiling point and easily ignited if released from the closed transport, processing, and storage system. There are a variety of failures that can occur. Most of them are small and cause no damage. However, there is always the potential for a small failure to either go unnoticed and propagate to a large failure or for the occurrence of a large failure per se.

One of the methods of estimating the probability that a failure will occur is through fault tree analysis. Such an analysis can be very complex and detailed, but in looking at LPG systems for only those failures that release product, significant simplifications can be made. The analysis was limited to those events that might cause product release because the goal was to estimate the probability of occurrence of events that might either endanger the public or operators or escalate to a larger event that could endanger the public or operators. In this context, danger to the public or operators was assumed to be possible only when the vessel was in port or traversing an inland waterway. Therefore, the major emphasis is on dockside operations because the cargo is then being transferred rather than in storage.

The fault trees generated during the study are too detailed and bulky to be presented here, but they are included in the report by Martinsen, et al. (1). Figure 7 is a fault tree diagram that summarizes the probabilities of various events during tank ship unloading and shows the pathways by which they might occur. The probabilities shown are for a single unloading sequence. Notice that the probability of a spill of less than 10 gallons is quite high, and can in fact be expected to occur on about three-quarters of the unloading operations. The reason the spill probability is so high is that in some operations the disconnect sequence requires draining a small quantity of LPG from the transfer arms. Small leaks from valve packing and gaskets are also expected to occur. While these leaks may not be corrected immediately, they are small enough that there is little chance that they will result in more than 100 gal being released over the unloading period. Larger spills are less likely to occur than smaller spills. In fact, for spills greater than 100,000 gal the most likely cause of the spill is an external force such as a ship collision. The reason is that even at the highest transfer rates, the flow would be shut off following a failure before such a large spill could accumulate.

Figure 7 shows a set of probabilities enclosed in parentheses. These probabilities are for transfer from vessels at docks where rubber hoses are used for ship-to-shore connections rather than metal transfer

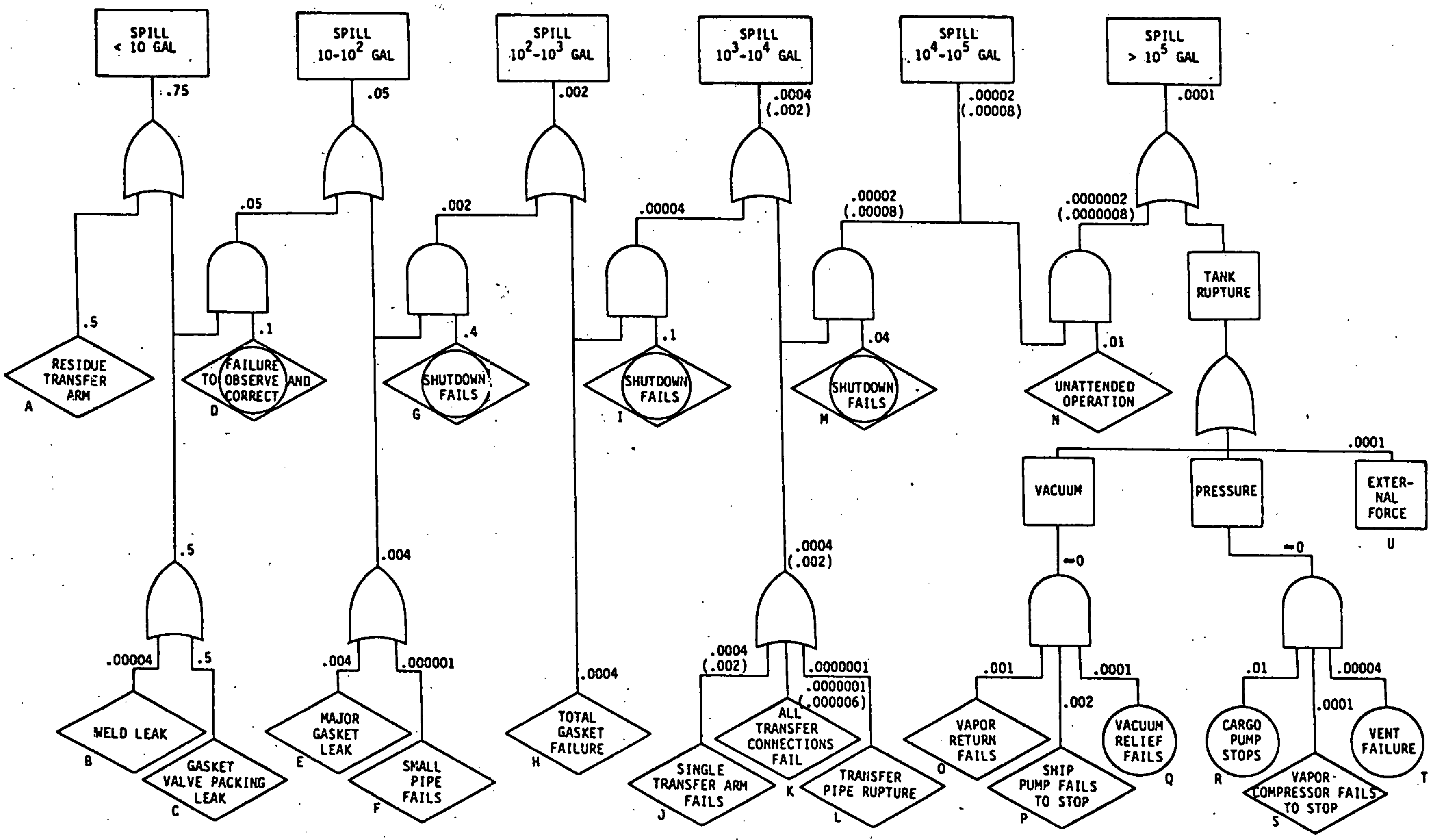


Figure 7. Fault Tree for Tank Ship Unloading.

arms. Transfer connection failure is more likely in the operations using hoses than those using metal arms.

Figure 8 is a graphical summary of the event probabilities from Figure 7. The event probability has been plotted as a function of spill size, where the spill size is taken to be about the middle of the spill range on a logarithmic scale. The plot is shown as a broad range rather than a line to emphasize the approximate nature of the failure probabilities.

The spill probability shown in Figures 7 and 8 is based on an analysis of 16,000 voyages of liquefied gas ships, during which there has been no loss of the liquefied gas cargo as a direct result of a collision. (LPG loss on the Yuyo Maru was a result of fire burning naphtha in the wing tanks. Flammable liquids are forbidden in the wing and topside tanks in U. S. ports.) Table 1 compares the resulting spill probability with similar estimates from other sources.

Figure 9 shows a fault tree for loading or unloading LPG barges. The events that lead to spills are similar to those for LPG tankers, but the spill probabilities may be different because of differences in design, operating pressures, and transfer procedures. Figure 10 shows a graphical summary of the spill probabilities for barges during transfer operations. Again the plot is shown as a broad line to emphasize the approximate nature of the spill probabilities.

It is interesting that the spill probabilities for barge and tanker operations are about the same. Intuitively, it might appear that barges would have more spills because of the pressurized cargo transfer and less sophisticated equipment and procedures. However, the transfer operations are simpler and the transfer time is shorter, so that the risk is reduced. Barge collisions causing spills are shown as being an order of magnitude less probable than ship collisions. The barge transport of LPG has a fairly long history and a much larger number of transfers than tanker transport, with only one known spill due to collision. Collisions involving tankers may in fact have a much lower probability than shown,

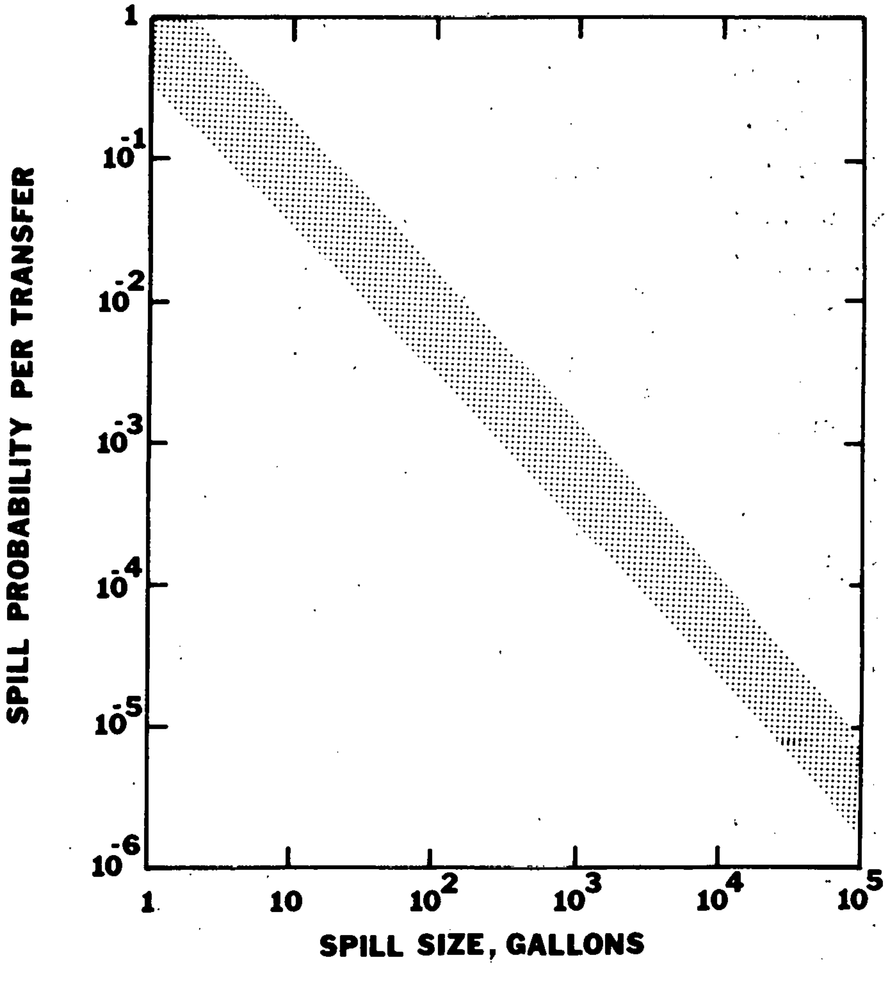


Figure 8. Spill Probabilities for LPG Tanker Transfer Operations.

TABLE 1. COMPARISON OF RISK PROBABILITIES

Source	Probability of Spill (per Cargo Delivery) Due to Ship Collision
Applied Technology Corp.	2×10^{-4}
FPC (3)	1×10^{-3}
SAI (4) for Los Angeles Harbor	1×10^{-4}
Cave and Kazarians (5)	3×10^{-7}*
University Engineers (6)	5×10^{-4}

*Probability given is for spills greater than 20,000 m^3.

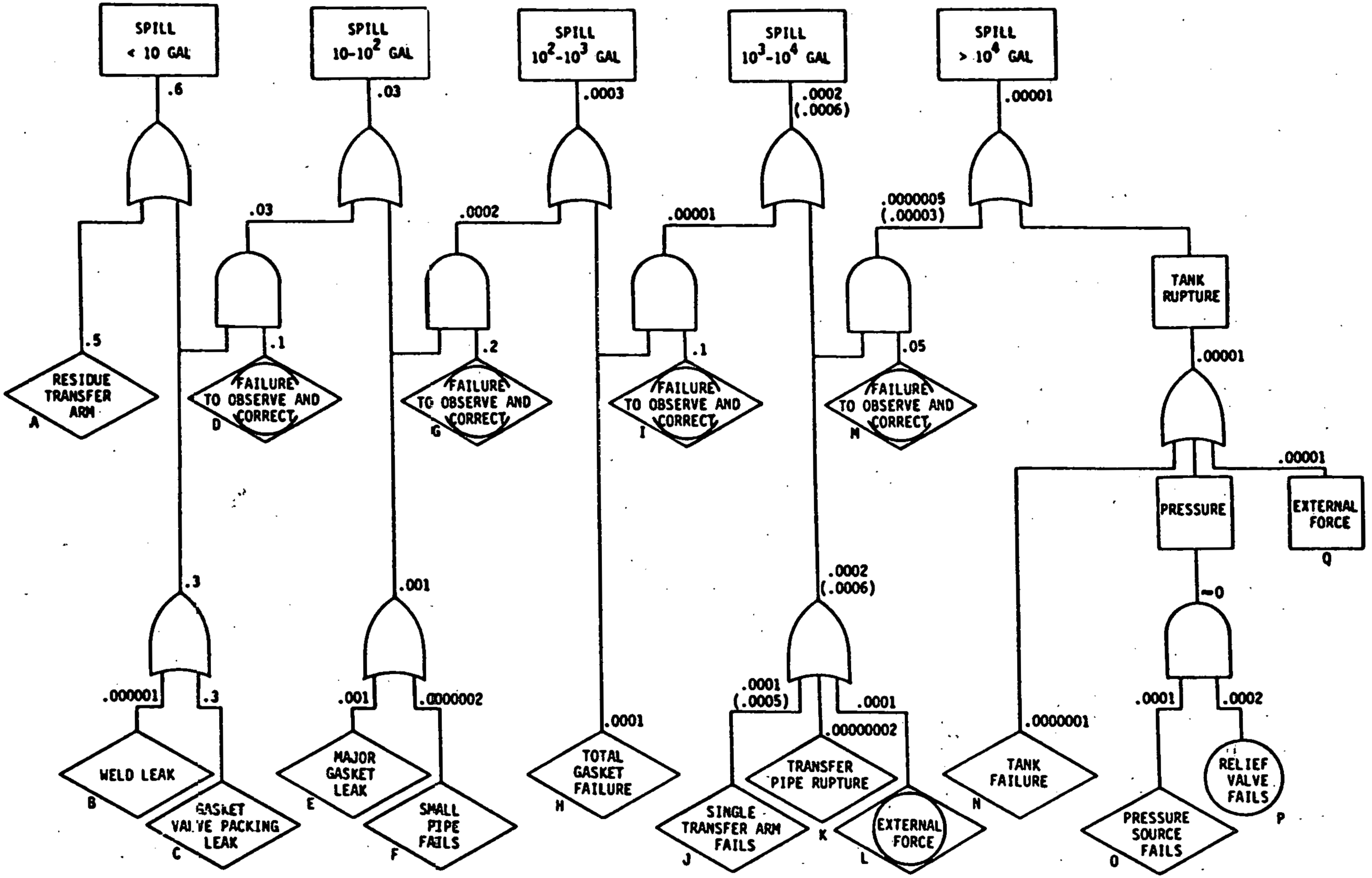


Figure 9. Fault Tree for Barge Transfer.

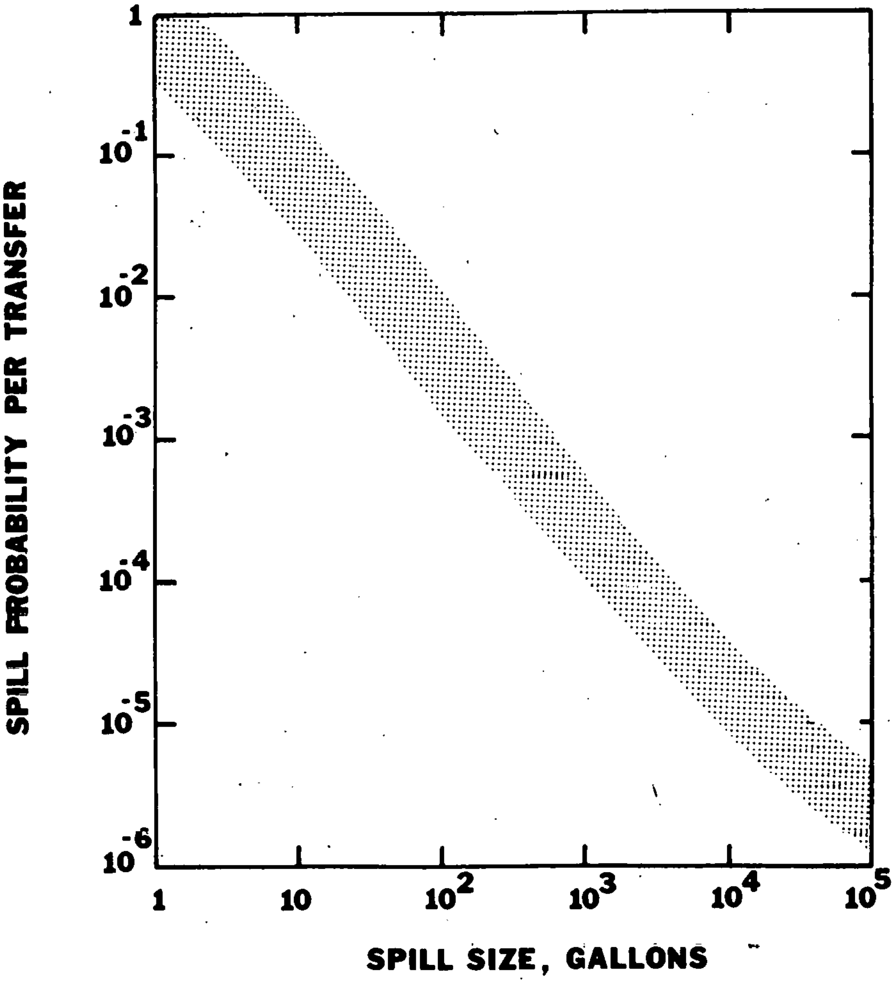


Figure 10. Spill Probabilities for LPG Barge Transfer Operations.

but there is not sufficient historical data to prove it. The comparison in Table 1 illustrates the point. All the spill probabilities except that of Cave and Kazarians are based either on no spills for limited numbers of liquefied gas ships or other ships and for no vessel traffic control in the harbors. The results are roughly comparable, even though different data bases were used. Cave and Kazarians' study was specific for large spills in Boston Harbor, and included the provisions for traffic control and Coast Guard escort required for gas tankers in Boston Harbor. The special precautions obviously result in a higher level of safety by reducing the collision probability substantially.

Even though the spill probability may be large for some parts of the operation, it does not necessarily follow that the operation is especially dangerous. The primary danger from LPG spills, particularly those less than a few hundred gallons in volume, is from fire. The ignition probability depends on the spill size, with ignition more likely for larger spills. Small spills, less than 10 gal in size, which occur during more than half the transfers, must have very low ignition probabilities. Otherwise, fires would be common occurrences at LPG terminals. On the other hand, spills involving more than 100,000 gal of LPG at a high spill rate are practically certain to be ignited. The probability of fire occurring during transfer can be estimated if ignition probabilities are known. As an estimate, the following are used to approximate ignition probabilities:

Spill Size, gal	Ignition Probability
< 10 gal	0.001
100 gal	0.01
5000 gal	0.1
> 100,000 gal	1.0

These ignition probabilities are assumed to apply regardless of whether the spill occurs at a barge or tanker operation. If the ignition probabilities are applied to the spill probabilities from Figures 8 and 10, the result is the probability of occurrence of fire during a transfer operation. Figure 11 shows the approximate fire probability for both barge and tanker operations for non-collision events.

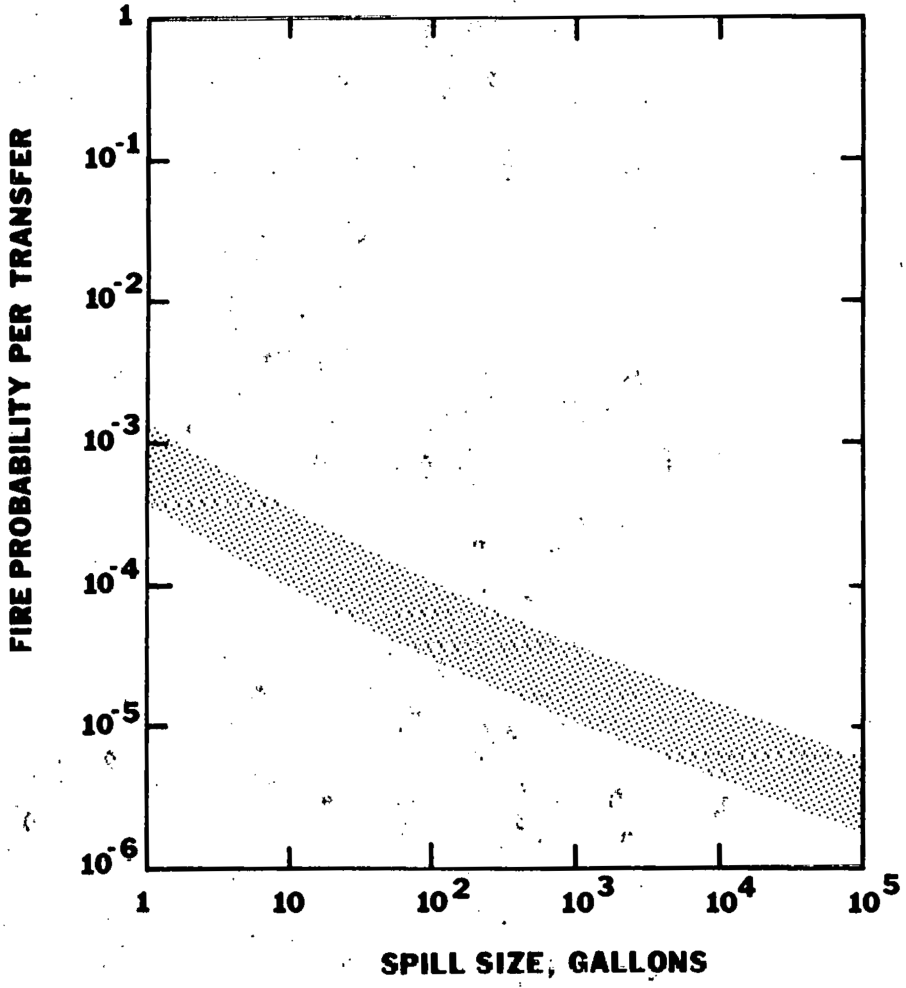


Figure 11. Fire Probabilities for LPG Transfer Operations.

The probability of a ship collision is estimated to be 0.0001 per transit based on historical data for gas carriers. However, the design of LPG ships will offer some protection from LPG spills (as the Yuyo Maru incident showed). Therefore, the spill frequency will be much less than shown in Figure 7. The frequency will also be reduced substantially if traffic controls are instigated, as shown by Cave and Kazarians. It should also be recalled that the collision frequencies for gas carriers may be less than estimated from historical data because the number of collisions is so small that statistical analysis can be misleading. Figure 11 omits the ship collision contribution to fire probability because it distorts the trend and makes the fire probabilities appear higher than they really are at the terminal.

HAZARD POTENTIAL

Fire damage and personnel injuries are related to fire size. Fires resulting from spills of less than 10 gallons are unlikely to cause substantial damage or result in fatalities, but fires involving thousands of gallons are nearly certain to cause substantial damage and are quite likely to result in fatalities or serious injuries as well. The overall probability of fatality from a spill during LPG transfer is therefore estimated to be in the range of 10^{-6} to 10^{-5} per transfer operation. This fatality probability is for operators near the transfer point and assumes continuous exposure during transfer. The fatality probability for the general public is much lower because of the greater separation from the transfer area.

LPG barge operations can result in a special hazard because the cargo is pressurized. If a cargo tank is heated by a fire, the internal pressure will rise and the emergency vent will open. As gas is vented, the vapor space in the top of the tank grows and the metal in the vapor space heats. At some point, the metal can weaken enough so that the tank ruptures. As the pressure is released, much of the liquid flashes to vapor and much is atomized by the force of the explosion. The fireball that results may be very large and cause a large amount of damage. This phenomenon is called a "boiling liquid expanding vapor explosion" (BLEVE) and has occurred following LPG tank car derailments. No fires at barge transfer facilities have been reported that resulted in BLEVE's.

BLEVE's cannot occur during operations for fully refrigerated LPG cargoes because the operations are all performed using liquids that are saturated near atmospheric pressure. The fraction of flash upon pressure release is therefore small and the liquid released from a storage tank is not disseminated explosively as it is from pressurized storage.

In general, refrigerated storage is used for larger quantities of LPG. If a large spill occurs, a vapor cloud will form, and until it is dispersed by mixing with the atmosphere, it can easily be ignited. Under most circumstances, the result will be a vapor cloud fire, but a vapor cloud explosion is possible. In either case, primary damage will be confined to locations near or within the vapor cloud at the time of the fire or explosion. Secondary damage may also be caused if the fire spreads.

CONCLUSIONS

The safety record for marine LPG transportation in the United States is very good, probably because of fairly careful attention being paid to design, construction, and operation of facilities. Spills of small quantities of LPG (less than 10 gal) are quite frequent, but are not particularly dangerous.

Most of the small leaks are "planned" in the sense that they are part of normal operations. They occur on nearly every transfer at some facilities and very rarely at others because of differences in operations. The spill frequencies for very small spills could be reduced substantially for some facilities by changes in design and operational procedure. Whether such changes would improve safety is debatable.

The spill probabilities estimated in this report are based on generic designs and overall estimates of collision frequencies. Obviously, if similar calculations are made for a specific facility, the results may vary. Fatalities for barge and tanker terminals are estimated to have an occurrence probability of about 10^{-6} to 10^{-5} per transfer operation. Based on the assumption of weekly to monthly transfer operations, the annual fatality probability for an operator at a given facility would be in the range of 10^{-5} or lower. That is in the same general probability range as an average individual would accept by exposure to automobile accidents. The risk to the general public is substantially less.

EXTINGUISHMENT AND CONTROL OF LPG FIRES

About 100 tests were run on free-burning LPG fires to determine the quantities of agent required to control or extinguish the fire. The tests were run using methods developed for hexane fires in earlier tests. The general procedure was to put about 3 inches of LPG in the bottom of a square concrete test pit about 2 feet deep. The LPG was allowed to remain in the pit for at least half an hour before it was ignited so that the vaporization rate was relatively low at the start of the test. After ignition, the fires were allowed to burn freely for at least a minute so that the burning rate could reach a steady state value before extinguishment was attempted.

Fire control tests using high expansion foam were run on fires in 5-, 10-, 20-, and 40-ft square pits. The foam was applied at the upwind edge of the pit and foam flow was continued long enough to control the fire or until all the LPG was burned. The minimum foam application time for non-controlled fires was 5 minutes.

Three types of dry chemical were used to extinguish fires in 5-, 10-, and 20-ft square test pits: sodium bicarbonate, potassium bicarbonate, and urea-potassium bicarbonate. The dry chemicals were usually applied from fixed nozzles located along the sides of the test pits, one nozzle in the center of each side. To insure uniform flow, the powder was supplied to each of the four nozzles through a symmetrical piping system. Powder flow rates could be varied by changing the nozzle sizes or by changing the dry chemical tank pressure. Upper limits on flow rates were fixed by the nozzles available and the maximum operating pressure of the dry chemical tanks. Some manual tests were also run in which dry chemical was applied by portable dry chemical units or hand-held dry chemical hoselines. Manual extinguishment tests were run using shallow earthen containment pits as well as the deep concrete pits.

A few tests were also run in which the boiloff rate of LPG was measured following rapid spillage onto concrete, polyurethane foam, and a sand-soil mix. Both the transient and steady state vaporization rates were measured.

LPG BOILOFF AND BURNING RATES

Figure 12 shows the mass of LPG remaining in a 5-ft^2 concrete test pit following a rapid spill of about 37 lb. The dashed line represents the measured quantity remaining and the solid line shows the predicted quantity remaining. The prediction of boiloff rate and quantity remaining was based on a film coefficient-limited model of heat transfer by conduction through the concrete with additional terms representing atmospheric convection, solar radiation, and sensible heat from the cooling LPG (2). The temperatures of the LPG pools reached a steady state value between -90°F and -100°F in most of the tests, so there was substantial subcooling of the LPG below its normal boiling point. In these tests the LPG was more than 90 percent propane.

Steady state evaporation rates were measured using insulated containers to reduce the conduction of heat through the container walls. Heat transfer to the liquid was limited to convection from the atmosphere and solar radiation. Mass transfer coefficients were calculated from the evaporation rates and are shown in Figure 13. They compare favorably with coefficients found in the literature for other organic liquids (7). The mass transfer coefficients can also be used to estimate convective heat transfer rates between the atmosphere and liquid pools because of the heat and mass transfer analogy.

The burning rates were found to vary with the fire size, and to a lesser extent with wind speed. Although not enough data were taken to provide quantitative relationships, the burning rates for smaller fires decreased for higher wind speeds. Figure 14 shows the measured steady state burning rates as a function of pool diameter. The data points are weighted averages of the measured burning rates for two or more tests.

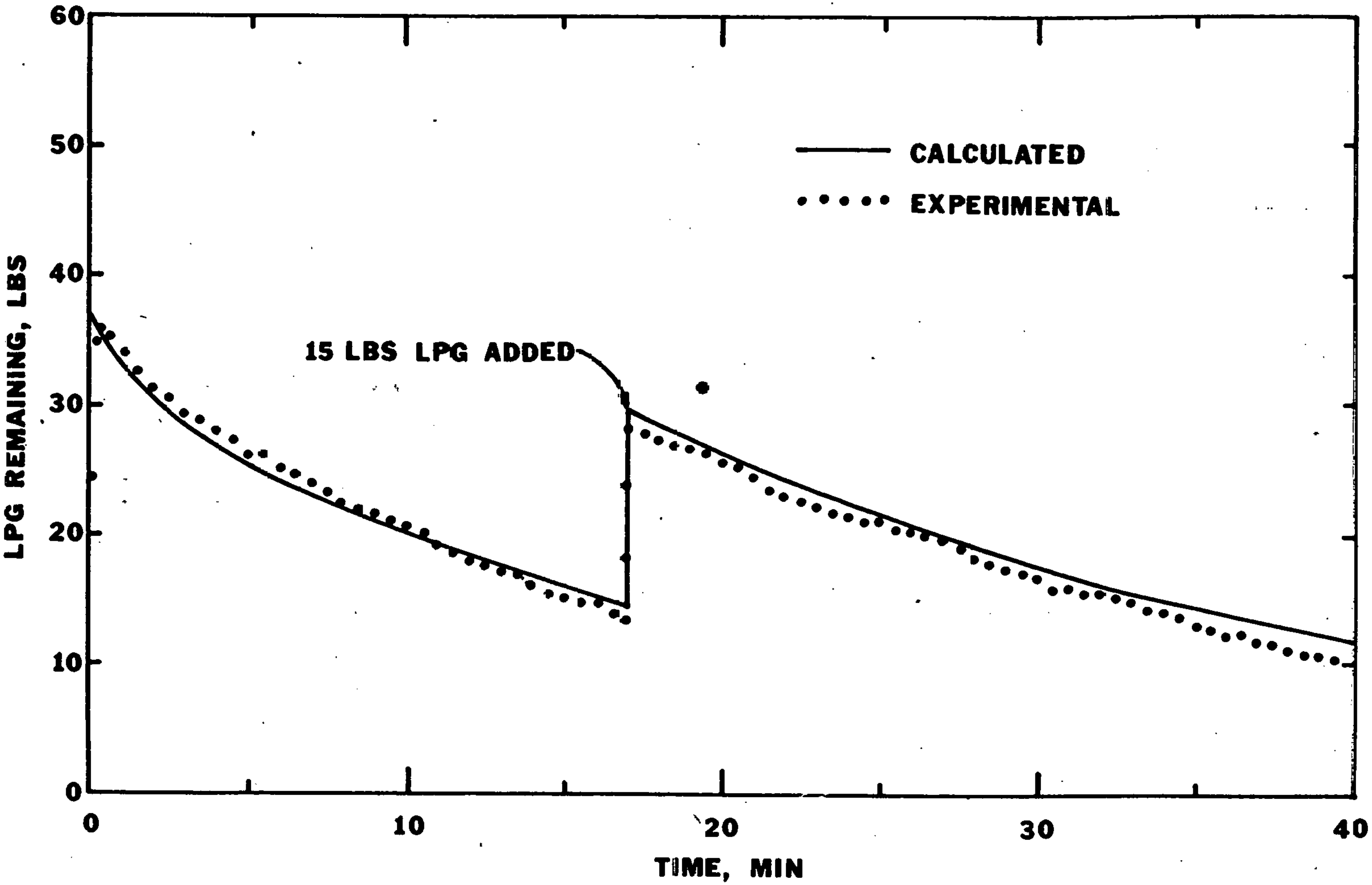
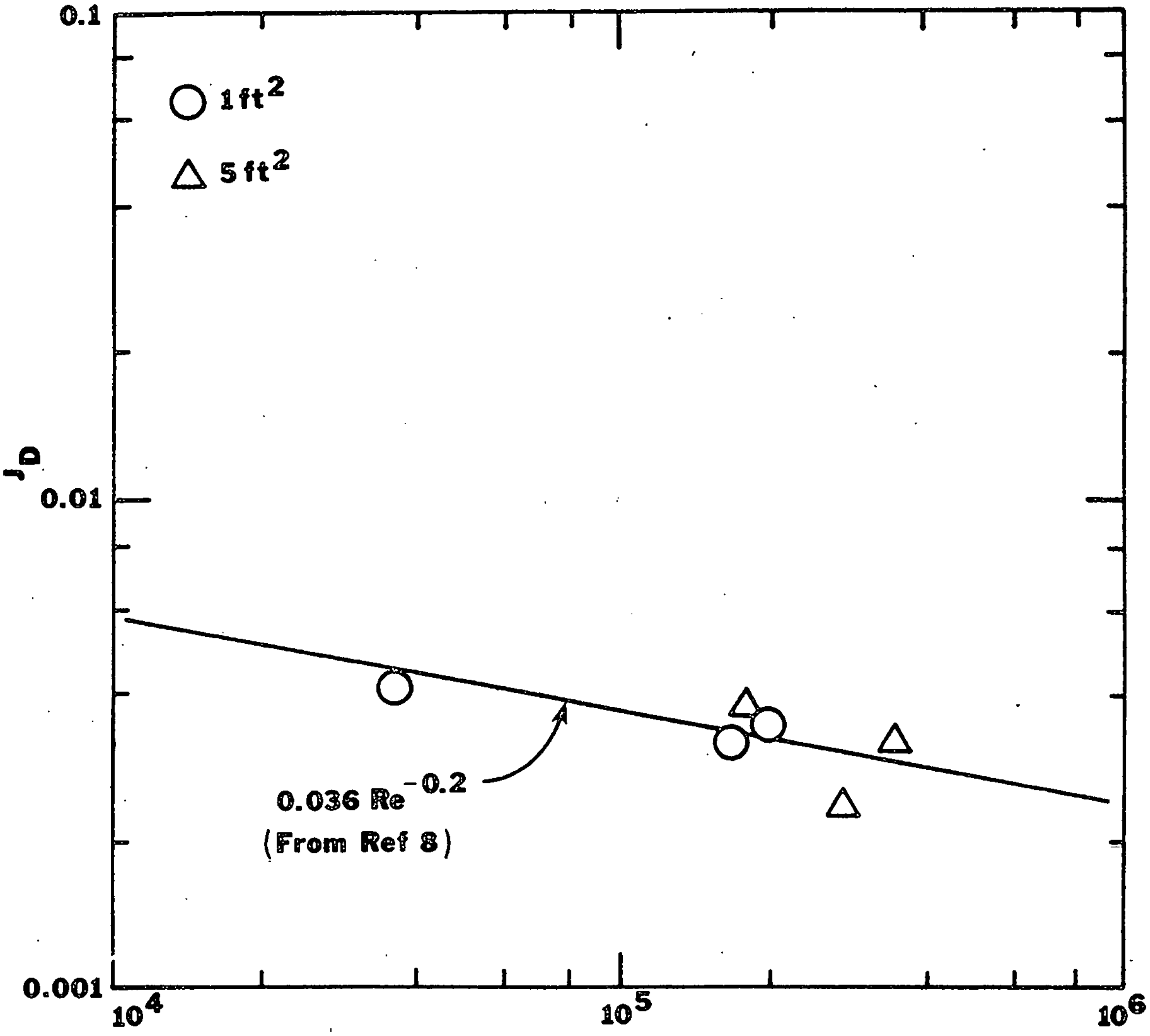


Figure 12. Comparison of Predicted and Measured LPG Vaporization.



REYNOLDS NUMBER

Figure 13. Steady State Mass Transfer Coefficients for LPG.

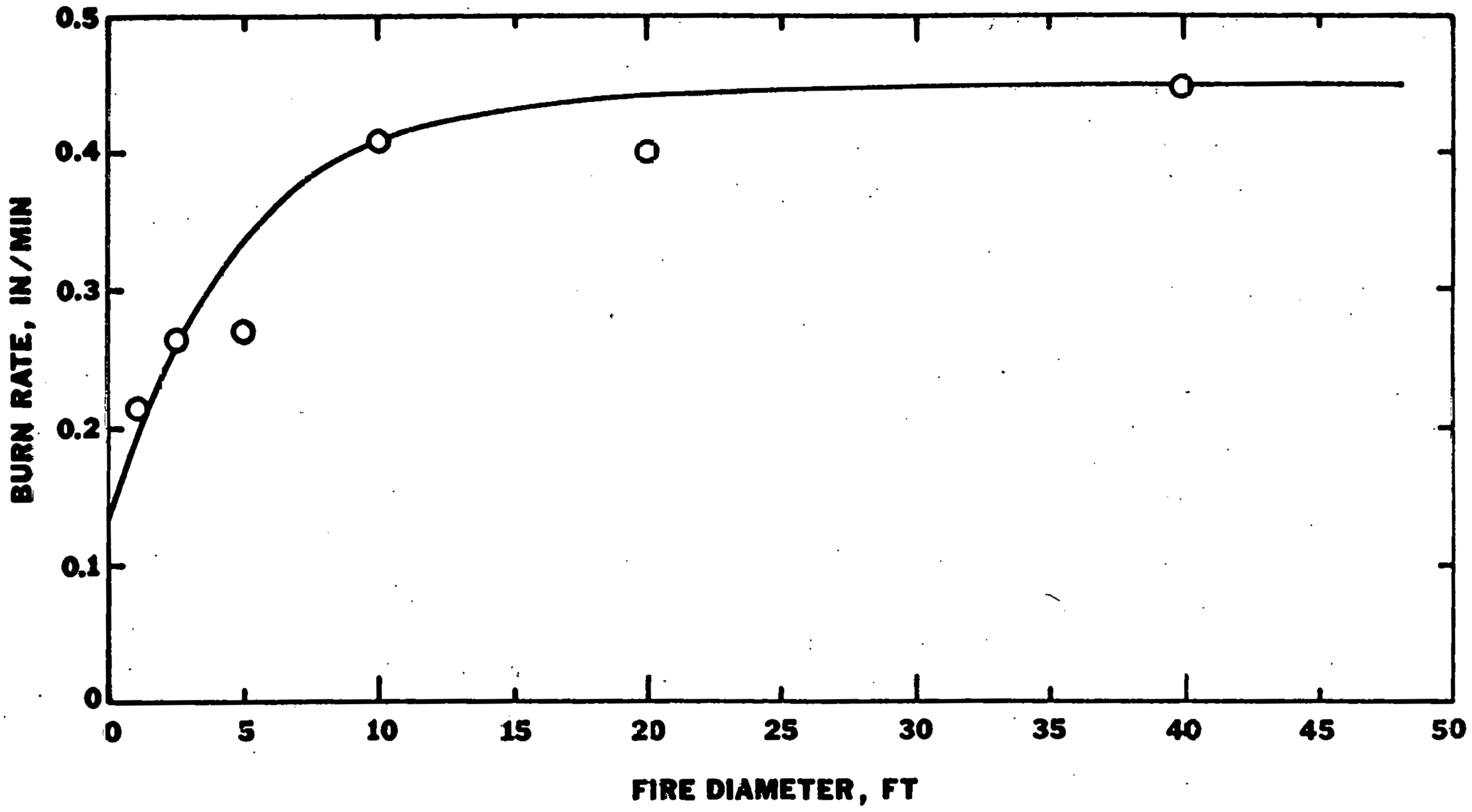


Figure 14. Burning Rates for LPG Fires.

If it is assumed that at least the surface of the burning pool is at the boiling point, a simple heat balance model can represent the results; the total burning rate being composed of vaporization rates due to convective and radiative heating from the flame, i.e.,

$$V = V_c + V_r \tag{1}$$

where V = burning rate, in/min

V_c = vaporization rate due to convective heating, in/min

V_r = vaporization rate due to radiative heating, in/min

By using the vaporization rate data from Figure 13 and assuming a flame temperature of 2000°F, V_c is estimated to be 0.13 /min and is approximately constant over the range of fire sizes involved.

The vaporization rate due to radiative heating is assumed to vary with pool diameter in the following manner.

$$V_r = V_{r,\,max} (1 - e^{-bD}) \tag{2}$$

where

$V_{r\,,max}$ = maximum vaporization rate due to radiation, in./min

b = flame extinction coefficient, ft^{-1}

D = flame diameter, ft

The values of $V_{r,\,max}$ and b can be determined from the data and are about 0.32 in/min and 0.208 ft^{-1} respectively.

The solid line in Figure 14 was calculated from Equations 1 and 2. It appears that the maximum burning rate for propane fires is about 0.45 in/min and that the maximum rate is reached for fires about 20 ft wide or larger. If the fuel is ignited before the ground is well frozen, the burning rate can be substantially higher, of course, because of the more rapid boiloff of LPG.

FIRE CONTROL

High expansion foam was chosen as the agent for fire control because of its effectiveness in controlling liquefied natural gas (LNG) fires. The foam application rates and expansion ratios were limited by the equipment available, so the number of tests was also somewhat limited. Figure 15 shows the control time as a function of the foam application rate. The control time is defined as the time at which the radiation flux measured at one pool diameter from the pool edge is reduced to 25 percent of its value before foam was applied.

The line drawn through the data points is based on a multivariate curve fit of the data, assuming an equation of the form

$$t - t_{min} = K\ (A - A_{min})^a (B)^b (E)^c \qquad (3)$$

where t = control time, sec

t_{min} = minimum control time

A = application rate, gpm/ft^2

A_{min} = minimum application rate, gpm/ft^2

B = burning rate, in/min

E = expansion ratio

K,a,b,c = constants

There is a minimum application rate below which the fire will not be controlled. It is dependent on the rate of foam breakdown due to heat transfer from the flame to the foam and contact with the cold LPG. The minimum rate was calculated to be about 0.03 gpm/ft^2. If foam was applied at a lower rate, the foam collapsed as fast as it was applied. The resulting foam solution drained into the fire and increased the burning rate. This same behavior had been found earlier in applying high expansion foam to LNG fires (8, 9).

There is also a minimum control time since it takes a finite time to cover the entire fuel surface with foam. For the test procedure used, the minimum control time was about 30 seconds.

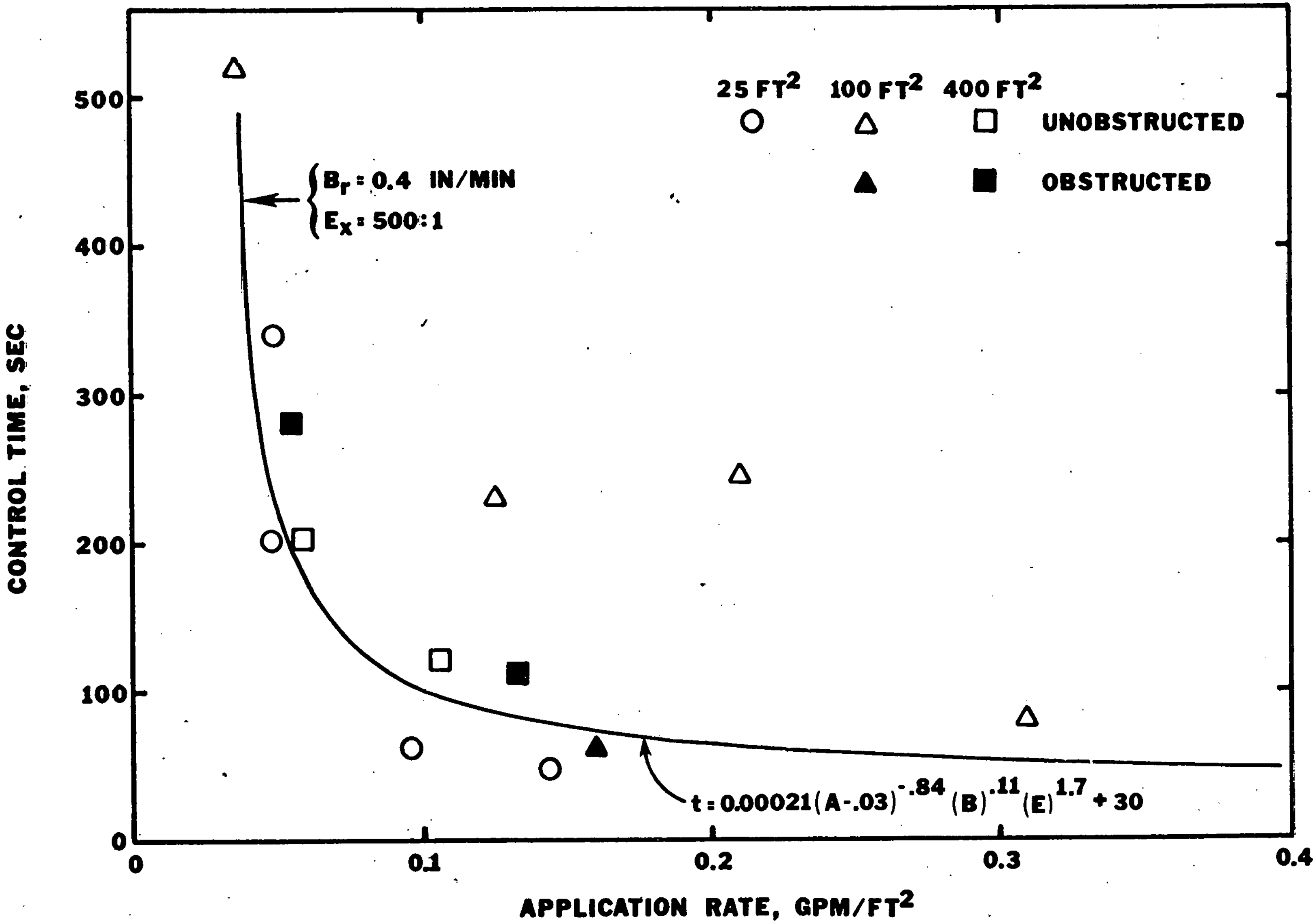


Figure 15. Control Times for High Expansion Foam.

It is known from the LNG fire tests that the fire control time and the extent of reduction in fire size ultimately achieved depend on both the foam generating equipment and foam concentrate used, because of differences in foam quality. In comparing the control times for LPG fires with those measured for LNG fires, it was found that LPG fires were controlled in less time than the LNG fires and that the reduction in radiant flux was about the same or larger than that for LNG fires using comparable foam. It is likely that faster control times and greater reductions in fire size after control can be achieved using higher quality foams. Practical application rates for LPG fires should be large enough to provide control within a few minutes after foam application is started. For the foam used in these tests, the application rate should be in the range of 0.1 - 0.15 gal/min-ft^2 at an expansion ratio of 500:1. Other foams may be more or less effective, and may require other application rates for assured control.

The LPG fire control times can also be compared with those found in earlier tests where n-hexane was used as the fuel. Hexane fires were controlled more rapidly than LPG fires and were ultimately extinguished. Thus the data confirm the results that might be expected intuitively: fuels with very low boiling points produce fires that are harder to control with foam and cannot be extinguished, while higher-boiling fuels produce fires that are easier to control and can be extinguished.

Three tests were run in which obstructions were placed in the center of the fire. These obstructions, which consisted of a set of concentric steel rings open 90 degrees on opposite sides, increased the control time only slightly. High expansion foam was fluid enough to flow around and over the obstructions and provide effective control. In practical applications, foam should be applied so that all areas of potential fire will be covered by foam.

FIRE EXTINGUISHMENT

Three dry chemical agents were used to extinguish fires in 5-, 10-, and 20-ft square pits. Figures 16 through 18 show the extinguishment

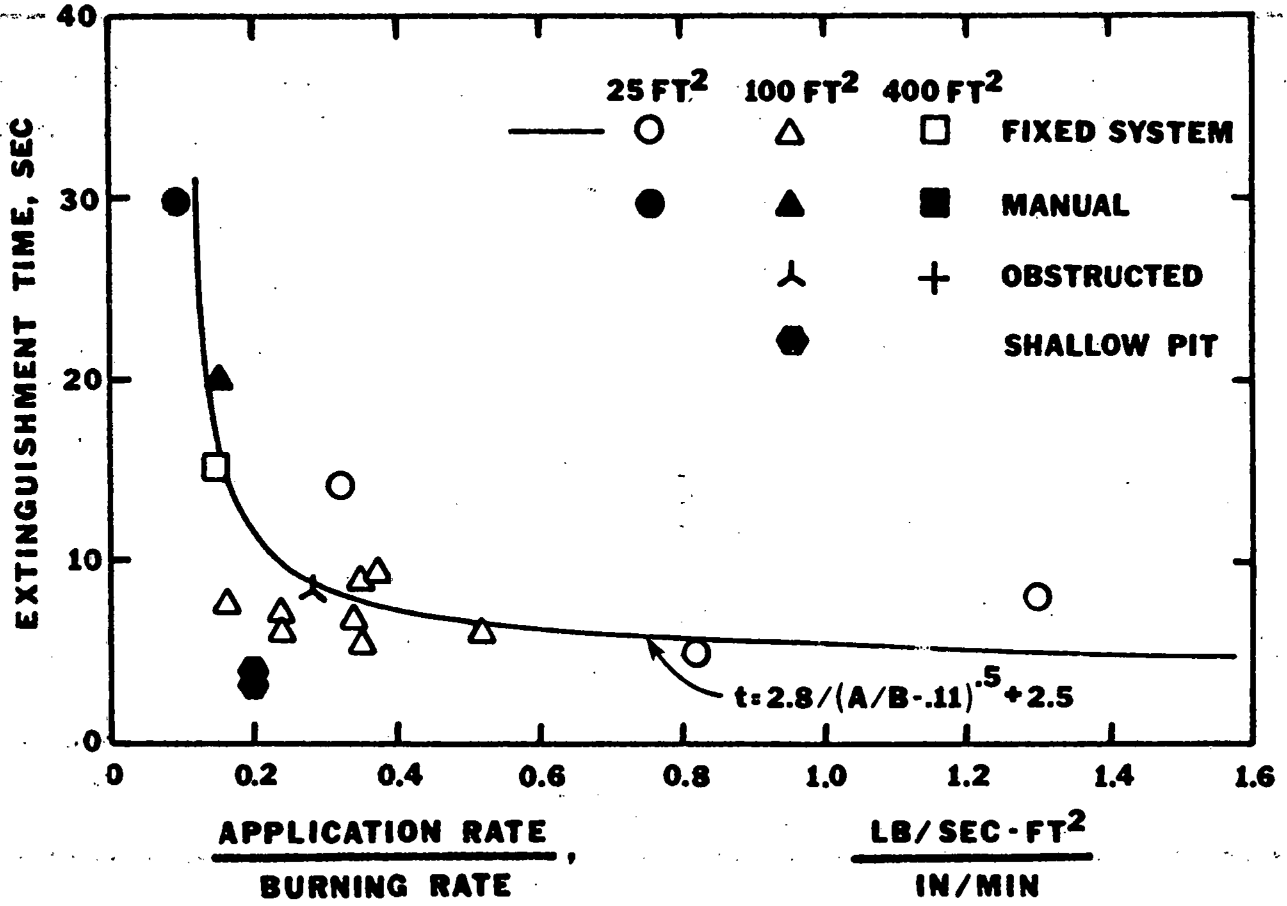


Figure 16. Extinguishment Times for Sodium Bicarbonate.

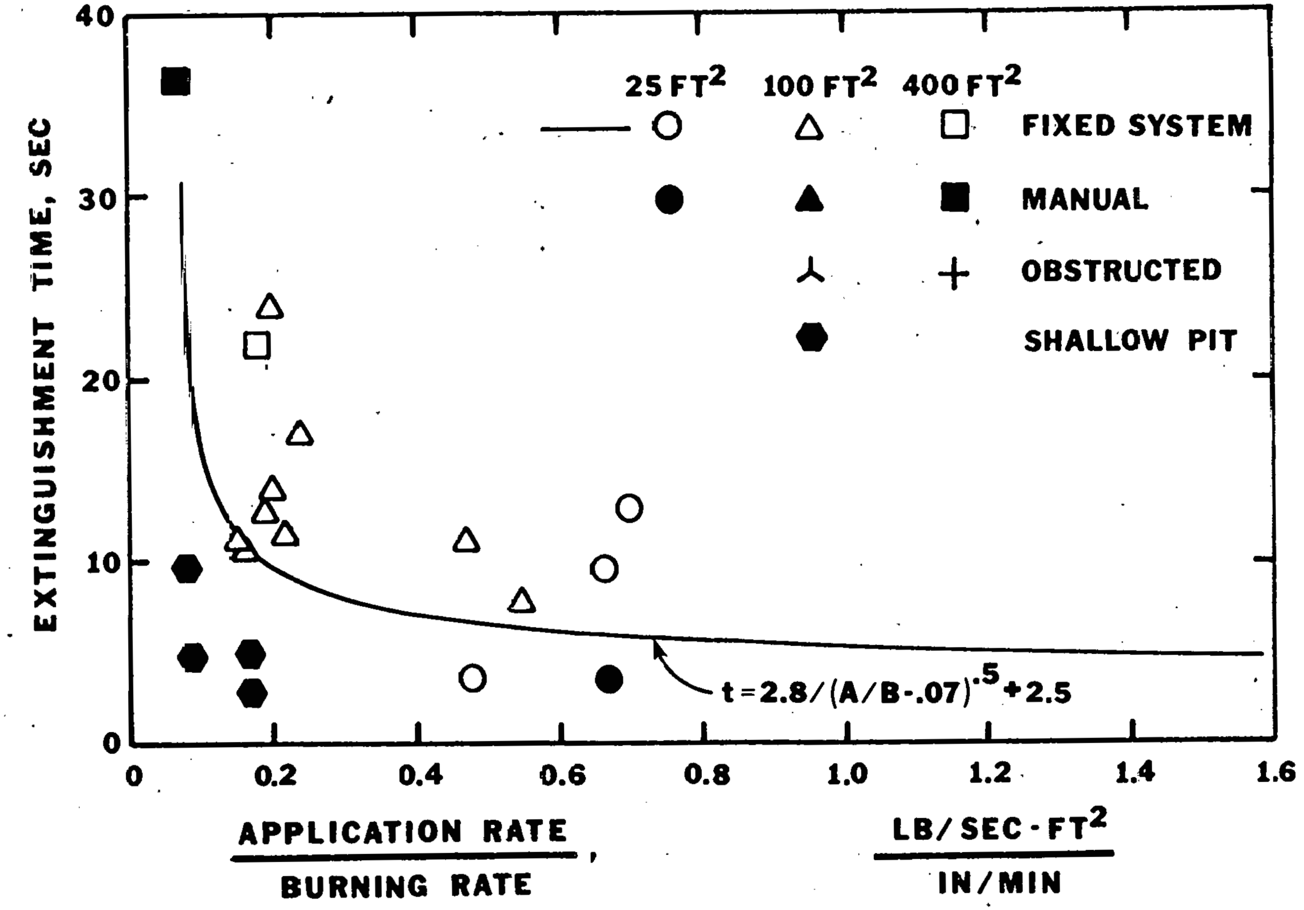


Figure 17. Extinguishment Times for Potassium Bicarbonate.

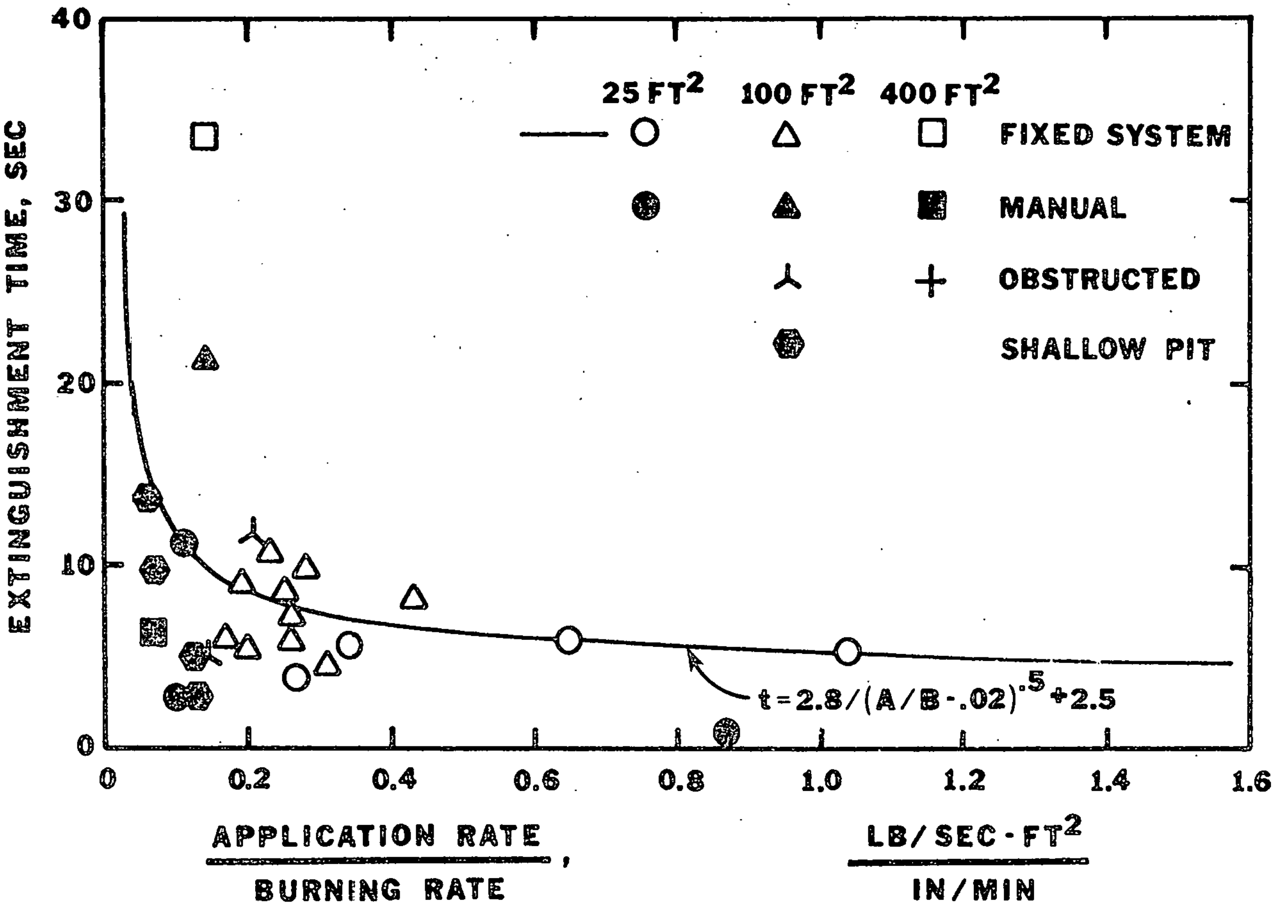


Figure 18. Extinguishment Times for Urea-Potassium Bicarbonate.

times measured for sodium bicarbonate, potassium bicarbonate, and urea-potassium bicarbonate, respectively. The extinguishment times are shown as a function of the ratio of dry chemical application rate to LPG burning rate because the quantity of powder required depends on the burning rate.

The lines drawn through the data points were derived from a least-squares analysis of the data assuming an equation of the form

$$t - t_{min} = \frac{K}{(A/B - C)^a} \qquad (4)$$

where t = extinguishment time, sec

t_{min} = minimum extinguishment time, sec

A = application rate, lb/sec-ft^2

B = burning rate, in/min

a, K, C = constants

There is a minimum application rate below which the fires cannot be extinguished; it is related to C in Equation 4. Part of the mechanism by which dry chemicals extinguish fires is by absorption of free radicals from the combustion chain. The minimum application rate is apparently related to the average free radical concentration in the flame. Since the effectiveness of absorption of free radicals varies according to the dry chemical being applied, the minimum application rate is different for the three agents. The data analysis indicated that the minimum rates were largest for sodium bicarbonate and lowest for urea-potassium bicarbonate.

There is also a minimum application time below which the fire will not be extinguished, even for very high powder application rates. This minimum application time is apparently related to the time required to mix powder and flame, so it is dependent on the application technique. Since all the fixed system extinguishment tests used the same application technique, the minimum time for extinguishment for all powders was about the same, around 2 to 3 seconds.

The LPG was contained in concrete pits about 2 ft deep, so that there was always a freeboard depth of at least 1.5 ft. The fixed nozzles were placed about 6 in. below the top of the pit wall, so that the powder was distributed evenly within the fire zone. Extinguishment was therefore quite uniform in most of the tests.

The same concentric circle obstructions used in the foam tests were also used in the dry chemical tests. The fires were more difficult to extinguish when the obstructions were used because the powder could not be uniformly distributed with the obstructions in place. In fact, potassium bicarbonate did not extinguish any fires when the obstruction was used because the powder could not be projected far enough into the obstructed area to cover all of the fire. Data from sodium bicarbonate tests showed less effect caused by the obstructions than found in the urea-potassium bicarbonate tests, probably because the projection range for sodium bicarbonate is greater than for urea-potassium bicarbonate.

Some manual fire extinguishment tests were also run using either hoselines or portable dry chemical extinguishers. The fires burning in deep pits (1.5-ft freeboard) were very difficult to extinguish. Additional manual tests on shallow pools resulted in much quicker extinguishment. No manual tests were run using the obstructions, but previous experience indicates that the fires would be harder to extinguish if obstructed. The additional difficulty is caused by the non-uniformity of powder distribution due to "shadowing" of parts of the fire by the obstructions. A well designed fixed system should show little or no effect in extinguishment time due to the presence of obstructions.

The dry chemical application rates required for extinguishing LPG fires were higher than those required for LNG fires of comparable size and burning rate in other tests (8, 9). However, the rates for LPG were comparable to those required for n-hexane. The reason LNG fires are more easily extinguished is probably related to the molecular structure and the combustion mechanism. The propane and n-hexane molecules have carbon to carbon bonds that are more easily broken than the carbon to hydrogen bonds of methane. This difference also affects the flame propagation rate, which is slower for methane, and the energy required to detonate unconfined vapor air mixtures, which is greater for methane than for propane.

Even though higher powder application rates are required for propane fires than for methane fires, practical extinguishment systems can be designed for propane. Care should be used in designing such systems so that reignition is prevented, because dry chemicals provide no long term control capability. Reignition must therefore be prevented.

CONCLUSIONS

The burning rates of LPG fires are primarily a function of the fire size and reach a maximum of about 0.45 in./min for fires larger than about 20 ft in diameter.

LPG fires can be controlled (but not extinguished) by application of high expansion foam. The foam rate required for LPG fires is less than for LNG fires at comparable burning rates, and the reduction in fire size is about the same as for LNG fires. For the foam used in these tests, the application rate should be in the range of 0.1 - 0.15 gal/min-ft^2 at an expansion ratio of 500:1 in order to provide control within a few minutes. Radiation fluxes from the fire were reduced by as much as 85 to 90 percent. Experience with LNG fires has shown wide variability in the effectiveness of various types of high expansion foam for controlling LNG fires. The same variability may be expected for LPG fires.

Dry chemical agents applied with properly designed fixed system or manned hoselines are effective in extinguishing LPG fires. Sodium bicarbonate will be less effective at low application rates than potassium bicarbonate or urea-potassium bicarbonate. However, the longer projection range and higher flow rates for a given system design and the lower cost of agent make sodium bicarbonate an attractive choice for large fixed systems discharging at high rates.

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REPORT V

State-of-the-Art of Release Prevention and Control Technology in the LPG Industry

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Subcontracted by
Pacific Northwest Laboratory for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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REPORT V

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SUMMARY

Release prevention and control technology encompasses all safety aspects of the actual handling, transportation, storage, or use of LPG. As such, it includes all construction, installation, and operational practices; codes and regulations dealing with LPG equipment and practices; analysis of the causes of accidents; research and development aimed at improved equipment; and efforts to develop better safety procedures. In this report the state-of-the-art of release prevention and control technology is presented for several modes of transportation and for consumer storage.

RELEASE PREVENTION

Release prevention encompasses all those activities whose objective is the avoidance of uncontrolled LPG spills with their attendant potential hazards. These activities include efforts by designers, constructors, installers, regulators, etc., to ensure the maximum integrity of all containers and appurtenances, and efforts by all appropriate segments of industry and government to develop safe procedures and to communicate safety information to all persons who handle or use LPG. Recent and current research and development directed toward improvements in these areas are included in this description of the state-of-the-art.

Pipeline Transportation

The importance of pipelines in the LPG industry is indicated by these statistics:

- There are some 220,000 miles of pipeline handling LPG in the United States

- Throughput in recent years has been in the neighborhood of 19 billion gallons (452 million barrels) per year, which is over 90 percent of LPG transported.

Accident Record

On the basis of accident reports filed with the Department of Transportation's Office of Pipeline Safety Operations (DOT/OPSO) by the operating companies, pipeline breaks in the ten year period 1968-1977 have resulted in 40 deaths, 69 seriously injured persons, and more than $5 million in property damage and the loss of 651,000 barrels of LPG product.(1) It can be argued that, relative to the number of miles of pipeline and the total LPG throughput, the accident record of the LPG industry is good. However, comparing the records of the LPG pipeline industry to that of pipelines carrying other liquids (crude, gasoline, middle distillates, and ammonia), LPG is accountable for two thirds of the deaths and half of the serious injuries, although it accounts for only 10 percent of all pipeline accidents. Also, although there appears to be a trend toward fewer accidents per year (183 in 1968-1972 versus 139 in 1973-1977), the dollar loss reported in the latter five-year period is double that in the previous period and the product loss is greater by 40 percent. In summary, there have been significant releases of LPG from pipelines, and serious consequences.

Design and Construction Practices

Prior to the establishment of mandatory federal regulations, industry standards and specifications provided a voluntary standard of practice for liquid pipelines. For example, the American Petroleum Institute (API) sponsored the development of specifications for the manufacture and testing of line pipe (API 5L, 5LX, 5LS specifications); the American National Standards Institute (ANSI) and the American Society of Mechanical Engineers (ASME) developed standards to guide the design and the construction of safe and serviceable pipelines. Numerous items of industry standards have been incorporated into the federal regulations.

LPG pipelines are subject to regulations detailed in the Code of Federal Regulations, Title 49, Part 195 (49CFR195) - Transportation of Liquids by Pipeline.(2) Part 195 "prescribes rules governing the transportation by pipeline in interstate and foreign commerce of hazardous materials that are subject to Parts 172 and 173 of this chapter, petroleum, and petroleum products". Part 195 specifies requirements for numerous details of material properties, design, construction, hydrostatic testing, operations and maintenance, and accident reporting. Many requirements are stated with reference to particular industry standards.

Perhaps the most significant items (with respect to release prevention) specified by Part 195 and by industry codes, e.g., ANSI B31.4,(3) include the following:

- Requirement for hydrostatic test of each new pipeline to a stress level in the pipe wall which is 125 percent of specified minimum yield stress (SMYS) (both 49CFR195 and ANSI B31.4).(2,3) This requirement seems justified by the record that, within thousands of miles of pipelines operated within this margin of safety, there have been no ruptures resulting from original manufacturing or construction defects.(4) Additionally, DOT recently published a notice of proposed rulemaking to amend Part 195 by requiring a hydrostatic test on all onshore pipelines carrying highly volatile liquids, which have not been previously tested, to at least 1.25 times their maximum operating pressure.(5)
- Requirement for coatings and cathodic protection on buried pipelines to limit corrosion damage (both Part 195 and B31.4). Although coatings and cathodic protection can be used separately, experience has shown that by far the best protection is provided by use of a combination of coatings and cathodic protection. The accident report records show that the number of accidents per year attributed to corrosion has declined from 229 in 1968 to 48 in 1976. This favorable trend reflects in large measure the requirements of Part 195 promulaged in 1967 with respect to cathodic protection, inspections for corrosion, reductions in operating pressure or replacement of pipe in cases of severe corrosion.

Although Part 195 and the industry codes prescribe many details of design, materials testing, construction, and quality control, the ultimate item of quality control is that of the field hydrostatic test indicated above. The requirement for coating and cathodic protection of buried pipelines obviously is an effort to preserve the integrity of a pipeline initially qualified by design to the codes, including the field hydrostatic test, against the ravages of corrosion over many years of service.

Other code requirements for LPG pipelines deserve mention. As already noted, Part 195 stipulates that no liquid pipeline may be operated normally at a pressure (MOP) greater than 80 percent of the hydrostatic test pressure (this corresponds to the margin of 125 percent mentioned above). In the operation of a liquid pipeline it is expected that internal pressures will occasionally exceed the normal operating pressure; these variations will be caused by the opening or closing of valves, starting or stopping of pumps, etc., which create surges of pressure. Part 195 (paragraph 195.406) stipulates that surges or other variations from normal must not be permitted to exceed 110 percent of MOP. This requirement can be met by the design and installation of surge suppressors, if needed.

It is to be especially noted that Part 195 (1977) referenced above refers to "Transportation of Liquids . . .", making no distinctions among the several categories of products carried by pipelines with respect to their characteristics or the hazards presented by them when released accidentally. In a Final Rule published on July 16, 1979, DOT/MTB has defined the term "highly volatile liquid" to be adopted under paragraph 195.2, to wit: "Highly volatile liquid" means a liquid which has an absolute vapor pressure of 40 psia or more at 100 F.(6) This notice and other notices of rulemaking thus provide a mechanism for and recognize the need for special requirements for pipelines when carrying highly volatile liquids.

Construction of steel pipelines for transportation of liquids is covered by 49CFR195, Subpart D, and by ANSI B31.4-1974, Chapter V. Generally, these regulations and standards deal with inspection of pipe and other components, welds, coatings, qualification of welders, pipe cover, construction records, etc. Part 195 requires that pipelines be constructed in accordance with comprehensive written specifications. Nondestructive inspection is required by the Federal Regulations on 10 percent of all welds (100 percent in some critical locations).

DOT/MTB published a final rule effective March 17, 1978, permitting and specifying requirements for conversion of existing pipelines to liquid service.(7) The announcement calls attention to the previous requirement that pipelines placed in liquid service after March 31, 1970, were to be designed and constructed in accordance with applicable Federal safety standards, and that the previous requirement was more stringent than necessary when applied to conversions subject to Part 195. Under the new requirements, a carrier prepares and follows a written conversion procedure, which must provide for visual inspection and historical review of the pipeline to identify actual or potential sources of failures. The review must be supplemented with appropriate tests where historical records are insufficient to judge the line's condition. Problem areas must be corrected by repair, replacement, or other alterations. A pressure test must be performed to demonstrate that the structural integrity of the pipeline is sufficient for safe operation. Applicable corrosion control requirements must be met within 12 months after the pipeline is placed in service. Records must be kept of the investigations, tests, and remedial measures conducted on the pipeline.

Finally we note that the DOT/MTB recently (February 5, 1979) issued an advanced notice of proposed rulemaking for pipelines carrying highly volatile liquids.(8) The proposed rules would:

- Make line pipe easier to weld and with tougher longitudinal seams
- Add water to anhydrous ammonia to inhibit stress-corrosion cracking
- Use lower design and operational stress levels in accordance with population density
- Require periodic hydrostatic tests.

Comments were to be filed with MTB by May 4, 1979.

Operations and Maintenance

The handling and transportation of highly volatile, flammable liquids require attention in normal operation to the potential hazards and to equipment and procedures to minimize risks. Part 195, in addition to requirements already identified, has established minimum safety requirements for pumping equipment, for written procedures for normal operation, maintenance, and abnormal operations and emergencies. Apparently the present requirements of Part 195 are not sufficiently specific in some respects, since changes to the regulations have been proposed, and made final, to clarify intent and to facilitate enforcement.(6) According to the new rules, it will be required that written procedures be incorporated in a manual, and the manual reviewed by MTB; if in MTB's view the procedures are inadequate, corrections could be required.

System Control. The overall control of liquid pipelines, as reported by Koch and Lutz(9) and verified by a survey(10), is from a central location. The type of control of operation of these pipeline systems ranges from manual call-in of parameters, which are then usually displayed on a control panel, to complete computer control. Over half of the 29 pipelines (LPG and NH_3) surveyed, representing over 19,000 miles of pipeline, have computers in their operations, but in varying degrees or modes. Some lines reported using a main computer in conjunction with various types of peripheral equipment such as hard wired controllers. Two computers of the same type, one on standby, are also used. A large number of pipelines also use a manually operated control panel with various types of peripheral equipment.

There appears to be a trend toward incorporating centralized control systems in pipeline systems transporting highly volatile liquids, but these are not truly computer-controlled systems.(10) The computer is used in an adjunct capacity, coding and decoding data, checking validity of transmitted data, calculating, receiving orders, and supplying information to the operator. The operator makes the key decisions.

In order to maintain throughput of product, keep a continuous account of the amount pumped, and protect against pipeline and equipment damage, numerous pipeline and equipment variables are monitored and logged, both at the pump stations and at central control. The specific variables used and the manner of use vary from pipeline to pipeline, but generally include pump suction and discharge pressures; commodity flow rate, temperature, and density; pump and drive running status; outputs of combustible vapor and flame sensors; and positions of pump station and mainline block valves. The transducers in a liquid pipeline control system are monitored by controllers which compare the instantaneous value against a set value. The controllers take action to minimize the differences; however, if the differences exceed certain limits, the system is shut down.

Operating variables that are used to shut down the pump station are mainly variables of the pump, such as: bearing failure, seal failure, case pressure, and case temperature. Some of the variables monitored for shutdown of the pipeline system are discharge pressure, suction pressure, and flow rate. The latter variables are good indicators of the condition of the pipeline, but only for a short distance down the line. Other transducers are needed along the line in order to monitor the condition of an entire line section.

Pump Station Control. In order to maintain operating parameters or to initiate a status change in the pipeline, controllers and actuators at the pumping stations are used. The types of pump station actuators reported in use are mainly, in order of the number reported, electronic pneumatic, and hydraulic.(10) The operating set points on these controllers are usually manually set at the remote sites. Most controllers being used are electronic because they are the most economical type that can provide the tight control necessary to run with the control valve normally wide open.(11) A good system is needed to prevent pressure overshoots, and some controllers, such as pneumatic types, may not respond fast enough, if the running pressure is close to the maximum operating pressure.

In the survey of pipelines carrying highly volatile liquids, almost all reported having pump stations with both automatic and remote shut down capabilities. The local automatic shut down capability protects the primary pumps from damage and prevents overpressuring of both pump station and trunkline piping.

The time required to isolate a pump station or shut down the pipeline system varies with the degree of automatic controls. Most pipelines require 2 to 4 minutes to shut down a pump station either automatically or remotely. Up to 2 hours is required to manually shut down a pipeline section due to the fact that all of the block valves are not automatic and must be manually closed to isolate a pipeline section. The fact that a majority of block valves must be manually closed indicates a very long time lag in closing off a section of a damaged pipeline. This is verified by the reported 2-hour estimate to isolate a section of pipeline by closing the block valves.

With regard to the shutdown capability of pump stations, 43 percent of those surveyed had an automatic shutdown capability and 87 percent had a remote control capability. Many pump stations have dual or triple means of shutting down the pump stations.(10)

195.262 of 49 CFR 195 requires that each pump station must be provided with (1) safety devices to prevent overpressuring, including auxiliary pumping equipment within the station, (2) a device for the emergency shutdown of each station, and (3) an auxiliary power supply, if power is required to actuate the safety device.

Third Party Damage. A large fraction of incidents involving release of products from pipelines involves damage by excavating equipment ("third party damage"). In a study of third party damage incidents on natural gas pipelines it was found that farmers were responsible for 35 percent of the incidents, government units 26 percent, utilities 11 percent, and developers 10 percent.(12) One type of effort directed toward reduction or elimination of third party damage is the institution of communication systems in particular areas, variously called "cooperative area notification plans" or "one-call systems". The idea is that, when any excavator plans to dig in a certain location, he can call one telephone number some time before hand, say 48 hours, and all utilities having facilities at or near the site will be notified. An NTSB report indicates a markedly downward trend in damages in areas covered by one-call systems.(13)

Maintenance Procedures. As noted above, Federal Regulations require that operators have written procedures for maintenance, the scope of which includes (1) maintaining maps and records, (2) maintaining line markers, (3) inspection of right-of-way, (4) external and internal corrosion control, (5) valve maintenance, (6) inspection and testing of overpressure devices and relief valves, etc. The potential benefits towards prevention of product releases to be derived from maintenance procedures of these types carried out at timely intervals is self-evident.

Accident Reporting. A requirement of Part 195 already noted is that pipeline operators must report to OPSO releases of commodity according to specified rules and on a specified form (Form 7000.1). The accident data so gathered could provide a basis for observing trends, analyzing for causes, determining whether changes in rules have the desired effect, etc. However, at least until very recently, OPSO has not analyzed the data gathered since 1968, other than to summarize them, and apparently has not monitored the operators' reports for completeness and accuracy.(14)

Research and Development

Most research and development which contributes to release prevention, directly or indirectly, can be considered in several categories: (1) that directed toward improvement of pipe steels, welding materials or procedures, coatings and other means of limiting corrosion, and appurtenances, (2) that directed toward understanding of causes of accidental releases, and (3) that directed toward better operating procedures or practices.

Hardware-oriented R and D will not be discussed in detail here. However, it can be said in general that any pipeline can be designed and constructed so that it will have a high degree of structural integrity. The incentives to provide an adequate degree of integrity include the safety of the general public, the safety of employees, avoiding loss of products and damage to company and non-company property, and preventing costly shut downs. Toward this objective, as previously noted, the pipeline industry, represented by the API, ANSI, ASME, etc., and the federal government have established specifications and regulations which are intended to produce the desired integrity and serviceability of pipelines. Committees which consider and promulgate changes in industry codes include a broad range of representatives, of manufacturers (steel, coatings, components, etc.), and of the pipeline operators, and various experts and researchers. A vast amount of research has been conducted over the years toward better pipe materials; better welding materials and techniques; more knowledge concerning fracture of pipelines; the significance of chemistry and metallurgy, residual stresses, and operating stresses in fracture behavior; and better understanding of the function and value of hydrostatic testing and other methods of quality control on reliability. To put the question of materials in pipeline systems in perspective, the results of a study by NTSB on liquid pipeline accidents indicate that the causes of 2294 accidents (1968-1976) for <u>all</u> liquid pipelines ranked as follows:(14)

Corrosion	45 percent
Equipment Rupturing Line	28 percent
Defective Pipe	7 percent
Defective Welds	5 percent
Incorrect Operations	2 percent
Other causes	13 percent

Some 12 percent of all accidents were attributed to defects in the pipelines themselves; these defects might have included manufacturing or field welding defects, damage to the pipeline due to handling during laying into the ditch or due to backfilling, damage by third parties after the pipeline is in service, etc.

Concerning causes of accidental releases of LPG from pipelines, we have, of course, the operators reports to OPSO on "reportable incidents", in which the general causes are given. The form provides the possibility of indicating as cause (1) corrosion, (2) defective pipe, (3) defective weld, (4) incorrect operation by carrier personnel, (5) equipment rupturing line, or (6) other (specify). These accident reports are summarized annually by OPSO(1) and have been analyzed by NTSB(14); some of the statistics have been cited above. Data and conclusions reached by NTSB, not already cited, include the following:

- Among the various possible causes of accidents, that of equipment rupturing line was the leader in losses of product as well as total casualties from 1968 to 1976.
- Michigan did not have any reported equipment caused ruptures in 1974, 1975, or 1976. NTSB attributes this in part to the state wide "one-call system"; all operators of underground utilities are required by State law to participate in the system.

- Instructions for filling out the Form 7000.1 are not adequate to insure consistency and thoroughness. Also, the form does not request sufficient kinds of data to support the formulation of safety regulations.
- There is no way to predict safe service life of a liquid pipeline using the currently available data.

The NTSB issued several recommendations on the basis of its study of liquid pipeline accident data:

- OPSO should publish a plan describing how it will use accident report data to formulate safety regulations and to develop a safe service life model for pipeline.
- OPSO should redesign the Form 7000-1 to include data similar to that collected for natural gas pipelines.
- OPSO should computerize the liquid pipeline accident reporting system to permit analysis and determination of meaningful relationships among leak rates per mile and various pipeline/product parameters.
- OPSO should expedite rulemaking concerning LPG pipelines.
- The API should urge member pipeline companies to participate in and encourage improvement in any one-call systems where they operate, and help organize systems where they do not exist. The Governors of Texas and Oklahoma were urged to take action to implement state wide one-call systems in their states.

Another source of information on releases of LPG/NGL (natural gas liquids) from pipelines are the reports of investigations of particular accidents by NTSB and the Bureau of Mines.(15-20) In addition to calling attention to the magnitude of combustible vapor clouds which can form and the damage which can be done by combustion of such clouds when an LPG/NGL line ruptures, the reports also indicate something about basic causes:

- In the case of a pipeline which ruptured in Missouri in 1970, 10 persons were injured in an explosion estimated to be equivalent to 50 tons of TNT. This pipeline had ruptured 12 times in the previous 6-year period, all due to failure of the longitudinal welds.

- Another pipeline, in Texas, ruptured in the longitudinal weld in February, 1976, killing 5 people. This pipeline had suffered a series of 14 longitudinal pipe seam failures in the period 1968 to 1976.
- In January, 1976, in an accident at an LPG compressor station in Oklahoma, 5 men were killed and 2 were burned seriously when NGL was released into a ditch by an error in procedure.
- Another accident occurred in Michigan in August, 1975, when an 8-inch propane pipeline ruptured due to previous mechanical damage. 9 persons were burned.

The feasibility of limiting of pressure to prevent pipeline failure due to overpressure was investigated for the DOT, as part of a larger study.(21) This study identified a variety of systems and devices which have been used for decades to limit pressures on pipelines. However, the study identified as a relatively new development the existence of supervisory control systems which link the various pipeline components, including pressure-limiting devices, into a coherent system. The report indicates that almost all liquid lines have some means of addressing the problem of pressure transients (surges), but the results of the questionnaire did not indicate surges as being a significant problem in liquid pipelines. The authors, however, question this result, suggesting that surges may, in fact, be the prime cause of mainline ruptures. The report also identifies the problem which arises when a liquid pipeline over a period of years is seriously weakened by corrosion; it suggests that some means of periodic evaluation and derating would be desirable.

In another project sponsored by DOT/OPSO "Transportation of Highly Volatile, Toxic, or Corrosive Liquids by Pipeline", the objective was to identify and catalog the specific design, construction, operation, and maintenance practices of pipeline operators, and the problems associated with the transportation of highly volatile, toxic, or corrosive liquids.(10) Information was gathered from questionnaires sent to operators of LPG and NH_3 pipelines, personal contacts, and survey of pertinent literature. This information was gathered and analyzed in order to provide a data base to OPSO for the rulemaking process. The most significant conclusions and recommendations reached in this project relative to release prevention are:

- In general, the design, construction, operation, and maintenance practices of pipelines transporting LPG and NH_3 do not differ significantly from those of pipelines transporting petroleum products or crude petroleum.
- Pipe quality and liquid pipeline safety can be enhanced at the pipe mill by control of the "carbon equivalent" to improve weldability, and by normalizing ERW longitudinal seam welds to improve the toughness of the heat-affected-zone.
- Continue Federal Regulations (in Part 195) calling for field tests to 125 percent of MOP on new construction and existing systems that have been relocated, replaced, or otherwise changed. Also, reconsider requiring such a test on existing pipelines that have not been tested in this manner.
- OPSO should consider modifying Part 195 to make it mandatory that any pipeline that is to be converted to highly volatile liquid service must have
  (1) The original design of the line reviewed
  (2) A hydrostatic test to 125 percent of MOP
  (3) Corrosion, construction, and maintenance records
  carefully examined before the system is put into service.
- OPSO should specify a review interval for the written procedures covering normal shutdown, emergency shutdown, and an accidental release of liquid.
- Encourage all pipelines and in particular those transporting LPG or NH_3, to consider the safety benefits of cooperative notification plans.

Recent rulemaking has taken many of these conclusions and recommendations into account as discussed earlier.

Railroad Transportation

Railroads have transported some 1.1 billion gallons of LPG per year in recent years, which is about 5.5 percent of the total transported. As of

1977 there were 22,000 railroad tank cars in LPG operation. LPG tank cars built before 1961 typically had a water capacity of 11,600 gallons (9,500 gallons of propane). After 1961 much larger tank cars became available which have water capacities up to about 34,000 gallons.

Accident Record

In the last several years there has been an increasing number of railroad accidents involving LPG. This is not because LPG in any way initiates accidents; on the contrary, most accidents are initiated by derailment of trains, and the derailments set off chains of events which release LPG. Some LPG accidents have done great amounts of damage, especially when they occur in urban areas.

Often, when LP-gas tanks rupture, large portions of the tanks are propelled several hundred feet, sometimes more than 1000 feet. These events are known as BLEVE's (boiling liquid expanding vapor explosions), which occur when flames impinge on LP-gas tanks above the liquid level; the vapor cannot carry heat away adequately and the steel becomes hotter and weaker. Eventually, as the steel heats up, its strength decreases to a level where it cannot sustain the pressure in the tank, and it ruptures. Typically, the fracture travels circumferentially around the tank, separating the tank into two parts, and the vapor pressure acting on the cross-sectional area of the tank accelerates the two parts axially. The tank parts then travel until the kinetic energy acquired during the acceleration is dissipated.

In the period 1950-1969 NFPA received 18 reports on incidents involving LP-gas tanks exposed to fire which resulted in BLEVE's; those 18 fires resulted in 22 deaths and 318 injuries. In the years 1970-1974 12 BLEVE incidents were reported, resulting in 24 deaths and more than 300 injuries.

Design and Construction Practices

As with pipelines, so, too, the railroads had developed industry standards and specifications before federal regulations became mandatory. The principal industrial associations providing specifications and standards services for pressure tank cars are the American Association of Railroads

(AAR) and the American National Standards Institute (ANSI). The AAR and the ANSI are referenced in the federal regulations, and, in fact, the AAR Committee on Tank Cars has an active role in reviewing and approving designs, materials and construction, conversion or alteration of tank car tanks.

Transportation of LPG by rail is covered by federal regulations under Title 49, in three parts:(2)

- Part 173 - Shippers - Federal Requirements for Shipments and Packagings.
  Rail transport of LPG is covered specifically in Subpart B, Preparation of Hazardous Materials for Transportation, paragraph 173.31, qualification, maintenance, and use of tank cars; also in Subpart G, Compressed Gases; Definition and Preparation, paragraph 173.314, Requirements for Compressed Gases in Tank Cars.
- Part 174 - Carriage by Rail.
  This part under various subparts covers general requirements (Subpart A), such as inspections, handling of astray shipments, etc.; general operating requirements (Subpart B), such as shipping papers, orders and billings, labels and placards, etc.; handling and loading requirements (Subpart C); Detailed Requirements for Gases (Subpart F), under paragraph 174.204, "Tank car delivery of gases", specifies that compressed gases may be unloaded only on private tracks, unless certain conditions are fulfilled.
- Part 179 - Specifications for Tank Cars.

Tank car specifications for LPG include 105, 106, 111, 112, and 114. Each tank car must be designed, constructed, tested, and certified to a specific test pressure (at a temperature $\leq$ 100 F), e.g., 100, 200, ---, 600 psi. In each case the permissible maximum operating pressure (at a specific temperature, e.g., 105 F) is 75 percent of the test pressure, as determined by the start-to-open setting of the safety relief valve. The test pressure is incorporated in the tank car designation, e.g., 105 T 100 means a car designed to 105 T specifications and tested to 100 psi. The particular tank car specification required will depend on the composition of the LPG, specifically, on the vapor pressure; propane, for example, requires cars tested to higher pressure than butane. General design requirements of Part 179 include:

- Requirement for approval of the manner in which tanks are attached to the car structure; also of welding procedures, welders, and fabricators.
- Limitations on capacity and gross weight of tank cars built after November 30, 1979, to 34,500 gallons and 263,000 lb on the rails, respectively. Existing tank cars cannot be converted to exceed these limits.
- All tank cars built after 1970 must be equipped with interlocking automatic couplers that will resist car telescoping and jackknifing in derailments and in emergency stops. These couplers must be approved by the Federal Railroad Administration.

As a result of a series of serious accidents involving uninsulated tank cars built to 112 and 114 specifications and transporting hazardous materials (especially LPG), the DOT/MTB issued amendments to Parts 173 and 179, effective October 19, 1977:(22)

- Existing and newly built specifications 112 and 114 tank cars used to transport flammable gases (including LPG) are required to have both thermal and tank head protection.
- All 112 and 114 cars, regardless of lading transported, are to be equipped with special couplers designed to resist vertical disengagements. These are referred to as "shelf couplers".
- Three types of 112 and 114 tank cars were established:
    1. (1) 112A and 114A cars are authorized to transport hazardous liquids (such as gasoline) and non-flammable compressed gases other than anhydrous ammonia (note that LPG is classified as "flammable gas").
    2. (2) Newly built 112 S and 114 S tank cars to transport anhydrous ammonia as well as commodities carried by 112 A and 114 A. Each must be equipped with head shields and shelf couplers.

(3) Newly built 112 T, 112 J, 114 T, and 114 J tank cars to transport flammable and non-flammable compressed gases, including anhydrous ammonia, and hazardous liquids. Each is required to be equipped with a thermal protection system, head shields, shelf couplers, and a safety relief valve meeting the requirements of paragraph 179.105-7. This last permits reduction of relief valve capacity on thermally insulated cars.

The meanings of the letters after the specification numbers indicated above are as follows:

"A" designates 112 or 114 specification cars which have as additional protection only shelf-couplers; these cars can carry non-flammable gases and hazardous liquids.

"S" designates 112 or 114 specification cars which have both shelf-couplers and head shields; they can carry anhydrous ammonia, non-flammable gases, and hazardous liquids.

"J" designates 112 or 114 specification cars with thermal protection enclosed in a metal jacket, plus shelf-couplers and head shields; these cars can carry flammable gases (LPG) in addition to products carried by "A" and "S" cars.

"T" indicates thermal protection without a metal jacket; such cars are otherwise similar to "J" cars and can carry the same products.

Recently the DOT/MTB issued a list of thermal protection systems which may be used on 112 and 114 tank cars without further test verification to satisfy the retrofit requirements.(23)

Operations and Maintenance

Operating and maintenance aspects of rail transportation of LPG are covered by 49 CFR 173 and 49 CFR 174, as noted above. Numerous details of practice are also specified in NFPA 58 "Storage and Handling of Liquefied

Gases - 1976",(24) and recommended practices have also been developed and promulgated by the National LP-Gas Association(25), and by the Compressed Gas Association(26).

Important operational aspects covered by regulations include inspections of tank cars and appurtenances before loading and before shipping; periodic retest and reinspection, including hydrostatic test of tanks and testing of safety relief valves; withdrawal from service or repair of tanks which have been subject to fire; filling densities; maximum vapor pressure (at specified temperatures) versus the test pressure; use of foreign tank cars in domestic use (tests and certifications required); respective responsibilities of shippers and carriers; proper handling of empty cars offered for transportation; handling of leaking cars; positions of cars carrying compressed flammable gases in trains with respect to cars carrying other hazardous substances.

Research and Development

Following a number of tank car ruptures in 1969, a research project was initiated in 1970 referred to as the RPI-AAR project (Railway Progress Institute-American Association of Railroads) and known officially as "Railroad Tank Car Safety Research and Test Project". In addition to the two organizations already named, sponsors included nine other interested associations and institutes; there were also government observers from the Canadian Transport Commission, The Federal Railway Administration (FRA), and NTSB. The program was directed by the Tank Car Research Committee under the Chairmanship of Frank J. Heller. The research was organized in phases, and, except for one continuing project (1978), the research effort has been concluded.(27,28) The research phases were as follows(27,29):

Phase 1 - Accident review
Phase 2 - Derailment Environment Study (including dollar loss)
Phase 3 - Materials Study-Steel (including fracture properties)
Phase 4 - Review of Literature and Related Experience
Phase 5 - Head Study (including head shields)
Phase 6 - Safety Valve in Liquid Study
Phase 7 - Safety Relief Devices-General

Phase 8 - Reduced Scale Model Studies (including derailment studies)
Phase 9 - Design Study - Tanks and Attachments
Phase 10 - Design Study-Car (including couplers and trucks)
Phase 11 - Thermal Effects Study (including thermal shield systems, and torch tests)
Phase 12 - Vessel Failure Research (including fracture and tub rocketing)
Phase 13 - Tank Head Shield Design (this phase conducted under DOT Contract, DOT-FR-00035)
Phase 14 - Stub Sill Buckling Study
Phase 15 - Switchyard Impact Tests.

Some 40 final or phase reports, plus 31 technical progress reports, were issued on the various phases of this project as of February, 1979.(29) This whole program apparently has been directed entirely toward release prevention, and has obviously provided the basis, at least in part, for the recent regulatory actions regarding thermal shields, shelf couplers, and head shields.

The DOT sponsored a 4-month study in 1970 at the Cornell Aeronautical Laboratory (DOT-FR-00028)(30). The objectives of this research included development of performance specifications and conceptual design and application requirements for safety devices to prevent catastrophic car failure. A number of technical conclusions were reached and a plan for a research program was developed. Apparently this was the basis in part for initiation of the RPI-AAR project described above, although the latter program was appreciably more comprehensive than envisioned by this study.

The NTSB held a public hearing in April 1978 and issued a report of their analysis and recommendations regarding means of reducing the risks from rail transport of hazardous cargo, including LPG.(31) NTSB examined safeguard installations for 112 and 114 tank cars, emergency notification and response procedures, the derailment problem, track standards, and other areas. Conclusions by NTSB pertaining to release prevention include the following:

- 112 A and 114 A tank cars were designed by the tank car and the railroad industry to maximize economics; no specific safety methodology to determine unreasonable risk to the public was employed.

- When the 112A/114 A car designs were accepted on special permit, the safety features of thermal insulation and a center sill were eliminated and the capacity was increased three-fold. No analysis nor full-scale testing were carried out before these designs and equipment were placed into service.
- No adequate safety methodology has been developed by Federal agencies to determine risks as a basis for regulation.
- DOT's accident data collection programs for train derailments and hazardous materials provide a limited capability for accident prevention research and countermeasure development.

Truck Transportation

Truck transport of LPG accounted for about 800 million gallons or about 4 percent of the total amount shipped in 1977. According to the NLPGA there were about 25,000 transport and delivery trucks in operation in the U.S. in 1977. These include some 7,000 trucks carrying between 3,500 and 10,000 gallons; some 18,000 trucks, called "bobtails", used for local distribution and carrying generally from 800 to 3,500 gallons; and a relatively small number of flat-bed trucks which carry skid tanks of 300 to 2,000 gallons capacity.

Accident Record

LPG truck accidents occur mainly in three situations: (1) in loading/unloading operations, (2) in repair garages, and (3) in collisions or overturns on the road. Statistics on LPG truck accidents are gathered by the Department of Transportation/Office of Hazardous Materials, (DOT/OHM), the Federal Highway Administration (FHWA), the Bureau of Motor Carrier Statistics (BMCS), agencies in several states, and private trucking organizations. However, the gathering of statistics on truck accidents is a major problem: accident data are incomplete, sometimes difficult to obtain even when they exist, and largely not dependable because different criteria are used in collecting data.(32, 33) A particularly significant problem with respect to hazardous materials is that many truck accident data are not differentiated by type of cargo, and there are many times more trucks hauling gasoline, diesel fuel, and other middle distillates than there are hauling LPG. However, some partial statistics are available from various studies:

- The NLPGA collected and analyzed LPG truck accidents for the period 1972-1976. The data include 178 highway accidents in the 6-year period, of which 96 involved no release of cargo, 50 produced minor spills, and 32 involved fire or significant releases.(34)
- The DOT/OHM collected and analyzed data for the period 1971-1977, showing a total of 124 spills from all sources except loading/unloading operations.(34)
- FHWA statistics, although quite incomplete in many categories, show that in the 5-year period 1973-1977 there was an annual average of 79 accidents involving LPG trucks. Of these, 9.4 were reported as spills.(34)
- Factory Mutual analyzed DOT data for hazardous materials for the period July, 1966, to December, 1968, finding that combustible compressed gases accounted for 139 accidents, 9 deaths, and 81 injuries.(33)
- There were three separate incidents in 1974 involving LPG tank trucks in repair garages. Fires resulted because the trucks were not emptied of LPG and purged before being moved inside. Several people were burned, there were 4 fatalities and large amounts of property damage.(35)

Design and Construction Practices

LPG trucking is regulated by the DOT and by NFPA 58. The extensive and detailed requirements specified by NFPA 58 and the DOT regulations for storage and handling of LPG are, of course, directly related to its hazardous nature. LPG is hazardous primarily because it exists as a liquid only under relatively high pressures (200 psi for propane at 105 F), and, when the pressure is released, a flammable fuel air cloud is formed which is denser than air, hence does not disperse readily. The general objective of regulations, then, is the prevention of accidental release of LPG fuel and the consequent production of a flammable cloud. The more important aspects of the regulations are presented below.

Interstate LPG trucking is regulated by the DOT under 49 CFR, Parts 172, 173, 177, and 178.(2) The general scopes of these parts are as follows:

- Part 172 contains a Table of Hazardous Materials (paragraph 172.101) identifying materials by name, the hazard classification of each, labels required on packages, and specific packaging requirements. In this part LPG is classed as a "flammable gas", and must be labeled so, unless excepted. This part also deals with (1) shipping papers and information required on them; (2) marking requirements, which refers to the shipping name (in this case "liquefied petroleum gas"); color, size, location, etc., of the marking; (3) requirements for labeling; and (4) placarding requirements.
- Part 173 defines hazardous materials for transportation purposes and prescribes certain requirements to be observed in preparing them for shipment. "Flammable gas" is defined in paragraph 173.300. Subparts pertinent to LPG include (1) Subpart A - General, (2) Subpart B - Preparation of Hazardous Materials for Transportation, and (3) Subpart G - Compressed gases Definition and Preparation. This part also covers specifically (in 173.33) the qualification, maintenance, and use of cargo tanks.
- Part 177 deals specifically with transportation by highway, and generally pertains to the vehicle and operations, rather than containers.
- Part 178 prescribes the manufacturing and testing specifications for containers. Subpart C gives specifications for cylinders, Subpart H for portable tanks, and Subpart J for containers for motor vehicle transportation (paragraph 178.337). "Portable tank" is defined as any packaging (except a cylinder having a 1000 pound or less water capacity) over 110 U.S. gallons capacity and designed primarily to be loaded into, or on, or temporarily

attached to, a transport vehicle, and equipped with skids, mounting, or accessories to facilitate handling of the tank by mechanical means (paragraph 171.8).

Intrastate trucking of LPG is subject to NFPA 58, specifically Chapter 6 "Truck Transportation of LPGas".(24) Paragraph 6002 of NFPA 58 indicates that "many of the provisions of Chapter 6 are identical or similar to DOT regulations and are intended to extend these provisions to areas not subject to DOT regulation", i.e., intrastate. The design and construction of containers is covered in Chapter 2, and filling of containers in Chapter 4, of NFPA 58.

49 CFR 173.315 stipulates that LPG shall be shipped only in cargo tanks, Specification MC-330 or 331, or in portable containers, Specification DOT-51, or as provided in 173.32 and 173.33. (Liquefied gases may also be charged into and transported in cylinders as indicated in paragraph 173.304; cylinders will be discussed in another section). Specification MC-330 is obsolete, and tanks have not been built to this specification since 1967; however, MC-330 tanks continue in use. Specification MB-331 is described in paragraph 178.337, and DOT-51 in paragraph 178.245. Both MC-331 and DOT-51 tanks must be built to the same ASME Code.(36)

The designs of vehicles to carry cargo tanks or portable tanks are not specified in regulations in detail, except with respect to certain items:

- Requirements for fire extinguishers
- Requirements for chock blocks
- Requirements on exhaust systems
- Requirements on lights and wiring
- Requirements on truck bodies for hauling cylinders (tie downs, etc.)

Specification MC-331 (49 CFR 178.337) includes the following items for containers to be used to haul LPG:

- General requirements - Tanks must be seamless or welded steel construction and designed and constructed in accordance with the ASME Code. The design pressure shall not be less than the vapor pressure of the commodity at 115 F. Excess pressure relief valves shall be located in the top of the tank or heads. Post weld heat treatment must be as prescribed in the ASME Code, except that each tank constructed in accordance with Part UH of the Code must be post-weld heat treated. In no event shall the post-weld treatment be at less than 1050 F.

- Materials - All materials used for construction of the tank and appurtenances must be suitable for use with the commodities to be transported and must comply with requirements of the Code and of the ASTM. Impact tests are required on steel used in fabrication of each tank constructed in accordance with Part UHT of the ASME Code.
- Design Stress Considerations - Specification MC-331 includes requirements on minimum thicknesses of shell, head, etc.; on minimum stresses, and prescribes a formula for calculation of stresses. A paper discusses these calculations and other aspects of MC-331.(37)
- Construction - Tanks are to be assembled generally according to requirements of the ASME Code. These requirements cover welding procedures, welder qualifications and performance tests, preparation of joints, cutting of openings, tolerances for misalignment, etc.
- Outlets and Safety Devices - Excess-flow check valves or backflow check valves may be used on vapor lines, but liquid-discharge lines must be fitted with internal, self-closing valves.(37) The latter function so that they are closed during transport, must be held open during unloading operations, and close automatically or manually in event of an emergency. Also, tanks greater than 3500 gallons capacity must have remote-control stations at each end of the tank and diagonally opposite each other for operation of valves. For smaller tanks, at least one remote-control station must be provided.(37)

Fittings must be protected against damage from collision with other vehicles or objects. Safety relief valves, in particular, must be protected so that in event of overturn of the vehicle on a hard surface, opening will not be prevented and discharge will not be restricted. There are specific requirements on the design of these protective devices or housings.

- Qualification - Every cargo tank used for the transportation of hazardous materials must be an "authorized" container by virtue of testing and inspections as prescribed in 49 CFR 173.33. A container, less any fittings, must be subjected to a hydrostatic or pneumatic test to a pressure 1.5 times the design pressure.

An amendment to 49 CFR 178 to be effective July 1, 1979, prohibits the location of manhole assemblies on the front head of MC331 cargo tanks. This is intended to reduce the probability of release of cargo in accidents because of collision damage to the manhole assembly.(38)

Operations and Maintenance

As noted above, operation and maintenance are regulated mainly by Parts 173 and 177 of Title 49, and by NFPA 58; Parts 390 to 397 of Title 49, "Motor Carrier Safety Regulations"(39) also apply.

Recommendations and procedures for safe operation of truck transport are included in "LP-Gas Safety Handbook" prepared and published by National LP-Gas Association, and "Handbook of Compressed Gases", a Compressed Gas Association publication.(25, 26)

The interstate truck transport of LPG is subject to regulation by the U.S. Department of Transportation, and thus, to CFR Title 49, Part 177. The NFPA No. 58 is essentially identical to the DOT regulations and is intended to extend the provisions of those regulations to intrastate operations. However, vehicles and procedures under the jurisdiction of DOT shall, in all cases, comply with DOT regulations.

Insofar as the truck transport of portable containers is concerned, provisions as to filling quantities, protection of valves, loading procedures and marking are specified in NFPA No. 58, Chapter 6. Similarly, provisions for cargo vehicles covering safety relief valves, filling connections, the need for remodeling controlled shut-off valves, gaging devices, drainage openings, necessary labeling and protection of container appurtenances are specified.

All pipe, tubing, fittings, valves, hoses and flexible connectors must be inspected daily to ensure that they are in good condition, free from leaks and not damaged in any way.

The regulations of the FHWA as detailed in 49 CFR 390-397, pertain to the driver and, generally, to the operation of LPG transports on public highways. The titles of several Parts indicate the general nature of these regulations:

Part 390 - Federal motor carrier safety regulations: General
Part 391 - Qualifications of Drivers
Part 392 - Driving of motor vehicles
Part 393 - Parts and accessaries necessary for safe operation
Part 394 - Notification, reporting and recording of accidents
Part 395 - Hours of service of drivers
Part 396 - Inspection and Maintenance
Part 397 - Transportation of Hazardous Materials; driving and parking rules.

Loading and Unloading. The usual method for transfer of LPG utilizes a liquid pump, although propane under some circumstances may not require mechanical assistance. On the other hand, butane in cold climates may require both liquid pump and vapor compressor. If a compressor is used, it draws vapor from the discharge vessel, compresses and discharges the vapor back into the delivery tank, thus creating a pressure differential and forcing the liquid to flow from delivery to receiving tanks.

When undertaking transfer operations, propane must never be loaded into a vessel designed for butane, although the converse is allowable. Overfilling must be guarded against by constantly monitoring the liquid level. Road trucks must be electrically grounded to prevent static electricity build-up before the transfer operation is initiated. In addition, transfer lines must have electrical continuity across any connectors. Also, chock blocks should be used to prevent rolling of the vehicle.

Maintenance and Repair. All vehicles should undergo a formal written schedule of preventative maintenance as well as a daily routine check by the driver. Any defects noted during inspection or operation should be reported in writing to the driver's supervisor. Repairs of tanks should be made only by persons qualified in pressure work and must meet requirements of the authority having jurisdiction. Repaired containers cannot be returned to service until their use is certified by a qualified pressure vessel inspector.

A recent amendment to Part 177, effective January 1, 1979, is intended to reduce the probability of accident involving hazardous materials as a result of maintenance or repair work on the motor vehicle by specifying conditions for such work inside a building.(40)

Research and Development

Recent research in connection with LPG trucking has involved analysis of accident data and of particular serious accidents, generally with the purpose of discovering causes so that corrective measures toward release prevention might be taken.

In 1974 the Alberta Manpower and Labor Department investigated accidents that occurred in Alberta in the period 1969-1974 and which resulted in fatalities.(41) There had been a trend of increasing frequency of such accidents (reflected also in the entire Canadian propane industry), and this study was carried out in an effort to determine their causes. It was found that each accident was caused by a human error. In most cases both management and truck drivers appeared to be unaware of safety requirements, of the hazards of putting trucks (with propane) in garages, and of the requirements for safe handling and transporting LP-gas. The study recommended that the industry provide for adequate training of employees, ensure proper maintenance of equipment, enforce safety practices, locate large storage tanks (2000 imperial gallons or more) at least 400 feet from all public and residential places, prohibit the garaging of LP-gas trucks, tanks, etc.

In 1977 the DOT/FHWA sponsored a project to assess accident data relating to cargo tank overturns and to determine whether the existing cargo tank specifications should be revised.(42) The report lists these recommendations pertinent to MC 331 tanks:

- A systematic effort should be made to collect cargo tank damage information and related data.
- Any truck or tractor used to carry or tow a cargo tank containing hazardous flammable materials should be subject to special performance and compliance requirements. The complete fuel system should be designed for a high level of safety performance more consistent with the risks associated with leakage in possible accidents.
- The requirements for automatic shut-off and excess flow valves should be clarified and improved. Positive shutoff internal to the shell and establishment of sufficient compliance lists and procedures should be specified. Required research includes the development of cost-effective systems and components.
- The requirements for fitting protection should be reviewed and clarified. Any opening in the shell should be closed internally except when transferring cargo, or be adequately protected for most accidents which the basic shell can survive.
- The requirements for shear section performance, (as presently specified in 178.337-12), should be clarified and compliance tests developed.
- The requirements for supporting and anchoring the shell should be reviewed and specific requirements established for overturn conditions.
- Manholes should be located in an area of low probability of accident damage. The design should minimize stress concentration and maximize damage resistance. Further research and testing is required to establish definitive methods of specifying design requirements.
- Baffles, bulkheads, and stiffeners, when used in MC 331 tanks, should be designed to minimize their contribution to adjacent structural stress concentrations. Further research effort is required to define cost effective methods of spreading out the connecting loads.

Note that some of these recommendations have been the subject of recent rulemaking, as noted earlier.

Consumer Storage

The LPG industry serves about 18 million customers, including business and government as well as homes, farms, and others. It is estimated that roughly 60 million people are dependent on LPG for one use or another. The major uses are:

- Home and Camping - Heating, cooking, clothes drying, water heating, barbecueing, air conditioning and refrigeration
- Farms - Crop drying, flame weeding, tobacco curing, defoliation, poultry and pig brooding, stock tank heating and frost protection
- Internal Combustion - Trucks, fork-lift trucks, buses, taxicabs, pumps, generators and other equipment
- Commercial - Same uses as home for restaurants, hotels, motels, laundries, etc.
- Industry - Brazing, soldering, cutting, heat treating, annealing, vulcanizing, etc.

In 1977, the NLPGA reported numbers of LPG retail customers as follows:(43)

Homes	-	10,772,600
Farms	-	1,394,000
Commerce and Industry	-	944,400
Recreation Vehicles	-	5,502,700 .

They also reported sales in thousands of gallons as follows:

Residential and Commercial	-	7,168,600
Internal Combustion	-	1,144,900
Industrial	-	1,043,500
Utility Gas	-	566,200
Chemical and Synthetic Rubber	-	3,578,200
Other Uses (including agriculture, SNG feedstock and secondary recovery of petroleum).	-	2,006,600

Total number of LPG tanks and cylinders are unavailable. Miniature cylinders containing 2 pounds or less of propane are widely used for hand torches, lights and camp stoves. Twenty-pound cylinders are most commonly used by small domestic users or for trailers, temporary installations, and other applications where portability is most important.

Accident Record

Apparently there is no single agency or private organization which has assembled comprehensive statistics over a period of years on accident experience with consumer LPG equipment. The NFPA has published brief stories describing accidents, fires, or explosions involving LPG.(44,45) Excluding those incidents not consumer-oriented, such as with truck- and rail-transport and also those involving consumer appliances, which are outside the scope of this study, the NFPA presents these statistics:

- For the period 1930-1951

Habitational	occupancies	5	incidents	7	killed	17	injured
Mercantile	"	12	"	27	"	128	
Manufacturing	"	5	"	15	"	3	
Storage	"	1	"	1	"	3	
Transportation Equipment		7	"	3	"	50	
Garages & Service Stations		7	"	12	"	9	
Miscellaneous		4	"	9	"	164	
		41	incidents	74	killed	374	injured

- For the period 1951-1961

Residential	occupancies	4	incidents	2	killed	11	injured
Public Assembly	"	3	"	1	"	16	
Mercantile	"	2	"	0	"	3	
Automobiles, trucks		5	"	1	"	11	
Miscellaneous		3	"	2	"	6	
		17	incidents	6	killed	47	injured

These statistics were extracted from the short news stories on the incidents by selecting only those cases where the cause of the incident appeared to involve the portions of systems containing liquid. In other words, numerous incidents involving heating equipment or other appliances, or the vapor pipeline beyond the regulator, have been excluded.

Causes of the incidents included in the tabulations above run the gamut of possibilities, including a large fraction caused by human error, resulting from insufficient awareness or knowledge of the hazards and behavior of LPG, lack of communication, etc. Other causes include corrosion of buried tanks or liquid lines, settlement of foundations, nonstandard equipment, installations not according to code, overfilling, fires of other materials impinging on tanks or cylinders, damage to LPG system by vehicles or by attempts to move or repair tanks containing liquid, leakage during LPG transfer, use of a propane cylinder to pressurize a paint sprayer inside a building, failure of pressure regulator, leakage through heat exchangers of butane systems, failure of plumbing on vehicles, improper handling of cylinders and portable tanks, etc.

The Consumer Product Safety Commission (CPSC) CPSC had on file 105 death certificates related to LPG tanks and fittings as of June, 1976(46) (presumably from March, 1967); of these, 64 deaths were caused by explosions, 30 deaths were attributed to inhalation of gas fumes, and 11 deaths occurred in incidents which could not be categorized under specific accident patterns.

Design, Construction, and Installation

The design and construction of LPG containers is covered by Chapters 2 and 3 of NFPA 58.(24) Chapter 2 includes the basic provisions for individual components, subassemblies, container assemblies or complete container systems. The field assembly and installation of components, subassemblies, container assemblies, or complete container systems into complete LP-Gas systems is covered by Chapter 3. Paragraph 2101 of NFPA 58 says that containers shall be designed, fabricated, tested, and marked in accordance with DOT regulations(2), the ASME Code(47), or the API-ASME Code.(48) Construction of containers to the last named code has not been authorized since July 1, 1961. Paragraph 2101 also states that containers fabricated according to earlier editions of any of these codes may continue in use, provided certain requirements described in other paragraphs are met, especially requirements pertaining to requalification or retesting.

The DOT Regulations pertaining to LPG containers are found in 49 CFR:

- Part 173 - Shippers - General Requirements for Shipments and Packagings, particularly in Subpart B - Preparation of Hazardous Materials for Transportation, and in Subpart G - Compressed Gases; Definition and Preparation
- Part 178 - Shipping Container Specifications, particularly in Subpart C - Specifications for Cylinders.

Note that the DOT Regulations govern only containers which are to be used to transport LPG; a container which is to be mounted permanently at a consumer's site, or a skid-mounted container which may be moved when essentially empty, is not covered by DOT Regulations.

The codes are quite voluminous, covering in considerable detail many aspects of design, materials, fabrication methods, testing and retesting, marking, and installation of cylinders, tanks, and their appurtenances. Some aspects are highlighted below:

- Design or Service Pressure. The term "service pressure" in DOT terminology designates the authorized pressure marking on the container, and is equal to the maximum allowed vapor pressure in the container at 70 F. The DOT further specifies in paragraph 173.301 that the pressure in a compressed gas (LPG) container at 130 F shall not exceed 5/4 times the service pressure. "Design pressure" in ASME terminology connotes design for the most severe condition of coincident pressure and temperature expected in normal operation. ASME containers for LPG must be designed to a minimum design pressure generally equal to 5/4 of the expected vapor pressure in the container at 100 F (containers for automotive use require a higher factor). See paragraph 2111, NFPA 58.
- Design. In addition to specification of a design pressure or service pressure as explained above, the codes also contain requirements on design temperature, on wall thickness of the

shell, thickness of the heads, concavity of heads toward the pressure, allowable stresses and methods of calculating stresses. On openings in cylinders the DOT (paragraph 178.37-12) deals only with the types of threads to be used and some details as to cleanness, lack of defects, number of engaged threads, etc.; the ASME treats the design of openings in much greater detail, including the possible need for reinforcements, the geometric limits of reinforcement, the strength of reinforcements, and methods of attachment of pipe and nozzle necks to vessel walls.

- Fabrication. Fabrication is regulated in part by stipulation of type of container (e.g., DOT, seamless cylinder), further by requirements on removal of dirt and scale, on rejection of defective material, repair of defects, etc; also, by stipulation as to when and where welding or brazing are permitted, and as to proper heat treatment of completed vessels. Again, the ASME Code is much more detailed than DOT Regulations, treating such items as permissible out-of-roundness of shell, tolerances for formed heads, details of lugs, fittings attachments, holes for screw stays, etc.
- Inspection and Tests. Tests required under specified circumstances include hydrostatic tests of completed containers; tests to measure mechanical, impact, and ductility properties of the materials; leakage tests. Inspections must be made by an independent inspection agency (i.e.., an agency not under control of the manufacturer). Required inspections include material inspections, verifications of chemical analyses, verification of compliance of containers with all requirements, inspection of interior before closing, verification of heat treatment, witness of all tests, verification of threads by gauge, reporting of volumetric capacity and tare weight and minimum thickness of wall.
- Appurtenances. Both ASME and DOT require positive shut off valves, internal excess flow valves, external excess flow valves, and back flow check valves on containers, depending on

the type, size, and mode of use of the container. External appurtenances must also be protected from physical damage while in transit, storage, when being moved into position for use, and when in use except in residential and commercial installations (paragraph 2130 and 2131 of NFPA58-1976).

In addition to the appurtenances mentioned above, other devices must be or may be used:

- Liquid level gaging devices must be provided on all containers filled by volume.
- Pressure gages, if used. shall be attached directly to the container opening or to a valve or fitting which is so attached.

- Pressure Relief Valves. ASME requires that containers be equipped with one or more safety relief devices designed to relieve vapor. These devices shall be spring-loaded valves set to start-to-discharge at pressures related to the design pressure as below:

	Minimum	Maximum
For ASME codes prior to 1949, and 1949, paragraph U-68 and paragraph U-69	110%	125%
For ASME code 1949 paragraph U-200 and paragraph U-201, and codes after 1949	88%	100%

- Hydrostatic Relief Valves. Hydrostatic relief valves are required to relieve pressure in sections of liquid piping which can be completely closed off by valves, and shall have pressure settings in accordance with Table 1 taken from NFPA 58-1976, paragraph 236.

TABLE 1. PRESSURE SETTINGS FOR HYDROSTATIC RELIEF VALVES

Located in Piping Directly Connected to	Pressure Settings Minimum	 Maximum
DOT (ICC) Cylinders	400.0 psig	500 psig
ASME Containers, 250 psig design*	350.0 psig	500 psig
ASME Containers, 312.5 psig design*	437.5 psig	500 psig
Pump Discharge Systems	450.0 psig	500 psig

* Or equivalent (see paragraph 2111 and Appendix C).

- Regulators. Requirements for regulators are described in paragraphs 247 and 314 of NFPA 58. Final stage regulators shall be equipped on the low pressure side with either a relief valve or a shut off device that shuts the gas off at the inlet side when the downstream pressure reaches certain limits, or both. The minimum and maximum limits for these devices are given in Table 2 reproduced from NFPA 58. The shut off device just mentioned shall not open automatically to permit flow of gas. Regulators used to control distribution or utilization pressure shall be as close to the container as possible. Generally, first stage regulating equipment must be outside of buildings. LPG vapor may not be piped into buildings at pressures exceeding 20 psig, except under certain prescribed conditions. On regulators installed inside of buildings, the discharge from the safety relief device and from above the regulator and relief valve diaphragms shall be vented to outside air in such a way as to minimize significant diffusion of the vapor back into the building (see paragraph 315, NFPA 58).

TABLE 2. LIMITS FOR DEVICES ON FINAL REGULATORS

Regulatory Delivery Pressure in psig	Relief Valve Start-to-Discharge Pressure Setting, % of Regulator Delivery Pressure Minimum	Maximum
1 or less	170%	300%
Above 1, not over 3	140%	250%
Above 3	125%	250%

LP-Gas systems must be installed according to the requirements in Chapter 3 of NFPA 58, and in accordance with other national standards which may apply. Paragraph 300 lists several such codes:

(a) National Fuel Gas Code, NFPA 54 (ANSI Z 223.1)
(b) Stationary Combustion Engines and Gas Turbines, NFPA 37
(c) Mobile Home Parks, NFPA 501A (ANSI A 119.3)
(d) Mobile Homes, NFPA 501B (ANSI A119.1)
(e) Recreational Vehicles, NFPA 501C (ANSI A 119.2)
(f) Removal of Smoke and Grease-Laden Vapors from Commercial Cooking Equipment, NFPA 96
(g) Ovens and Furnaces, NFPA 86 A
(h) Incinerators and Rubbish Handling, NFPA 82
(i) Motor Craft (Pleasure and Commercial), NFPA 302
(j) Grain Elevators and Bulk Handling, NFPA 61B (Grain Dryers).

Chapter 3 deals with (1) location of containers, (2) installation of containers and regulators, (3) piping system service limitations, (4) installation of pipe, tubing, fittings, valves, hose, and hydrostatic relief valves, (5) testing piping systems, (6) equipment installation, (7) distribution and industrial LP-Gas systems, (8) LP-Gas systems in buildings or on the roofs of buildings, (9) installation of appliances, (10) ignition source control, (11) installation of LP-Gas systems on vehicles, and (12) fire protection.

Operational Aspects

Experience has shown that a large fraction of leaks and spills of LPG have involved improper filling procedures, or equipment, and also defective equipment including hoses and cylinders. Safety involves several aspects: (1) Existence of codes or regulations prescribing important items of equipment and procedures, (2) development of detailed procedures by the industry or by individual dealers to implement the codes and regulations, and (3) education and training of employees and of consumers in safe handling of LPG.

Chapter 4 of NFPA 58 titled, "LP-Gas Liquid Transfer" covers many aspects of transfer, including especially the following:

- Locations and Precautions - Liquid shall be transferred into containers only outdoors or in structures especially designed for the purpose; tank trucks unloading into storage containers shall be at least 10 feet from the container and positioned so that shut-off valves on both truck and container are readily accessible.
- Personnel - Transfer operations shall be conducted by personnel trained in proper handling and operating procedures, and at least one such person shall remain at or near the operation from the time connections are made until lines are disconnected.
- Containers to be filled - Containers shall be filled only by the owner or upon his authorization; containers shall be filled only after determination that they comply with the design, fabrication, inspection, marking and requalification provisions of NFPA 58; disposable containers shall not be refilled; containers shall comply with requirements for service or design pressure with respect to the vapor pressure of the LPG to be transferred.
- Venting - LP-Gas either liquid or vapor normally shall not be vented to atmosphere except under specified conditions.
- General Arrangement and Operation of Transfer Systems - It is recommended that transfer hoses be fitted with a shutoff valve at the discharge end, so that the hose normally contains liquid.

- Control of Ignition Sources - Internal combustion engines within 15 feet of the point of transfer shall be shut down during transfer operation, and other ignition sources such as smoking, open flames, portable electric tools, shall not be permitted.
- Quantity of LP-Gas in Containers - In order that containers will not become liquid-full at elevated temperatures due to thermal expansion of the liquid, NFPA 58 provides bases for determining container capacity, specifies maximum quantity to be put into a container and methods for verifying this quantity.

Similarly, Chapter 2 of NFPA, titled "LP-Gas Equipment and Appliances", stipulates requirements for containers; container appurtenances; piping and hose, fittings and valves; and other equipment such as pumps, compressors, vaporizers, etc. Requalification requirements for containers are specified in paragraph 2101 and paragraph 2102 and in Appendix B of NFPA 58. Hence, it appears that both hardware and major aspects of procedures are prescribed by NFPA 58.

The LPG industry has been involved in a continuous effort to promote safe practices by the development and publication of guidelines, detailed procedures, and recommended practices. The NLPGA has published an "LP-Gas Safety Handbook", which contains some 68 individual bulletins in loose-leaf notebook form, with titles identified in the following categories:(25)

Distribution Operations
Emergency Procedures
Safety Meetings
Residential
Agricultural
Industrial
Recreational
General

Selected titles which indicate the nature of these bulletins are:

"Safe Practices Around LP-Gas Installations"
"Plant Inspection Check List"
"Safety Considerations in Truck Deliveries"
"Recommended Procedures for Filling Cylinders"
"How to Control LP-Gas Leaks and Fires"

"Safe Use of LP-Gas in Industrial Trucks"

"Safe Camping with LP-Gas on Recreational Vehicles".(25)

Other efforts at educating LPG consumers and employees of LP-gas distributors include publication of articles in trade magazines (e.g., LP-Gas and Gas Industries) on pertinent topics, including accidents which have happened, specific procedures, discussions by experts on hazards and proper procedures. Examples of the latter include such titles as:

- "Colorado Fire Chief Says Dealers Face New Threats to LPG Facilities", LP-Gas, October, 1976, p 31.
- "Check Lists for Truck Maintenance", Gas Industries, September, 1976, p 8.
- "The Flaming Inferno", a story of an LPG fire at a distribution facility in Dallas, Texas, January, 1975; "How to Handle an LP-Gas Emergency"; "What Price Tragedy", description of an LP-truck accident in West Virginia and how it might have been prevented; and "The Decatur Disaster", the story of a jumbo LPG rail car explosion at Decatur, Illinois, July 19, 1974. All of these articles in LP-Gas, October, 1975.

Safety information is also provided by numerous other organizations, such as:

- A manual on safety "LP-Gas, Safe Handling and Use", published by Engineering and Safety Service, American Insurance Association, 85 John Street, New York, New York 10038, 1972, 64 p.
- A film "BLEVE", produced by and available from NFPA.
- A film "Handling LP-Gas Emergencies", also from NFPA and available also in slide-version.
- A slide series "LP-Gas Explosion, Kingman, Arizona", July 5, 1973, from NFPA.
- An "RV (Recreational Vehicle) Owners Manual Copybook", a guide for RV manufacturers in making up future owner's manuals, covering electric, LP-gas, and other systems published by Recreational Vehicle Industry Association, P. O. Box 204, Chantilly, Virginia 22021.

Research and Development

Research and development activities directed toward prevention of product releases from consumer storage have been limited mainly to some analysis of accidents to determine causes and to review of code requirements.

The National Bureau of Standards (NBS) recently investigated incidents involving injuries associated with LP gas tanks and fittings(46). Tank sizes were in the range 20 to 100 lb of gas. Information on incidents was obtained through the National Electronic Injury Surveillance System (NEISS) and the Consumer Product Safety Commission (CPSC). The NEISS system reported that 154 injuries related to LPG systems were treated at NEISS hospital emergency rooms from FY 1973 to FY 1976 (4 years). In that period, the distribution of the more frequent injuries was: thermal burns, 38 percent; lacerations, 12 percent; contusions and abrasions, 10 percent. For FY 1976, the mean severity index of LPG-related injuries was 263 as compared to the average mean severity of 101 for the product group "General Household Appliances". Examples of severity values are shown in Table 3 which is reproduced from Reference 46.

NBS also has reviewed 31 in-depth investigations done by CPSC and summarized the incidents as in Table 4. It is apparent that leakage from tanks or fittings is the primary hazard (20 out of 31 incidents investigated). NBS also reviewed the standards relevant to the safety of LP gas containers and concluded from its analysis of the strength of LPG containers that both DOT and ASME containers should withstand the vapor pressure even at high temperatures (up to at least 38 C), if the container is not corroded or otherwise structurally weakened. NBS also concluded that, generally, code requirements for appurtenances (relief valves, regulators, shut off valves, plugs, level gages, and pressure gages) appear to be satisfactory. However, they questioned the requirements for the pressure settings of relief valves on ASME tanks, which can result in relief valves opening (for propane) at a temperature as low as 43 C (110 F); such temperatures are not uncommon in parts of the U.S. NBS also questions the standards for requalification of cylinders, particularly by the method of visual inspection, which can be quite subjective.

TABLE 3. MEAN SEVERITY*

Severity Category	Examples of Injuries in Each Category	Severity Value*
1	Mild injuries to small areas, for example, sprained foot	10
2	Contusion to lower trunk; dislocated arm, hand puncture, non-hospitalized poisoning	12
3	Arm fracture, sprained neck	17
4	Finger crushing, head laceration, punctured eye	31
5	Concussion, fractured neck, ingested foreign object	81
6	Amputation, anoxia, arm crushing, hospitalized poisoning	340
7	All hospitalized category 6's	2,516
8	All deaths	2,516

* Incomplete or otherwise not acceptable data are assigned a severity value of 0 and are not included in calculations of mean severity.

TABLE 4. SUMMARY OF LP GAS CONTAINER INCIDENTS

Type of Incident	Reported Cause	Number of Cases
Explosion	Gas leak from tank; ignition by spark or flame	7
Explosion	Gas leak from fuel line; ignition by spark or flame	7
Explosion	Gas leak from unknown source; ignition by spark or flame	6
Explosion	Overpressurization; rusted container; no safety relief valve	1
Explosion	Undetermined	1
Inhalation of gas fumes	Leak; no explosion	1
Other incidents not involving defective containers or fittings		8
	Total	31

NBS concluded that "there may be a significant risk of serious accidents associated with the use of LP gas containers", and cited data indicating that explosions were responsible for most of the injuries and deaths. Further, leakage was reported to be the primary cause of explosions. They note as important possible causes of accidents:

- Faulty requalification of cylinders, particularly by visual inspection (as noted above)
- The low setting of start-to-discharge of ASME cylinders
- Poor installation and maintenance.

It was emphasized that detection and immediate reporting of leaks to qualified service personnel would avoid many accidents. The addition of odorant is ineffective in many instances; more positive means of leak detection and education of consumers would be helpful.

RELEASE CONTROL

If and when LPG is spilled, for whatever reason, it is important that the quantity of spill be as small as possible and that the potential hazards be controlled. Thus release control implies design and planning aspects which will facilitate the limitation of the quantity of spills, and implies also development of procedures, training programs, and equipment to deal with the hazards after spills occur. All of these activities involve designers, constructors, installers, owner/operators, regulators, and even to some extent, the public, especially those people who live near pipeline rights-of-way or near LPG storage. The status of release control in each area is described below.

Pipeline Transportation

Because of the fact that a pipeline can fail at any point along its length, it is more likely to be discovered by people other than pipeline company personnel and to affect anyone who happens to be near the break at the time. These may include residents near the right-of-way, travelers on nearby roads, farmers or others operating machinery, etc. Accident histories indicate that people can become engulfed in a flammable vapor cloud without recognizing the danger, and others are injured because their own activity has broken a pipeline (third party damage). In any case, control of the quantity of spill depends on several factors:

- Early detection of leak or break
- Shut down time of pipeline section
- Shut down time of pump stations
- Quantity of liquid between block valves.

The last item - the quantity of liquid between block valves is, of course, determined during design and construction of the pipeline, and is also a matter of regulation, as discussed earlier.(49) From the safety point of view, it is obviously desirable for the block valves to be spaced close together.

In a survey of LPG and NH_3 pipeline operators, it was reported that almost all pipelines have both automatic and remote shut down capabilities for the pump stations, and that pump stations can be shut down in 2 to 4 minutes either automatically or remotely.(10) (The local automatic shut down capability protects the primary pumps from damage and prevents the overpressuring of pump station and trunk line piping.) In this connection, the survey posed a question to operators concerning their policy regarding continued pumping of LPG or other hazardous liquid when a failure of significant magnitude exists at a known location on the right-of-way. All answers to the question were that the system would be shut down and repairs made, with qualification by only one operator: this pipeline company, which batches propane, indicated that it would continue to pump providing the leakage was small and the site isolated, and the pumping would continue until a less volatile product was across the site of the leak. Responses indicated generally that emergency procedures require shutting down up-stream pump stations as soon as possible, diverting or stopping the upstream flow, while continuing to pump on the downstream side of the leak as long as possible.(10)

The time required to shut down a pipeline section, i.e., to close the block valves, depends on whether they can be operated remotely or manually. Manual operation requires that personnel go to the valve, which may require trips of many miles, sometimes over back roads or in rough country. Typically these trips require appreciable time, up to 2 hours, or even more. Unfortunately also, the vast majority (>80 percent) of block valves on LPG pipelines are manually operated;(10) however, recent proposed rulemaking regarding block valves includes provisions to limit their spacing in critical areas and to require that they be automatically or remotely operable.(50) Until these proposed rules become final rules, and pipeline companies have an opportunity to upgrade the pipelines by installing more valves within the specified spacing limits and by making more valves remotely operable, times required to block pipeline sections after breaks will continue to be a matter of up to a few hours.

Early detection of a leak or a break could be accomplished by means of pressure or flow transducers closely spaced along the pipeline; however, at present such equipment is limited almost entirely to pump stations. Presently, shut-down of a pipeline is based largely on the experience of the operator, using the data from pressure transducers and over/short instrumentation at stations. The latter consist of turbine or positive displacement meters, plus integration equipment. In the survey,(10) only 50 percent of operators reported having over/short equipment, and for these the intervals over which they made checks ranged from 2 minutes to monthly. Three of the most interesting systems reported were: (1) comparative metering, ±2 percent of flow on an hourly basis, (2) hourly check, leak detection to 1 percent (10 barrels per hour), and (3) average compensated flow rate with 2 minute interval checks, sensitive to 1 barrel per hour with the alarm set at 5 barrels per hour. Due to the compressibility of the product, leak detection systems cannot detect small outages. Operators commented that leak detection systems are not sensitive enough.(10)

The above discussion of release control has dealt mainly with pipeline design and system characteristics. Other aspects of hazard control with respect to accidental releases from LPG pipelines have to do more with information systems, procedures, and communication. As in any area where safety is an important concern, it is axiomatic that safety will be promoted and injuries and damage reduced if people know something specifically about the particular hazards, how to cope with them, and if detailed procedures have been developed, frequently reviewed, and released. There is abundant evidence, based on reports and analyses of LPG pipeline accidental releases, that written procedures have often been non-existent or inadequate, procedures had in some cases not been reviewed recently, personnel have been inadequately trained, and the public who reside or work near rights-of-way have not been sufficiently informed as to the product, its hazards, or how to respond to a pipeline break. Even emergency personnel such as police and fire departments in many cases have never had experience in dealing with a large conflagration typical of large pipeline breaks, and have not had training on appropriate procedures in these cases. In order to improve this state of affairs, the DOT/MTB recently published a final rule to increase the present requirements of 49 CFR 195, by aiming to establish the essentials of procedures; by requiring that normal, maintenance, and emergency procedures be incorporated in a manual; and by requiring that the manual be reviewed by MTB.(6,50) The rules also establish new requirements governing the training of carrier personnel and educating public agencies and the general public about the hazards of liquids being transported. This final rule also establishes a definition of "highly volatile liquid" as one having a vapor pressure of 40 psia or greater at 100 F; LPG is by definition a "highly volatile liquid".

Actions which may be taken for safety at the actual site of a pipeline break include, most importantly, (1) stopping traffic or otherwise limiting approach of the public to the site, taking into account the wind and possible or likely changes in wind direction, (2) if possible, the installation of temporary plugs in the pipeline to limit further the quantity of liquid which can be released, and (3) to consider intentional ignition of the vapor cloud, taking into account its present extent and weighing the damage which will be done by the combustion of the cloud and continued combustion of the pool at the break, versus the risks of allowing the cloud to continue unignited. If fire has already started, it will generally be better not to attempt extinguishment. Probably all liquid pipeline operators have plugging equipment available, or have arrangements with contractors to provide plugging service on a normal or an emergency basis; the techniques for temporarily plugging and by-passing a section which has broken or which is to be repaired are well developed and are incorporated in standard operating procedures. The procedures require excavation, welding, insertion of plugs, and laying of a by-pass pipe, all of which will normally require several hours, even if the equipment is readily available at the site.

To the authors' knowledge there has not been recently, nor is there currently, research and development (other than that already cited, e.g., References 10, 12, 13, and 21) aimed at improvements in release or hazard control technology for LPG pipeline breaks. Activity in this area has been mainly regulatory, as described above. The NFPA has recently developed, under contract to MTB, a training course titled "Handling Pipeline Transportation Emergencies", which consists of 139 slides, 2 cassette tapes, a course work guide, and a performance manual for student use.(51)

Railroad Transportation

LPG is released accidentally from tank cars mostly as a result of train derailments; accidents have also occurred in railroad yards, e.g., in humping operations. The actual mechanisms of release in most cases are rupture of a tank car by impact with other cars, rails, or other objects during derailment, or rupture due to overheating of the tank because of impingement of flames from another already-ruptured tank. A third mechanism was illustrated at Waverly, Tennessee, in February, 1978: in a derailment two LPG cars were dented and overturned, but there was no leak and no fire; about 2 days later, while preparations were being made to transfer LPG from the derailed cars, one of them ruptured, the vapor ignited, and the fireball caused 15 deaths and more than 40 injuries.(52) This rupture was caused by weakening of the tank wall in the dented area; a contributing factor was the increase of pressure in the tank in the intervening 2 days due to moderation (i.e., increased temperature) of the weather.

Frequently, when a car is punctured during derailment, the volume leak rate is limited, that is, the contents of the tank are released through a relatively small opening, such as would be made by impact of a coupler against a head. In these cases the LPG emerges from the tank with significant velocity because of the pressure in the tank; due to numerous impacts during the derailment providing ignition sources, the leaking tank is usually ignited and the flame may impinge on the shell of another tank nearby. If flames impinge on a tank below the liquid level, the liquid temperature will gradually rise, increasing the vapor pressure until eventually (perhaps in a few hours) the relief valve will release vapor. On the other hand, if the flames impinge on the tank above the liquid level, the temperature of the steel will increase rapidly because of poor heat transfer to the vapor, soon (within a fraction of an hour) weakening the steel so that the tank ruptures. In this latter case, the rupture usually results in separation of the tank into two "tubs" which are accelerated by the vapor pressure and rocketed distances of several or many hundreds of feet; these are called BLEVE's (Boiling Liquid Expanding Vapor Explosion), and can cause great damage, both by impact of the flying pieces of tank car and by thermal radiation from the large fire.

Control of LPG releases from tank cars after derailments consists primarily of applying water to tanks on which flames are impinging in order to avoid BLEVE's, and attempting to extinguish flames from leaking cars. This work must be done from appreciable distances because of the risk of exposure to a BLEVE, and also because of the chance that a tank not leaking nor subject to flame impingement may rupture because of damage incurred during derailment.

The NTSB recently held a public hearing and issued a report "Safety Effectiveness Evaluation" with respect to derailments and hazardous materials.(31) Several conclusions in this report pertain to release control:

- DOT 112 A/114 A tank cars still pose serious threats to local and state emergency response personnel when hazardous materials are released during a train derailment.
- Current methods of alerting emergency response personnel to the presence of hazardous materials at the scenes of railroad accidents often are unreliable, untimely, and rely upon unstructured individual actions to provide information in time to influence early response decisions.
- An adequate procedure does not exist for linking distant diagnostic experts on hazardous materials to on-scene emergency personnel. Such linkage would be more responsive to immediate decision making needs than existing procedures based on manuals, training, or computer readouts.
- Effective channels need to be established for communication of post accident safety lessons to all emergency response personnel.
- A full hazardous materials emergency response system documenting emergency response alternatives, information needs of emergency personnel at risk, and coordination of all Federal efforts in railroad emergencies is not operational.
- DOT's accident data collection programs for train derailments and hazardous materials provide a limited capability for accident prevention research and countermeasure development.

With regard to information systems which have been used (although not universally) for emergencies, the railroads themselves have used several techniques. First, Part 172 of the regulations requires that the shipper include the proper shipping name, the class and other describers on the shipping papers. Also, the train crew must have a document indicating the position in the train of each placarded car containing a hazardous material, and a member of the train crew must have a copy of the waybills of the hazardous materials being transported. MTB and FRA regulations do not require that railroads have an emergency response preparedness capability. However, most major railroads have developed or are developing their own systems, such as accelerated use of the AAR's Bureau of Explosives Standard Transportation Commodity Codes, which are computerized and printed out for each train's consist. These printouts include emergency actions appropriate for each hazardous material on the train. Other techniques used by some railroads include coordination with local officials along rights-of-way, use of specially denoted hazardous materials trains, and special railroad hazardous materials teams. However, the NTSB reports, there have been informational difficulties, such as (1) not obtaining prompt notification from railroads of an accident, (2) only one copy of the shipping papers is inadequate, and (3) emergency manuals not located on trains.(31)

The NFPA recently developed an audiovisual training package "Transportation BLEVE's--Causes, Effects, Guidelines" consisting of 140 color slides, cassette tape, an instructor's guide, and a student workbook.(53)

Truck Transportation

LPG truck accidents occur mainly in three situations: (1) in loading/unloading operations, (2) in repair garages, and (3) in collisions or overturns in transit. Regarding accidents involving LPG in repair garages, Section 65 of NFPA 58 requires that LPG be removed from a vehicle and that the tank be purged before moving the vehicle into a public garage for parking or for repair; if the garage is owned by the vehicle operator, the vehicle may be moved into the garage without removing the LPG if the provisions of Chapter 7, NFPA 58 are followed. Chapter 7 provides for proper construction, ventilation, and heating of structures housing LP-gas systems. Construction requirements include use of non-combustible materials for floors, ceilings, and wall materials, and that the floor shall not be below grade. The structure shall be ventilated utilizing air inlets and outlets arranged to provide air movement across the floor as uniformly as possible, at specified rates, and outlets shall discharge at least five feet away from any other opening into the garage or any other structure. Heating shall be by hot water or steam radiation or other heating transfer medium with the source remotely located.

It appears that adherence to these regulations would prevent LPG accidents in garages. Reported accidents in garages have all involved public garages where the LPG had not been removed.(35)

Accidents during loading or unloading of LPG can involve any of a gamut of human errors and equipment failures or malfunctions. These will often involve releases at relatively small rates, sometimes with fire immediately, sometimes not. The NLPGA has published bulletins which offer guidance on controlling such releases:

- "How to Control LP-Gas Leaks and Fires"(54)
- "How to Stage LP-Gas Fire Control Demonstrations"(55)
- "How to Handle Small LP-Gas Fires With Portable Fire Extinguishers"(56).

These bulletins describe basic precautions in approaching a leak or a fire, when and how to extinguish a fire, protection of a tank from radiation by water spray (to avoid a BLEVE), policing the area, etc. The bulletins are applicable generally to releases from trucks during loading or unloading, or from piping connecting the truck tank to storage, or from the storage tank.

If a truck tank has an accident on a highway which results in leakage, as contrasted to a major rupture and large spill, the same procedures referred to above in connection with releases in loading/unloading operations are applicable.

In any case of leakage or fire at or near a truck tank, there is the possibility of a BLEVE, as with rail tank cars or with stationary tanks, and the NFPA slide-cassette package on Transportation BLEVE's should be applicable and useful.(53)

Other than the educational and procedural packages prepared by the NLPGA and the NFPA, the authors were unable to identify any recent or current research or development efforts directed toward control of LPG releases in trucking.

Consumer Storage

Attention here is restricted to that part of a consumer's LPG system containing liquid, that is, releases from appliances or from the vapor piping beyond the regulator are excluded from consideration. Causes of spills from consumer storage, as noted earlier, include a large fraction from human error, resulting from insufficient awareness of the hazards of LPG, lack of communication, etc.; corrosion of buried tanks or liquid lines; settlement of foundations; non-standard equipment; installation not according to code; damage by vehicles; leakage during LPG transfer from truck (covered in previous section); failure of pressure regulator; leakage through heat exchangers of butane systems; improper handling of cylinders and portable tanks; etc.

Present methods of control of releases of LPG from consumer storage are generally very similar to those already discussed under Truck Transportation. Probably the first action to be taken, at least for relatively small leaks, is to report the suspected leak to qualified service personnel, who can then determine the exact cause or location of the leak and correct the problem.(46) A bulletin is available from NLPGA dealing specifically with procedures for finding leaks in LP-gas piping systems.(57) For large leaks which obviously pose immediate and serious danger, the procedures described in the NLPGA bulletins should be applicable.(54-56) These procedures would generally involve these precautions:

- If possible, shut off the source of LPG to the leak
- If there is fire at the leak, do not attempt to extinguish until the source has been shut off
- Evacuate people from the general area downwind from the leak where there is risk of flammable mixtures
- Approach the leak or fire from the upwind side (for purposes of attempting to shut off or to extinguish fire).

These precautions are presented more fully in the bulletins. NLPGA has prepared a bulletin also for multiple LP-gas customers: "A Guide for Developing Emergency Procedures for Multiple LP-Gas Customers Using a Common Source of Supply".(58)

Research or development projects or reports dealing with improvements in the technology of release control for consumer storage have not been discovered.

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REPORT W

Ammonia: An Introductory Assessment of Safety and Environmental Control Information

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CONTENTS

SUMMARY

The Government and the ammonia industry are addressing safety aspects of handling, storing, transporting and using ammonia. Agencies involved in ammonia spill research include: the U.S. Coast Guard, Federal Railroad Administration, DOE, and Fertilizer Institute. The use of ammonia is expected to increase in the future, both in conventional and in new applications. The increasing use of ammonia may result in more emissions and more frequent accidents. The purpose of this report is to provide appropriate background information and a basis for the ammonia assessment study being performed by PNL.

Literature pertaining to the production, storage, transportation, and use of ammonia is reviewed. This report also describes ammonia properties, potential hazards, production methods, accident reports, regulations, and control techniques. Finally potential research and development needs are identified in the area of ammonia, safety and environmental control that need to be considered in more detail as part of the PNL assessment study.

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1.0 INTRODUCTION

Ammonia is a natural part of the nitrogen cycle and, as such, life cannot exist without it; however, in massive doses, it is hazardous to all forms of life. It is easily assimilated into the environment and, once dispersed, does not present any significant ecological problems. Ammonia readily evaporates and is also very soluble in water under ambient conditions. The vapor, although generally less dense than air, is often detected at considerable distances from accidental spills. In water, it greatly increases the pH and the temperature and can endanger aquatic life (Harsh, 1978).

To ensure adequate protection of man and the environment in the transportation of energy materials, it is necessary to understand the safety and potential environmental effects of the shipment of energy materials, both in normal transportation and under accident conditions. Interest by both the government and the ammonia industry in the safety aspects of handling, storing, transporting, and using ammonia has led to the ongoing assessment of ammonia hazards. Some agencies involved in ammonia spill research include the United States Coast Guard, the Federal Railroad Administration, and the Department of Energy (DOE), as well as the Fertilizer Institute. The objectives of these spill studies, particularly in the DOE, are to: 1) determine the dispersion behavior of ammonia releases, 2) improve models describing this behavior, 3) provide experimental data on the extent of the hazard posed by ammonia vapors, and 4) assess and recommend control and mitigation measures to improve safety. The size and shape of the vapor cloud, ammonia concentration profiles, and vapor cloud buoyancy are some of the characteristics that will be described as well as the effects attributable to varying release and weather conditions.

The basic concerns associated with ammonia have been the environmental and safety aspects of production, transportation, storage, and use; including the health consequences of exposure and the possibilities of explosions and fire. The use of ammonia is expected to increase in the future, both in conventional and in new applications. The expanded use of ammonia as, for example, a fuel, (direct burning or hydrogen storage medium) a heat-transfer medium in power plant cooling systems, a coal-processing solvent, an agent in stack gas cleaning, or as a fertilizer in the biomass production of ethanol may result in more regular emissions of ammonia and more frequent accidents. Before usage is substantially increased, additional research may be required on such issues as atmospheric chemistry interactions, and the suitability of current control measures and corrosion prevention techniques. The ongoing ammonia research of the fertilizer industry will contribute significantly to the assessment of environmental and safety issues.

The purpose of this report is to provide appropriate background information for planning a more complete assessment study. The literature pertaining to the production, storage, transportation, and use of ammonia is reviewed along with safety and environmental control concerns. These concerns are associated with a potential increased use of ammonia directly as an energy material or possible increased transport if imported ammonia displaces domestic production to free natural gas feedstocks for alternative energy uses. This report describes the properties, potential hazards, production methods, accident reports, regulations, and control techniques for ammonia and provides a foundation for identifying and describing environmental and safety needs for research and development.

An assessment report on the medical and biological effects of ammonia prepared by the National Research Council (1979) was a significant resource for this study. The National Research Council (1979) report is recommended for background reading although its assessment objectives differ from those of the LGF Safety and Environmental Control Assessment Program.

This report is divided into six sections with supportive appendices. The appendices describe ammonia spills, conversions for units commonly used in ammonia studies, and a reproduction of research recommendations provided in the National Research Council report.

The extensive use of ammonia in energy-related applications could cause several new concerns in addition to those associated with the current widespread use of ammonia as a fertilizer. Some impacts of increased ammonia usage and potentially more spills are briefly summarized below:

1. An increased use of ammonia could present a greater potential for accidents and large spills, especially during bulk transportation. There is very little experimental data to assess the nature of such spills, and the accuracy of available prediction methods is also uncertain. For example, whereas hundreds of cubic meters of ammonia may be risked in transporting a shipment, the largest controlled experimental spills on water to date are approximately 0.2 m^3. The potential behavior and consequences of large-scale spills of ammonia are, at this point, uncertain. Field tests simulating large-scale spills are needed, and data from these tests should be used to confirm existing models and scale relationships or to develop improved analytical models.

2. Ammonia and its oxidation products may perturb the atmospheric nitrogen cycle, possibly influencing acid precipitation problems. The increased energy use of ammonia as a fuel may impact the atmospheric levels of ammonia and oxides of nitrogen. Leakage and incomplete combustion are the sources of atmospheric ammonia while the oxides of nitrogen in the atmosphere are by-products of combustion.

3. Progress in the control of stress-corrosion cracking of system components should be reviewed. The use of trace amounts of water in ammonia may be very effective as corrosion inhibitor for some materials during bulk transportation and storage, but it may not be an adequate control in all uses since ammonia and water are also corrosive to some materials.

4. Ammonia, when stored as a refrigerated liquid, poses handling and storage problems compared to other common energy materials. Distribution personnel and users could be exposed to objectionable, and possibly harmful, doses of ammonia vapor.

5. Current spill control methods may be inadequate for the small-scale user. The methods that seem suitable for controlling large-scale spills, e.g., dikes around storage tanks, are unsuitable for the small spills, which cause injuries and could become a more frequent hazard if ammonia use were increased.

6. The procedures for responding to accidental spills at ammonia facilities and along transportation routes should be reviewed.

7. Ammonia has a lower heating value ($\sim$50%) than gasoline and hence vehicles fueled by ammonia would have to carry larger volumes to have the same travel range. A comprehensive risk assessment may be required to determine whether the increased fuel capacity would significantly change the level of risk to the fuel users.

2.0 PRODUCTION, STORAGE, TRANSPORTATION, AND USE OF AMMONIA

The major uses of ammonia are for fertilizer and associated products. In 1976, 15.2 million metric tons of synthetic anhydrous ammonia were produced in the United States (Rawlings and Reznik 1977). Approximately 80% of this ammonia was used as a direct application fertilizer and in the production of other fertilizer products such as urea, ammonium nitrate, and ammonium phosphates. The remaining ammonia was used to manufacture nonfertilizer materials such as ammonium nitrate for explosives, urea for feeds and resins, nitric acid, acrylonitrile, and various amines (Kirk-Othmer 1978).

2.1 AMMONIA PRODUCTION

Ammonia is produced by reacting nitrogen taken from air with hydrogen. The hydrogen is obtained from: 1) natural gas, 2) petroleum, 3) coal, 4) chemical operations by-products, or 5) electrolysis. In the United States, 98% of the synthetic ammonia is produced by steam reforming natural gas to produce hydrogen. The remaining 2% is produced using hydrogen from electrolysis cells in chlorine/caustic soda plants. There are six major production steps when natural gas is used as a feedstock: 1) natural gas desulfurization, 2) catalytic steam reforming to produce hydrogen, 3) a carbon monoxide shift to produce more hydrogen, 4) carbon dioxide removal, 5) methanation to convert residual carbon dioxide to methane, and 6) ammonia synthesis. The first, third, fourth, and fifth steps are designed to remove impurities such as sulfur, CO, CO_2, and water from the feedstock, hydrogen, and synthesis gas streams. In the second step, hydrogen is manufactured and nitrogen is introduced into the process. The sixth step produces anhydrous ammonia from the synthesis gas. Since the second step is an endothermic reaction, additional energy is required to generate process steam and to complete the reforming reaction. Approximately 60 percent of the natural gas requirements are for feedstock, 35 percent for process requirements (reformer), and 5 percent for fuel use as required (steam generation). Many plants have had to switch to No. 2 fuel oil for use in the place of process gas and steam generation during the winter months when natural gas supplies are curtailed (Rawlings and Reznik 1977).

2.2 AMMONIA STORAGE AND TRANSPORT

Anhydrous ammonia is ordinarily stored and handled as a refrigerated liquid (-33°C at 1 atm). In a few cases, ammonia is stored at about 2.7 atm and some of the ammonia is evaporated to keep the liquid cooled; in these cases, the vented ammonia is usually compressed and condensed or absorbed in water to make a by-product, aqua ammonia. Seasonal variations in the fertilizer market require large-capacity, single- or double-walled storage tanks on the order of 35,000 to 47,000 m^3 (9 to 12 million gal) (Kirk-Othmer 1978).

Anhydrous ammonia is normally shipped in tank trucks (23 to 30 m^3 [6000 to 7800 gal]) or railcars (up to 130 m^3 [33,800 gal]), barges, or pipelines. In the last decade, two major pipelines have been constructed: 1) the Mid-American Pipeline system going from Texas to Minnesota through Oklahoma, Kansas, Nebraska, and Iowa, and 2) the Gulf Central Pipeline system going from Louisiana to Nebraska and Indiana through Arkansas, Missouri, Illinois, and Iowa.

2.3 POTENTIAL USES OF AMMONIA

The energy-related uses of ammonia are increasing. Ammonia has potential for use as:

- a fuel;
- a heat transfer medium;
- an agent in oxides of nitrogen removal in combustion engines;
- an agent in coal gasification;
- a storage medium for hydrogen; and
- as a fertilizer for biomass production of ethanol.

Ammonia importation can also be considered in relation to energy since it has the potential of displacing domestic production which would use hydrocarbon fuels as feedstock. The fuel use option is discussed in more detail below because of its potential for wide-spread impacts. The use of ammonia as a heat transfer medium is expanding and it is currently used as a refrigerant and may be applied in future dry cooling towers, and as a heat transfer medium such as the Ocean Thermal Energy Conversion Program of DOE. Ammonia has been mentioned as an agent in NO_x scrubbing for large emission sources and in internal combustion emission reductions. The use of anhydrous ammonia as a solvent for enhancing coal reactivity for gasification has also been studied.

Ammonia is not presently in wide use as a fuel; however, it is considered a suitable substitute for hydrocarbons. The U.S. Army conducted a number of tests in conjunction with its "Energy Depot Concept" where ammonia would be produced from water using nuclear energy and used under field conditions (Grimes 1964). The use of ammonia and ammonia mixtures as fuels for internal combustion engines has been investigated in Europe.

The combustion products of ammonia in air are water and nitrogen. The heating value of ammonia is about 50% of gasoline. The stoichiometric fuel-air ratio for ammonia is 1:6.06 compared to a much leaner ratio of about 1:14.5 for gasoline. Based on equal volumes of stoichiometric fuel-air mixtures, the heat content of an ammonia-air mixture is about 80% that of the gasoline-air mixture; thus, in a reciprocating type engine, the power produced would not exceed about 80% of that produced by a gasoline and air mixture. Ammonia does however have a high octane rating (greater than 111 research octane number) permitting higher compression ratios and the use of a supercharger, both of which significantly improve performance. Ammonia's heat of vaporization is 4.4 times that of gasoline and an engine consumes 2.4 times as much ammonia as gasoline by weight for an equal output of power. Because ammonia requires 10.3 times as much heat of vaporization as gasoline, a vaporizer would be necessary if ammonia were to be used as a fuel (Cornelius 1965).

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3.0 AMMONIA IN THE ENVIRONMENT

Ammonia is a natural constituent found in the atmosphere, the soil, and waters of the earth. It plays an essential role in sustaining life and, as such, it is an integral part of the nitrogen cycle.

Ammonia does not remain inert in any phase of the environment and is not itself a major pollutant because the mechanisms for taking up ammonia are plentiful and effective. Plants and animals have active, efficient, and rapidly operating enzyme systems to trap and use ammonia. However, it is a definite industrial and agricultural hazard because: large doses from accidental spills can be hazardous to human health and the environment; under certain conditions it may burn or explode; and it is highly soluble in water where it greatly increases the pH and the temperature to the detriment of aquatic life.

3.1 AMMONIA SOURCES

More than 99.5% of atmospheric, soil, and water ammonia is produced by natural biologic processes. The ammonia produced as a result of human activities, although a minor fraction of the total, creates concentrations that are harmful to health and safety. The sources related to human activities include:

- the production of fertilizers;
- the use of fertilizers;
- the combustion of fossil fuels;
- cattle feedlots;
- the incineration of waste materials;
- refineries and petrochemical plants;
- leakage from refrigeration equipment and other operations such as electroplating, galvanizing, and printing (National Research Council 1979);
- sewage treatment.

3.2 ENVIRONMENTAL EFFECTS

Ammonia reacts with a number of constituents in the atmosphere. These reactions include 1) aqueous-phase oxidation of sulfur dioxide leading to the production of ammonium sulfate aerosols, 2) heterogeneous interactions with soot particles, 3) thermal reactions with sulfur dioxide and ozone, and 4) photochemical dissociation to form amino (NH_2) and NH radicals. The oxidation of ammonia in the atmosphere and oxides of nitrogen from ammonia combustion may influence acid precipitation formation. The major constituents of acid precipitation are sulfate and nitrate ions originating from sulfur oxides and nitrogen oxides, respectively. Oxides of sulfur appear to be the major contributor to acidity in precipitation (60%) but the contribution from nitrogen oxides (40%) is increasing. Nitrogen oxides come mainly from combustion processes. The relative contribution from ammonia oxidation and generally increased ammonia usage is uncertain (National Research Council 1979).

High atmospheric concentrations of ammonia injure flowers and foliage through leaf damage, which is characterized by large, dark green, water-soaked spots that later turn brown or black (National Research Council 1979). Eventual recovery occurs in the affected green areas.

Nitrogen is present in the soil largely in the organic form. Before it is assimilated by plants, it is normally changed by microbial processes to ammonium or nitrate ions. This nitrogen is used by the plants and either consumed by animals or returned directly to the soil. The cycle of nitrogen from soil to living things and back to the soil is a rapid one (National Research Council 1979).

Ammonia occurs in freshwater from precipitation, dissolved and particulate solids in runoff and ground water, animal wastes and decomposition of organic wastes, agriculture, sewage, industry, and other sources. Ammonia dissociates in water and the ammonium ion is oxidized to form nitrites and nitrates, which are readily adsorbed on soil and sediment particles. Water with excessive amounts of ammonia are subject to massive algae growth. Ammonia concentrations in polluted water may be high enough to be lethal to fish (National Research Council 1979).

3.3 MATERIALS EFFECTS

Ammonia corrodes a number of metals and alloys, and the corrosive effects are generally increased by the presence of water; however, trace amounts of water also act as corrosion inhibitors for other steels and alloys. Copper, tin, zinc, and their alloys corrode rapidly in the presence of ammonia at ordinary and high temperatures. The metals recommended for use in the presence of anhydrous ammonia include aluminum and its alloys, iron and steel, essentially all stainless steels, and the noble metals. Steels are generally used in ammonia and construction, but some carbon steel ammonia storage tanks have experienced severe stress-corrosion cracking, which has led to vessel failure.

The contact of ammonia with mercury leads to reaction products that are highly explosive and detonate easily (National Research Council 1979).

3.4 HUMAN HEALTH EFFECTS

People are routinely exposed to low concentrations of ammonia. In high concentrations, it irritates skin, eyes, and the mucous membranes of the upper respiratory tract and the lungs. When ingested, it strongly irritates the mouth, esophagus, and stomach. The effects of ammonia on human health can result from accidental acute toxic exposure or from chronic low concentrations in the living or working environments. Table 1 presents the physiological effects of ammonia at various concentration levels. Because of its great affinity for water, it is particularly irritating to moist skin surfaces. Liquid ammonia vaporizes rapidly when exposed to the atmosphere and will absorb heat from anything it contacts, which may lead to 'freeze burns' that are similar to regular burns on skin contact. Exposure to high concentrations may result in skin burns and/or death from respiratory injury (Kirk-Othmer 1978).

The current U.S. federal standard for atmospheric exposure to ammonia is an 8-hr time-weighted average of 50 ppm. This applies only to work place conditions; no ambient air-quality standard for ammonia exists (National Research Council 1979).

The quality criteria for unionized ammonia in water is 0.02 mg/ℓ. This level is recommended to protect freshwater aquatic life rather than human

TABLE 1. Physiological Effects of Ammonia in Air (Kirk-Othmer 1978)

Concentration, ppm by Volume	Effects
20	First perceptible odor
40	A few individuals may suffer slight eye irritation
100	Noticeable irritation of eyes and nasal passages, after a few minutes exposure
400	Severe irritation of the throat, nasal passages, and upper respiratory tract
700	Severe eye irritation; no permanent effect if the exposure is limited to less than 1/2 hr
1700	Serious coughing, bronchial spasms, less than 1/2 hr of exposure may be fatal
5000	Serious edema, strangulation, asphyxia; fatal almost immediately

health since the odor associated with high levels of ammonia in water make it objectionable for human use thus eliminating the need for a health effects standard.

4.0 SPILL HAZARD ASSESSMENT

A review of accidental ammonia spills (Section 4.1) indicates that most incidents causing injury involve small quantities related to agricultural use and the impacts are limited both spatially and in consequences. Larger scale accidental spills related to production, storage, and transportation have occurred and indicate a need for hazard assessment for spills on water (Section 4.2) and land (Section 4.3).

4.1 ACCIDENTAL SPILLS

Accidents in a range of sizes have occurred in production, storage, transportation, and utilization of ammonia. The increased production of ammonia may increase the frequency and magnitude of such spills if adequate environmental and safety precautions are not taken. This section summarizes the current experiences with spills; more extensive details are presented in Appendix A.

Material failures in reformers and/or piping are the major causes of accidents in production. Corrosion is the principal cause for metal failures. So far rapid plant shutdown capabilities have limited the consequences of ammonia spills in their cases.

There are three main sources of leaks and spills in storage operations: 1) pin holes in tanks, 2) spills while the tanks are being filled, and 3) brittle fracture of metal storage tanks. Of these, the last two pose the most serious health and safety concern. One brittle fracture accident in South Africa killed 18 people and many others required medical treatment.

Hundreds of spills have been reported during the transportation of ammonia. Barges, trains, ships, trucks, and pipelines have been involved, although most of the major spills have been associated with trucks and trains. As a result of one truck spill in 1979, five people were killed and almost 200 required medical treatment. In a single train derailment in 1969, ammonia fumes killed five people and over fifty required medical treatment (see Appendix A).

A large number of accidents from the farm use of ammonia have been reported. Local doctors in agricultural areas routinely see the results of human exposure to ammonia; however, statistics on such exposures appear to be unobtainable. There are, undoubtedly, many small accidents that are not reported where people receive skin and respiratory irritation. The few deaths from the agricultural use of ammonia have been caused by massive exposures to ammonia.

4.2 ASSESSMENTS OF SPILLS ON WATER

The Federal Water Pollution Control Act, as amended in 1972, focused attention on hazardous materials spills on water. As a result, in the last few years, work has been done to develop analytical methods of modeling and assessing the potential impacts of hazardous material spills. Ammonia is a hazardous material even though it is a very familiar one in all phases of the environment. The large-scale transportation of ammonia and its potentially harmful impact on living things in the event of an accident require that it be thoroughly studied. Water spills are important because of both the generation of toxic vapors for airborne transport and its toxic effects as it is dispersed in water.

The impacts of spilled ammonia depend on environmental conditions, i.e., land, water, ambient temperature, weather, and other factors. Very few controlled spill experiments have been conducted. The largest test was an instantaneous spill of 0.19 m^3 (50 gal) of anhydrous ammonia on a small lake for the U.S. Coast Guard (Raj et al. 1974). Most of the other available test data on controlled ammonia spills come from very small laboratory-type experiments where a few milliliters of ammonia were released in or on a known quantity of water.

The major findings of the spill tests on water for the U.S. Coast Guard (Raj, Hagopian, and Kalelkar 1974) follow:

1) For the larger surface spills (0.19 m^3 (50 gal) range), the partition ratio is between 0.5 and 0.6.(a)

2) For submerged releases, very little vapor enters the atmosphere when the discharge depth is greater than 10 times the outlet diameter of the leak.

(a)The partition ratio indicates the fraction of the total ammonia spill volume that remains dissolved in the water.

3) In surface spills, a rapid reaction occurs and results in the liberation of a vapor cloud, possibly containing a fraction of aerosols though not a large enough fraction to make the density of the cloud greater than that of air.

4) The vapor cloud formed from ammonia spills on water is very buoyant and rises as it travels downwind.

5) The ammonium hydroxide formed in a surface spill remains close to the top of the water surface and spreads radially at about 0.06 m s^{-1} (0.2 ft s^{-1}).

Analytical and experimental work in the dispersion of ammonia as NH_4OH has also been limited. Models for the spread of toxic substances have been presented or reviewed by Raj and Hagopian (1974), Jensen (1970), Benedict (1978), Tsahalis (1978), and others, but insufficient information is available for the models to be completely formulated or validated. Raj and Hagopian (1974) note difficulties in concurrently predicting both ammonia's spread and the associated temperature increases when comparing the results with spill tests of different scales.

4.3 ASSESSMENT OF SPILLS ON LAND

Analytical work in the United Kingdom (Kaiser and Walker 1978) to assess the dispersion of anhydrous ammonia from pressurized containers on land indicated that:

1) a cold ammonia/air mixture is formed;

2) the density of the cloud will most likely be greater than that of the surrounding air;

3) gravity causes the clouds to slump near the ground and spread laterally; and

4) wind speed is a critical parameter in determining whether the dispersing ammonia cloud will lift off the surface.

In further studies, Haddock and Williams (1978) present an analytical study of the ammonia density versus air density relationships expected as a result of a pressurized or refrigerated ammonia release. For this study, they considered air/ammonia chemistry, droplet formation and interactions, coagulation, and precipitation, and atmospheric moisture.

5.0 SAFETY STANDARDS AND ENVIRONMENTAL CONTROL PROCEDURES

The demand for ammonia will continue to increase, due to its use as fertilizer, and the anticipated expansion of other uses. Additional environmental and safety standards and control procedures may be required in the production, storage, transportation, and use of ammonia to reduce the frequency and severity of future spills.

Many techniques have been proposed for controlling ammonia spills, which depend on the nature and conditions of the spill. Some methods which have been mentioned include:

1) spraying water on leaking valves, pipes and vessels;
2) constraining leaks or spills from storage tanks with dikes (Brown 1978);
3) using wet foams to reduce evaporation and flammability (Clark 1975);
4) absorbing ammonia with sorbents such as activated carbon, zeolites, and ion exchangers; and
5) neutralizing the ammonia in water spills with acids such as hydrochloric, phosphoric and/or sulfuric acid (Bauer et al. 1976).

5.1 SAFETY IN PRODUCTION

In production, safety-related controls are primarily required because of equipment failures in the primary and secondary reformers, compressors, and turbines. The reformers usually fail when the catalyst is poisoned and/or the tubes overheat, leading to a material failure. Flange fires are a problem when flammable process gas leaks out of hot valves and fittings into the air. These fires may be precluded by proper scheduled maintenance and the use of flange guards (Sawyer, Williams, and Clegg 1971). Stress-corrosion cracking(a) of pipes, transfer lines, and vessels is also an occasional problem in production plants.

(a)Stress-corrosion cracking is the preferential corrosion on a molecular level in a line or crack in an area of stress (Clark and Crackness 1976).

Programs to minimize these production problems are the responsibility of the design engineer, the engineer in construction and maintenance, and the engineer operating the plant. Plant design, construction methods, and operation conditions all impact the production safety problems. While it is essential to inspect for developing cracks, an inspection program cannot overcome errors in design and construction. However, many potentially serious failures can be forestalled by adequate operator training to insure that units are operated properly.

5.2 SAFETY IN STORAGE

The storage of large quantities of ammonia poses several potential problems including:

1) stress-corrosion cracking in the storage tanks because of improper materials and welding techniques (Clark and Cracknell, 1976),
2) settling or heaving of tank floors due to poor construction methods and materials (Esrig, Ahmad, and Mayo 1974), and
3) spills during ammonia transfers (National Research Council 1979).

Dikes can probably be used to contain spills from ruptured tanks and are either required or a standard practice in the storage of petroleum products and other hazardous liquids. More expensive double-wall construction or other alternative designs might also be considered to reduce hazards, but, whatever the design or method, the principle of containing a natural or accidental release of ammonia into the environment, where it would flow to the nearest water-course, should be considered. Vapor formation occurs simultaneously with the release of the liquid so the proximity of storage to surrounding residential areas should be considered. Safe distance figures are found in the American National Standard K61.1-1972, subsection 2.5, paragraph 2.5.4, "Location of Containers." The container locations listed in Table 2 comply with K61.1-1972.

The pressure tanks used for the storage and delivery of ammonia to the consumer and farmer may vary in capacity from tens of liters to thousands of

TABLE 2. Safe Location of Ammonia Containers[(a)]

Nominal Capacity of Container, m^3 (gal)	Minimum Distance, m (ft), from the Container to: Line of Adjoining Property that may be Built on Highways and Main Line of Railroad	Place of Public Assembly	Institution Occupancy
Over 1.9 to 7.6 (Over 500 to 2,000)	7.6 (25)	46 (150)	76 (250)
Over 7.6 to 114 (Over 2,000 to 30,000)	15 (50)	91 (300)	152 (500)
Over 114 to 379 (Over 30,000 to 100,000)	15 (50)	137 (450)	229 (750)
Over 379 (Over 100,000)	15 (50)	183 (600)	305 (1,000)

(a) Data from American National Standard K61.1-1972, paragraph 2.5.4.

liters and are manufactured with a design pressure (working pressure) of about 1,720 kPa (250 psig) (the American Society of Mechanical Engineers (ASME) construction code for unfired pressure vessels). Although these tanks are designed for a maximum working pressure of about 1,720 kPa (250 psig), they are hydrostatically tested at the time of manufacture to about 1.5 times the design pressure, or about 2,580 kPa (375 psig). The internal pressures of stored anhydrous ammonia in these tanks may vary according to the temperature.

The tanks are also to be equipped with pressure-relief valves (American National Standard K61.1-1972, subsection 2.9, "Safety Relief Devices") to direct the vented material to the atmosphere upward and away from the container. The recommended relief device pressures are given in Table 3.

American National Standard K61.1-1972, "Safety Requirements for the Storage and Handling of Anhydrous Ammonia," a consensus standard, also covers many other topics, including first aid and personal protection equipment and their use, equipment identification and marking, operational procedures, location of containers, various kinds of storage containers (refrigerated and portable), transport systems mounted on trucks, and farm applications.

TABLE 3. Start-to-Discharge Pressures of Relief Devices of Ammonia Containers[(a)]

Containers	Relief Pressure, % of Container Design Pressure Minimum	 Maximum
ASME-U-68, U-69	100%	125%
ASME-U-200, U-201	95%	100%
ASME 1952, 1956, 1959, 1962, 1965, 1968, or 1971	95%	100%
API-ASME	95%	100%
U.S. Coast Guard	as required by USCG regulations	
DOT	as required by DOT regulations	

(a) Data from American National Standard K61.1-1972, paragraph 2.9.2.

The Code of Federal Regulations (CFR 29-1910:111) established requirements for the storage and handling of anhydrous ammonia. Section (a), (1) "General Scope," states that this standard is intended to apply to the design, construction, location, installation, and operation of anhydrous ammonia storage systems but not to manufacturing or refrigeration plants where ammonia is used as a refrigerant. Section (b), "Basic Rules," deals with such items as the approval of equipment and systems; requirements for construction; the original testing and requalification of nonrefrigerated containers; nonrefrigerated and refrigerated container marking; container instrumentation; piping, tubing, and fittings; hose specifications; safety relief devices; container charging; tank car unloading points and operations; liquid-level gauging devices; container painting; and electric equipment and wiring. Subsection (10) of this portion of the requirements mentions personnel training and specifies personnel protective devices including first aid water supplies for permanent and transport vehicles, excluding farm applicators. (Stationary storage installations must have an easily accessible shower or a 0.2 m^3 (50 gal) drum of water available, and each vehicle transporting ammonia in bulk must have a container carrying 0.02 m^3 (5 gal) of water and a full-face mask.) Section (c) describes systems hat use stationary nonrefrigerated storage containers; Section (d), refrigerated storage systems; Section (e), systems that use portable DOT containers; Section (f) tank motor vehicles for the transportation of ammonia; Section (g), systems mounted on farm vehicles other than for the application of ammonia; and Section (h), systems mounted on farm vehicles for the application of ammonia. In these sections, specific points and requirements are made concerning the safe handling and movement of ammonia to minimize or eliminate the hazards related to liquid or gaseous ammonia (NRC 1979).

5.3 SAFETY IN TRANSPORTATION

The potential problems faced in the transportation of anhydrous ammonia include primarily the accidental rupture of containers during loading, unloading, and transit. Transportation-related ammonia spills have been largely uncontrolled due to the accident locations. Cases have been recorded where spilled ammonia was contained with peat moss (an ammonia sorbant) dams and neutralized with hydrochloric acid.

The Department of Transportation requires MC-330 and MC-331 cargo tanks to be constructed of quenched and tempered steel and requires that the anhydrous ammonia contain a minimum of 0.2% by weight of water to inhibit stress-corrosion cracking. The Interstate Commerce Commission has this same requirement for ammonia shipped by pipeline.

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6.0 CONCLUSIONS

The accidental release of substantial quantities of ammonia has occurred a number of times, as exemplified in Appendix A. The consequences of such releases can be serious concerns and may increase in magnitude if substantially greater quantities of ammonia are produced and used in energy applications. Since gaps currently exist in the understanding of ammonia spills, their effects and consequences need to be assessed in a detailed manner. This should involve the further development of analytical models supported by data from field experiments. Spills of ammonia in or on water warrant particular attention. To date, all experiments have been limited to 0.2 m^3 (50 gal) spills; these data are not adequate to extrapolate and infer the consequences of larger spills. Improved analytical models are needed to describe the partitioning of ammonia in water and air and its subsequent transport in the environment.

The major areas of research recommendations presented by the National Research Council (Appendix C) are oriented toward 1) the effects of ammonia in trace amounts on the nitrogen cycle, 2) the transport and removal of ammonia in the ground/water/atmosphere system, 3) identifying new ammonia production methods and feedstocks, and 4) a further examination of toxicology and health effects. The safety aspects of ammonia use, including fire hazards, need to be assessed. The following topics are recommended for further assessment:

1) the sensitivity of ecosystems to increases in the environmental ammonia levels that are associated with increased routine and accidental ammonia releases;
2) the fire hazards and control potential associated with ammonia use;
3) methods to predict ammonia transport and diffusion in water as NH_3 and NH_4OH;
4) vapor generation and dispersion of ammonia in air;
5) stress-corrosion cracking in ammonia facilities and the use of corrosion inhibitors;
6) ammonia handling methods and controls, particularly for small-scale users; and
7) response procedures for accidental ammonia spills.

The assessment of these topics as part of the DOE Ammonia Safety and Environmental Control Assessment Program would enlarge the information base for planning program activities that address the knowledge gaps in ammonia safety and environmental control.

APPENDIX A

ACCIDENTAL SPILLS

APPENDIX A

ACCIDENTAL SPILLS

Accidental spills of ammonia occur in production, storage, transportation and use. This section includes summary descriptions of some of these spills.

PRODUCTION

In November 1975, a metal failure in a high-temperature shift conversion unit occurred at the BASF A.G. plant in Rotterdam. The accident happened during restart of the 1,300 m^3/day (340,000 gal/day) plant. "Hydrogen cracking" caused the metal to fail at a weld in the converter vessel. The plant was shut down before any serious leakage of process gas occurred (Appl, Feind, and Liebe, 1976).

In May 1975, a tee in the primary-to-secondary reformer transfer line at Nipak's ammonia plant in Texas ruptured suddenly and violently. The 416 m^3/day (110,000 gal/day) plant was shut down, and no injuries resulted. The precise cause of the failure was not determined; however, it was theorized that severe erosion of the part contributed to its failure (Isabell 1976).

In January 1976, a 0.3 m (11 in.) diameter process-gas line failed at the Farmland Industries, Inc., plant in Kansas. The gas ignited causing a shock wave felt 6 miles away but no injuries were reported. The flash fire was quickly extinguished. After shutdown, the carbon steel pipe was checked and found to be only 75% of its original thickness due to carbonic acid corrosion. This results when, during the cooling of the process gas, the carbon dioxide forms carbonic acid, which attacks the carbon steel pipe. Stainless steel pipe was used as a replacement (Pebworth 1976).

In 1974, an explosion and fire occurred at the Irish Nitrogen Ltd. plant in Arklow, Ireland. Corrosion had caused the ammonia shift conversion unit to rupture. The damage was confined mainly to the conversion unit, and no one was injured (Casey 1975).

STORAGE

At the Hills Chemicals, Inc., plant in Early, Iowa, a new 52,000 m^3 (13.5 million gal) low-pressure storage tank was being filled when ammonia vapor was observed under the insulation drain. Vapor leakage was caused by two problems: 1) corrosion was occurring on the galvanized conduit mounted on the foundation, and 2) the concrete was spalling in areas near ammonia vent points. When the tank was emptied, pinhole leaks were discovered and repaired. The numerous pinholes were attributed to the construction and testing activities conducted on the tank bottom during the cold winter months (Lichtenberg 1971).

In 1970, 208 m^3 (54,000 gal) of ammonia were spilled at Gulf's refrigerated ammonia storage in Blair, Nebraska, while the tank was being filled from barges. The high-level alarm and shutdown system failed to operate and, as a result, the ammonia spilled causing a cloud that spread over the surrounding area. No residences were evacuated in town but school children were sent home and several farm residences were evacuated after they were alerted by the county sheriff through a loudspeaker from a low-flying plane. Three firemen were treated for fume inhalation but no serious injuries occurred (MacArthur 1971).

In 1973, a brittle fracture caused 65 m^3 (17,000 gal) pressure-storage tank in Natal, South Africa, to fail releasing an estimated 39 m^3 (10,000 gal) of anhydrous ammonia. The ammonia caused the deaths of 18 people. One employee, 45 m from the tank, was killed outright by the blast; 8 employees were killed by gas while attempting to escape and three others died within a few days as a direct result of having been gassed. Outside the plant fence, four people died immediately and two others died several days later. Another 65 required hospital treatment and an unknown number were treated by private doctors (Lonsdale 1974).

TRANSPORTATION

Between 1971 and 1975, 239[(a)] accidents involving transportation or transfer of anhydrous ammonia were reported to the U.S. Department of Transportation. From 1971 to April 1977, 61 of these accidents caused injury or death (NRC 1979).

Extremely small quantities of anhydrous or aqua ammonia are the predominant cause of injuries during transportation. These releases commonly result from pressure releases before a safety-valve shutoff, caused by either defective or accidentally ruptured fitting valves or by closures of the container. Usually, hospitalization is not required since injuries are usually limited to eye irritation, minor skin burns, or fume inhalation.

In 1977, a hose failed while transferring ammonia from a truck to a 76 m^3 storage tank at a farm chemical service station in Cedarville, Ohio. Water was sprayed on the hose to reduce the evaporation of ammonia; the water subsequently ran into a nearby creek. Several peat moss dams were built downstream to block the water, to lower and buffer the stream pH, and to absorb ammonia. Hydrochloric acid was then added to the stream to neutralize the effect of the ammonia. The chemicals killed all stream life within 13 kilometers of the spill; however, the hydrochloric acid neutralization and peat moss dams did reduce the impact. An after-the-fact study concluded that quicker action could have saved more of the stream and that a dam could have been built to prevent the water from going into the creek (Harsh 1978).

In 1976, a 0.05 m (2-in.) liquid transfer hose burst while a tractor-trailer was unloading at a bulk storage plant. The failure of the safety devices resulted in the discharge of 21 m^3 of anhydrous ammonia. Nine townspeople were treated for fume inhalation and released. Exposure to the fumes also hospitalized two persons who assisted in the rescue.

In another incident, which involved unloading a tank-truck in 1971 in Indiana, the driver had completed unloading, bled off the pressure, disconnected the hoses, and laid them on the ground. While capping the unloading

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(a) Data from Office of Hazardous Materials Operation, U.S. Department of Transportation, Washington, DC.

pipe, he accidentally opened the valve for the unloading line. Anhydrous ammonia between the valve and the safety valve sprayed him. He ran to a water tank and placed his head and shoulders in the water. By the time a witness ran to him, he was limp; he never regained consciousness. He was not wearing safety clothing.

In 1973, a cylinder used to service air-conditioning equipment, which contained 8.3 ℓ, was being transported in the cargo space of a half-ton van truck. The cylinder ruptured (for unknown reasons) as the truck was moving at approximately 60 mph on a freeway in Industry, California. The driver stopped the truck, opened the door, and fell out. Although he was attended by highway patrol and a fire rescue squad, he died either at the scene or on the way to the hospital.

A catastropic accident involving a truck occurred in May 1976 in Houston, Texas, when the semitrailer containing 28.5 m^3 (7,400 gal) of anhydrous ammonia overturned, due to the lateral surge of the liquid and excessive speed of the truck on a curve of a freeway overpass, and plunged 4.6 m (15 ft) to the freeway below. The truck's tank exploded and split one of the overpass support columns. A 30-m (100 ft) high cloud of ammonia developed. The absence of wind under the overpass prevented the dispersion of the gas and hampered rescue efforts. The danger persisted for approximately 2 1/2 hr. Five people died and 178 were injured from inhaling the ammonia fumes.

Two trains were involved in an accident in Glen Ellyn, Illinois, in May 1976. It was caused by a faulty outside rail of a curved track, which did not comply with federal track safety standards. The lateral force on the faulty track caused the locomotive and 27 cars of a freight train to overturn, and a second train traveling in the same direction on an adjacent track collided with the derailed train. A tank car in the second train ruptured, releasing 76 m^3 (20,000 gal) of anhydrous ammonia. The accident occurred in the early morning. Three thousand residents were evacuated and kept away for more than 16 hr. There were no deaths, and the injuries suffered by 15 people were not serious.

Anhydrous ammonia was spilled from a moving tank car of a train as it traveled over a kilometer along the track in Reese, Michigan, in April 1976. The accident occurred when a train uncoupled one of its cars onto the track where a tank car was being unloaded. The tank car coupled with the car from the train, so the conductor pulled the cutting lever then signaled the engineer. However, the cars failed to uncouple, and the discharge pipes on the tank car were pulled away, pulling the hoses apart and releasing 33 m^3 (8,600 gal) of ammonia. Local residents were evacuated and only two people were injured (NRC 1979).

In February 1969, a catastrophic train accident occurred in Crete, Nebraska. A train derailed on a curve and struck cars on a siding. A tank car was fractured by the impact and 11 m^3 (2,860 gal) of anhydrous ammonia were released. At 6:30 a.m. when the accident occurred, a temperature inversion was present with ground fog, mid-level thin scattered clouds, and no wind. Flying parts from the derailed cars and the burst tank car damaged several houses close to the railroad. The houses quickly filled with ammonia gas, forcing the residents to abandon them and try to escape. Several residents of other houses smelled the gas, left their homes, and sought shelter. The people who ventured into the vapor cloud without adequate protection were either killed or seriously injured. Five people were killed immediately by ammonia, another died later, and 53 were injured (28 of them seriously) (Phillips 1970).

The anhydrous ammonia pipeline of the Mid America Pipeline Company (MAPCO) ruptured at Conway, Kansas, in December 1973, and released 340 m^3 (88,400 gal) of anhydrous ammonia into the atmosphere. The accident was caused by the failure of a remote-controlled valve to open and relieve excessive pressure when the station at Borger, Texas, began pumping. By the time pumping was stopped, 36.6 m^3 (9,500 gal) of anhydrous ammonia had been pumped into the line but the indicator light on the console in Tulsa, Oklahoma, still showed that the valve had not opened. The 0.2 m (8-in.) pipeline ruptured under an initial pressure of at least 8.3 x 10^6 Pa (1,200 psig). At the time of the accident, the ground was covered with snow and ice, the temperature was near -7°C, the sky was clear, and the wind was at 2 to 5 ms^{-1}. The drivers of two trucks on U.S. Highway 56, within a 0.8 km (0.5 mi) of the ruptured line, were injured and hospitalized with ammonia burns to the eyes, nose, throat, and lungs. The ammonia vapor was visible 0.8 km (0.5 mi) from the leak, and invisible but very irritating to the eyes, nose, and throat for another 5.6 km (3.5 mi). Beyond that point, an ammonia odor was detectable for another 6.5 km (4 mi) but did not irritate the eyes, nose, or throat.

According to U.S. Coast Guard records from 1971 to mid-1977, few accidents or spills have occurred that involved ammonia-carrying vessels and those on record involved tank barges rather than ships. The spills mostly were from the leaky fittings, valves, or hoses used in transfers. During this period, only one catastrophic accident occurred. In October 1974, a barge containing 10,600 m^3 (2.7 million gal) of anhydrous ammonia and 5300 m^3 (1.4 million gal) of bulk urea broke from the towline during a storm, grounded, and sank off Kekur Peninsula, Baranof Island, Alaska. The entire cargo of anhydrous ammonia and urea discharged into the marine environment and the atmosphere. Some mussels and starfish died, and approximately 2.6 km^2 (1 mi^2) of forest in the immediate vicinity was laid waste by ammonia fumes, but no humans were exposed to the spill (NRC 1979).

USE

Reports of small delivery or nurse tanks overturning on the highway or accidents involving other vehicles can be found in newspapers and police records, but these accidents usually cause little danger and few injuries. In most instances, only the driver or people engaged in the rescue or cleanup were involved. Statistics on such accidents appear to be unobtainable.

In agricultural areas, local doctors have been seeing the results of on-the-farm exposure of farmers to ammonia. Reports of accidental exposure to a minimal amounts of ammonia (a spray of liquid, ruptured hose, leaky valve, etc.) have involved eyesight loss, respiratory problems, and skin burns.

A 40-year-old employee of an anhydrous ammonia distributing company was injured while transferring liquid from a rail car to a nurse tank. The employee was standing on the side walkway of the rail car. The nurse tank filled more rapidly than expected and, before the employee realized how full it was, the safety relief valve emitted a spray of ammonia. (This valve is designed to prevent the tank from being overfilled; it relieves at 85% of capacity to ensure that there is space for the anhydrous ammonia to expand when the temperature rises.) The victim, who was standing about 2 m above the valve, was sprayed on the face and chest. He immediately jumped to the ground and washed his face in a water tank that was on the premises for such emergencies. He was taken to a local hospital but quickly transferred to a larger hospital. Although his facial burns were not extremely serious and both eyes were unaffected, pulmonary edema and pneumonitis resulting from inhalation developed quickly as well as inflammation and edema of the upper airways. A tracheostomy was performed, and aspiration was necessary. Treatment included pressurized oxygen, aminophylline, and several antibiotics. The patient recovered gradually and was discharged after 11 days in the hospital without residual lung damage (NRC 1979).

A 17-year-old farm boy who applied fertilizer for a commercial concern was injured while transfering aqua ammonia (25% ammonia in water). He and his employer were installing a new transfer pump when the accident occurred. With the new pump in place, they started to move the liquid from the nurse tank to the applicator tank. One hose had not been tightened sufficiently and began to leak. Without shutting off the machine, the boy grasped the hose and began to rotate it to make a tight connection. As he did so, the opposite end of the hose flipped out of the applicator tank and sprayed him with several liters of aqua ammonia. He was knocked down but did not panic; he scrambled to his tractor and used his jug of water to wash his eyes. He then ran 65 m (∿200 ft) to a nearby creek and immersed himself, but he did not remove his ammonia-soaked clothing. He noted some tightness of his throat during the first few minutes after the accident. After being driven home by his employer, he removed his clothing and rested. He soon noticed, however, that he had received burns to the buttocks from contact with his clothing during the 3 km (∿2 mi) ride home. Taken to a local hospital, the victim was treated for second-degree burns and recovered completely within a few days. No eye injuries were sustained.

A 36-year-old manager of an anhydrous ammonia retail operation was injured in a farmer's field to which he had been summoned because of improperly functioning equipment. The farmer was using 3.8 m^3 (1,000 gal) nurse tank connected by direct supply to a seven-row tool bar applicator. Anhydrous ammonia runs from the nurse tank through a hose and quick-coupling device to a flow regulator on the tool bar and from there out through the individual knives into the ground. Since the coupling device had been leaking, the manager installed a new one. Leakage occurred again. When the new device was tested by opening the liquid-out valve at the supply tank and permitting ammonia to pass through the hose, the man closed the liquid-out valve and attempted to make a tighter connection by jiggling the coupler. The coupler flew apart, spraying him in the face with the anhydrous ammonia that had remained under pressure in the portion of the hose between the coupler and flow regulator. Muscle spasms in his eyelids prevented him from seeing clearly as he got away from the escaping ammonia stream. The farmer who was with him at the time took him to the rear of the nurse tank and helped him pour a 20ℓ (5 gal) emergency water supply over his face. He washed with water from a Thermos bottle while being driven 40 km (25 mi) to a doctor's office where his eyes were irrigated for several minutes. During the washing, the victim had concentrated on the left side of his face, believing that only that this was the part affected. His right eye sustained greater damage because it had also been sprayed and was somewhat neglected. Irritative conjunctivitis and superficial corneal ulceration resulted; second-degree facial burns were also sustained. Palpebral edema of the left eye developed to such magnitude that the eye swelled shut several times during the following week. Recovery took a week.

APPENDIX B

AMMONIA UNITS CONVERSIONS AND PROPERTIES

APPENDIX B

AMMONIA UNITS CONVERSIONS AND PROPERTIES

Tables B.1 and B.2 are presented to facilitate units conversions among ammonia mass/volume relationships and various pressure units. Table B.1 assumes that the density of ammonia is 0.7 g cm^{-3} at -33°C.

Table B.3 presents a list of the properties of ammonia (NH_3).

TABLE B.1. Units Conversions for Anhydrous Ammonia at -33°C

	Liters	m^3	Metric Tons	kg	Tons	Gallons
Liters	1	10^{-3}	7×10^{-4}	0.7	7.7×10^{-4}	0.26
m^3	10^3	1.43	0.7	700	0.77	260
Metric Ton	1428	1.43	1	10^3	1.10	377
Kg	1.43	1.43×10^{-3}	10^{-3}	1	1.1×10^{-3}	0.38
Ton	1299	1.3	0.91	909	1	324.7
Gallon	3.79	3.79×10^{-3}	2.65×10^{-3}	2.65	2.91×10^{-3}	1

TABLE B.2. Units Conversions for Pressure

	Atmosphere	psig	Nm^{-2}
Atmosphere	1	14.70	1.01×10^5
psig	6.8×10^{-2}	1	6.9×10^3
Pa	9.9×10^{-6}	1.45×10^{-4}	1

TABLE B.3. Properties of Ammonia

Molecular Weight	17.032
Liquid Density (-33°C; 1 atm)	682.5 kg m^{-3}
Vapor Density (-33°C; 1 atm)	0.84 kg m^{-3}
Boiling Point	-33°C (-28°F)
Flammability Limits	16 to 25%
Ignition Temperature	850°C
Heat of Vaporization (-33°C; 1 atm)	5,581 cal/mole
Special Heat at Constant Pressure (25°C)	8.523 cal/mole (°C)
Heat of Formation (25°C)	-11,040 cal/mole
Heat of Solution (25°C)	-7,290 cal/mole

APPENDIX C

NATIONAL RESEARCH COUNCIL RECOMMENDATIONS ON AMMONIA RESEARCH

APPENDIX C

NATIONAL RESEARCH COUNCIL RECOMMENDATIONS ON AMMONIA RESEARCH

The National Research Council (NRC 1979) has provided an excellent review of the medical and biological effects of ammonia, which is valuable in assessing the increased energy-related uses of ammonia. The recommendations suggested in this study are reproduced here as a contribution to this introductory report. It is fortunate that these recommendations are available for guidance even though the priorities must be modified and the recommendations supplemented to satisfy the mission of the DOE Ammonia Safety and Environmental Control Assessment Program.

10

Recommendations

It is easy to make recommendations, particularly for research. If all recommendations of all committees were given equal priority, nothing would happen. We have therefore placed our recommendations into two categories; the more urgent of these are printed in italics. The word "urgent" is used in a special sense: italicized recommendations are those of broad current importance as well as those that deal with subjects in which there is substantial public interest. In addition, italics are used for recommendations that involve important questions or uncertainties about potential health or environmental effects. The nonitalicized recommendations are not less real, but they encompass narrower subjects, and those with primary interest in them may be groups, individuals, or agencies with objectives different from those of the Environmental Protection Agency. Other broad environmental recommendations are nonitalicized because the Subcommittee feels that although the questions raised are of interest, the environmental problems addressed are of less immediate public importance.

To illustrate: sections on the nitrogen cycle and denitrification are italicized because there is at the moment a public question of whether or not fertilizer application, followed by denitrification, leads to ozone depletion. A definitive answer cannot yet be given, so relatively high priority is attached to acquiring information on the subject. However, although studies of the inflammatory response to ammonia burns of the eye are of great importance to both patient and doctor, they are of less general public interest and are perhaps better addressed by more specialized agencies.

NITROGEN CYCLE

The evaluation of the interrelationship of ammonia and ammonium relative to other components and processes in the nitrogen cycle necessitates more quantitative information on a number of processes and reactions. Particular needs are:

1. *Global figures on nitrogen fixation by all biologic and other processes in terrestrial and oceanic environments.*
2. *Estimation of the amount of ammonia produced and volatilized from tidal areas, estuaries, and marshland.*

3. *Determination of the comparative significance of nitrification and denitrification as sources of nitrous oxide on land and in the sea.*
4. *Accurate estimates of the emission, movement, and degradation of ammonia in the atmosphere.*

GENETIC MANIPULATION OF PLANTS FOR NITROGEN FIXATION

Research in genetic manipulation of plants to insert nitrogen-fixing genes should continue to be pursued actively, although success is by no means ensured. In addition, the survey of existing species should continue: some strains of Rhizobium *compete better in a particular soil than other strains. Understanding the basis of soil-plant interaction would improve chances for the development of more useful agricultural strains. Thousands of different species of legumes grow wild around the world. It is important that these be screened to determine their value for food and for enriching poor soils.*

DENITRIFICATION

Additional information is needed regarding denitrification. This process can result, ultimately, in the production of nitrous oxide from nitrogen fertilizer. Atmospheric nitrous oxide concentrations should be monitored, and field, aquatic, and waste-disposal sources should be evaluated as nitrous oxide sources. The rates of natural processes of nitrous oxide production and destruction should be better assessed.

ATMOSPHERIC TRANSFORMATIONS

Several subjects should be explored further to improve our understanding of the physical and chemical transformations of ammonia in the atmosphere. More specifically, the following studies are recommended:

1. *Kinetic and mechanistic studies of the ammonia-nitric oxide-oxygen system should be directed to establishing whether destruction of ammonia in the atmosphere represents a source of nitric oxide or a sink for nitric oxide. The rate constants for the reaction of the amino radical with oxygen and nitric oxide should be established.*
2. To understand better the formation and fate of acid rain and of ammonia-containing particles, the dynamics of ammonia gas-to-particle conversion processes should be further investigated. This would require field measurements of aerosol and particulate concentrations and study of the thermodynamics and physics of aerosols.

3. The processes for the removal of ammonia from the troposphere should be better described. These processes include reactions of gaseous ammonia with receptors and washout as particular ammonium-containing materials.
4. Global nitrogen budgets for the troposphere should be refined to include a broad spectrum of often-neglected nitrogen compounds.

WATER

The capability of monitoring ammonia in surface and ground waters in the United States is inadequate for obtaining good descriptions of ammonia concentrations in various regions. Such information should be obtained, mapped (with available computer mapping techniques), and utilized in combination with mapping of rainfall data, to show nationwide trends in ammonia concentrations.

The growth of organisms in coastal waters is nitrogen-limited. A knowledge of nitrogen budgets in wetland areas would improve our understanding of life in coastal waters.

Reservoirs can cause stratification of ammonia concentrations in surface waters. The effect of this phenomenon on plants, animals, and nitrifying bacteria should be assessed.

PRODUCTION AND USES OF AMMONIA

Ammonia production requires a source of energy and of hydrogen. Natural gas can furnish both and can be both a fuel and a feedstock. The shortage of natural gas has led to studies of alternative feedstocks for ammonia production. It is recommended that priority be given to a search for potential feedstocks that will minimize pollution problems or safety hazards during ammonia production and that will permit industry to meet pollution abatement and safety standards with relatively low capital investment. Naphtha and electrolytic hydrogen are feedstocks that create environmental problems comparable with those related to natural gas. Other feedstocks should be sought. No changes in current air-pollution standards are considered necessary for emission from ammonia plants that use natural gas as a feedstock and natural gas or light fuel oil (No. 2) as fuel for the reformers.

At modern ammonia plants, about 972 kg of water condensate is obtained per tonne of ammonia produced. The condensate contains about 1 kg of ammonia per tonne of ammonia produced. Effluent guidelines limit the amount of ammonia that can be discharged, and about 98% of the ammonia must be removed before the effluent can be discharged as a waste. With present water-treatment technology, ammonia-plant condensate is steam-stripped, and ammonia removed from the wastewater is emitted into the air. *It may be possible to recycle the condensate in the ammonia-plant process and thereby eliminate emission of ammonia to the air. Furthermore, recycling the condensate would decrease the consumption of energy in the steam-stripping operation. It is recommended that studies be undertaken to investigate recycling of the ammonia-plant condensate in the process.*

Of all ammonia losses from production and application in industry and agriculture, the major portion occurs during the direct application of ammonia to soil. Although this process is relatively efficient (only 5% of ammonia applied is lost to air), the loss accounts for 60% of the total industrial–agricultural loss. For resource conservation, efforts should be directed toward reducing further the loss of ammonia during production, distribution, and application. The amount of total nitrogen lost in air and groundwater when nitrogen fertilizers are applied to the soil is about 8 times as much as the loss, as ammonia, during the production and distribution of fertilizers. The nitrogen losses in air and groundwater result from denitrification and leaching, respectively, of soil nitrogen. *It is recommended that major effort be directed toward development of improved nitrogen fertilizers that are less susceptible to such losses. This should be part of a continuing effort to improve agricultural practices and to decrease nitrogen losses in air and groundwater.*

AMMONIA VOLATILIZATION FROM ANIMAL WASTES

Methods should be developed to reduce the volatilization of ammonia from feedlot surfaces to conserve nitrogen for agricultural use. Study of the ammonia flux from feedlot areas into surface water and plant leaves would provide useful background data.

ATMOSPHERE

Polluted air contains particles and droplets that in turn contain nitrate and sulfate, which may constitute a health hazard to human populations in urban areas and contribute significantly to the reduction of visibility. Some of these particles contain ammonium ion, but it is not known whether the ammonium moiety lessens or heightens toxicity. Present evidence suggests that ammonia lessens toxicity. Furthermore, particulate ammonium, sulfate, and nitrate compounds may affect the radiative climate of the earth and are directly involved in acid-rain precipitation.

Ammonium-containing particles have received more limited attention than other substances in air-pollution research. Specific recommendations related to the atmospheric concentrations of ammonia are as follows:

1. An improved inventory of ammonia emission from stationary and automotive sources should be developed.
2. Methods should be developed or refined for the routine measurement of ambient ammonia at parts-per-billion concentrations. These methods should be suitable for continuous measurement of ambient ammonia as part of a limited monitoring network.
3. *Simultaneous measurements of ammonia and of particulate hydrogen (acidity), ammonium, sulfate, and nitrate content are needed to elucidate further the role of ammonia in the formation of particulate ammonium, nitrate, and sulfate and to formulate improved strategies for the control of these major inorganic pollutants.*

PLANT AMMONIA FIXATION

Plants may play a role in the absorption of ammonia and ammonium aerosols. Research is needed to distinguish gaseous and particulate components in the cycling of ammonia between the atmosphere and vegetation.

OCEANS

Ammonia is important in the nitrogen dynamics of coastal waters. Municipal sewage effluent is a major source of ammonia in these waters. The effects of municipal sewage on the nitrogen economy of coastal waters should be examined.

Ammonium fluxes across the sediment-water interface should be measured for the range of sedimentary conditions found in coastal water.

TOXICOLOGY AND HEALTH EFFECTS

Despite much effort, the metabolic basis of ammonia toxicity is insufficiently understood. Sound research in this area should be encouraged. The basis of hepatic coma should continue to be studied, and the functional importance of depletion of citric acid-cycle intermediates and ATP depletion should be examined. The possible role of ATPase, acetylcholine, and other neurotransmitters requires further investigation.

The treatment of urea toxicity in ruminants is not as effective as could be desired, and additional studies are needed on the causes of death due to urea feeding or rumen ammonia production.

Both short- and long-term tolerance limits for ammonia in fishes should be established, so that guidelines can be developed for safe concentrations in natural waters.

Proper ventilation and waste management can prevent the buildup of ammonia in the ambient air in confined livestock facilities. Information about proper technical construction and utilization is available and should be disseminated to livestock producers.

Bats can tolerate extremely high concentrations of atmospheric ammonia; their mechanism of tolerance should be studied in the hope that the information could be used to protect more sensitive species, including man.

Animal studies of pulmonary effects have been limited in number and sometimes inadequately controlled. Additional studies of physiologic and biochemical effects of ammonia on pulmonary ultrastructure and function would therefore be useful.

Studies of late sequelae of acute toxic inhalation of ammonia and of responses to chronic low exposure to ammonia need to be performed. Ammonia needs to be investigated as a sole pollutant and in mixtures with other pollutants, such as carbon monoxide, nitrogen oxides, sulfur dioxide, and hydrogen sulfide. Because studies of the synergistic effects of various combinations of pollutants at various concentrations could involve a large number of permutations and require a tremendous expenditure of effort and resources, these studies should be selected and designed carefully. Available empirical observations on man suggest that gaseous ammonia as encountered in air pollution adds little to the toxicity of other pollutants. Thus, it appears appropriate to suggest here, as well as for some of the recommendations to follow, that such studies be preceded by careful, well-controlled epidemiologic surveys. These will permit proper identification of the problem, if present, and of the specific combinations of pollutants that need be investigated. The following subjects warrant evaluation to determine threshold and safe limits for acute and chronic exposure to ammonia (alone or with carefully selected synergists) with respect to age:

1. Functional changes of the terminal airways, i.e., frequency-dependent compliance, closing volume, and flow rates at low lung volume.
2. Structural changes, as studied by ultrastructural techniques, scanning electron microscopy, autoradiographic techniques of cell turnover in the lung and bronchial tree, and electron microscopic tracer studies of pulmonary capillary permeability.
3. Biochemical changes *in vivo* and *in vitro*, particularly with respect to collagen and elastin metabolism; mucin production; protein, carbohydrate, and lipid (surfactant) metabolism; histamine and serotonin release; lysosomal enzyme alterations; and effects on other enzyme systems.

4. Changes in lung defenses, as manifested by changes in humoral and cell-mediated immunologic function, macrophage function, and *in vivo* and *in vitro* responses to bacterial and viral challenge.

The continued study of metabolic ammonia toxicity and of hepatic encephalopathy should be encouraged to elucidate the various intracerebral biochemical mechanisms and to assess their significance for human hepatic coma and other types of ammonia intoxication.

The initiation and perpetuation of the acute inflammatory response to ammonia burns of the eye should be studied further. Study is also needed of the various cellular interactions that result in protease degradation of the cornea and of the question of why ammonia-burned eyes are slow to epithelialize.

Monitoring of the industrial environment and workplace should continue to accumulate accurate measurements of ammonia in air and, if necessary, to refine industrial standards.

Additional well-controlled human inhalation studies should be conducted. They should last at least a few hours and should include monitoring of such metabolic and respiratory characteristics as blood urea nitrogen, urinary urea nitrogen, serum and urinary ammonia, closing volume, frequency-dependent compliance, alveolar-arterial oxygen gradient, maximal midexpiratory flow, and flow rates at low lung volumes.

Epidemiologic studies on selected industrial-rural populations chronically exposed to accurately monitored ammonia concentration are recommended. Other air pollutants, if present, should be identified and monitored. Detailed and accurate epidemiologic histories and tests of respiratory and metabolic characteristics are necessary, and there should be well-studied control groups. Smokers and nonsmokers should be specifically identified because the effect of cigarette smoke may obscure the effects of air pollutants. The incidence of neoplasm in the group should also be determined.

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REPORT X

Ammonia as a Fuel

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Prepared for the
Environmental and Safety Engineering
Division
U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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CONTENTS

SUMMARY

The future uses of ammonia as an energy material are under study as part of the ammonia safety and environmental control assessment being performed by PNL. The report presents a general overview of ammonia characteristics and provides a perspective on its potential use as a fuel. Significant conclusions are that ammonia may be an important hydrogen storage medium as part of a future hydrogen fueled economy and may be producible at low cost from inexhaustible resources.

1.0 INTRODUCTION

Ammonia is a liquefied energy material. It has been identified as a topic for analysis in the LGF Safety and Environmental Control Assessment Program because of its potential as a direct energy source in supplementing or replacing hydrocarbon fuel use and its uses in alternative energy technology (e.g., as a heat transfer medium). This report describes and assesses the utilization of ammonia as a fuel.

Because of declining domestic oil production and an increasing dependence on imported oil, alternative fuels have been studied for energy use in transportation, process industries, and electric power generation. However, existing research projects have not dealt specifically with the benefits or problems of ammonia fuel utilization. Therefore, our present knowledge is based on experience and investigations that are mostly ten or more years old. This report is designed to present a general overview on the characteristics of ammonia as a fuel and to provide a perspective on its potential.

The report which follows describes the physical characteristics of ammonia as a fuel and discusses its suitability through a historical perspective, a review of factors favorable to its use, and a description of actual use in various types of engines. Additional sections describe the potential for alternative ammonia fuel blends, the environmental impacts of its use, a comparison of ammonia fuel use to that of hydrogen, and a brief discussion of the availability and costs of ammonia.

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2.0 AMMONIA FUEL CHARACTERISTICS

At standard conditions, anhydrous ammonia is a colorless gas with the chemical formula NH_3. At a temperature of 21°C (70°F) and a pressure of 900 kPa (129 psia), ammonia will become a liquid with a density of 616 kg/m^3 (38 lb/ft^3). Ammonia burns readily in oxygen, but combustion in air without a catalyst is more difficult. When heated in the presence of a catalyst to 482°C (900°F) or above, ammonia decomposes into hydrogen and nitrogen. Ammonia is sometimes used as a source of hydrogen, such as in portable welding units, because a volume of liquid ammonia will yield more hydrogen than will an equal volume of compressed hydrogen gas. Additional properties of anhydrous ammonia are provided in Table 1.(a) Note that the net heating value of ammonia is 4445 kcal/kg (8,000 Btu/lb) compared to a heating value of 10,557 kcal/kg (19,000 Btu/lb) for gasoline. This indicates that for equal combustion efficiencies, approximately 2.4 times more ammonia will be needed to equal the energy output of gasoline.

The vapor pressure of liquid ammonia ranges from 138 kPa (20 psig) to 1,725 kPa (250 psig) over the temperature extremes of -29°C (-20°F) to 43°C (110°F), respectively. This indicates that an automobile storage tank would have to be pressurized to approximately 1,725 kPa (250 psig) to maintain the ammonia in liquid form. The flammability characteristics of ammonia in air and oxygen at atmospheric pressure are shown in Figure 1.

(a)A comprehensive updated compilation of the thermodynamic properties of ammonia has recently been prepared by the National Bureau of Standards (Haar 1978).

TABLE 1. Physicochemical Properties of Anhydrous Ammonia (Pangborn, 1974)

Chemical Formula	NH_3
Molecular Weight	17.031
Melting Point	-77.7°C (-108°F)
Normal Boiling Point (NBP)(a)	-33.4°C (-28°F)
Density at Normal Boiling Point	
Vapor	0.901 kg/m^3 (0.0556 lb/ft^3)
Liquid	690 kg/m^3 (42.6 lb/ft^3)
Density at 21°C (70°F)	
Vapor	0.702 kg/m^3 (0.0433 lb/ft^3)
Liquid	616 kg/m^3 (38.0 lb/ft^3)
Heating Value, Liquid	
Lower Heating Value	∿4450 kcal/kg (∿8,000 Btu/lb)
Lower Heating Value (at 21°C or 70°F)	∿2700 kcal/ℓ (∿40,600 Btu/gal)
Products of Combustion, Liquid	
Heat of Vaporization at NBP	325 kcal/kg (591 Btu/lb)
Flammable Limits in Air	16-27 vol.%
Autoignition Temperature	651°C (1204°F)
Stoichiometric Mixture (kg air/kg fuel)	6.1
Research Octane Number	130
Critical Data	
Critical Temperature	55.6°C (132°F)
Critical Pressure	11,200 kPa (1632 psia)
Critical Density	235 kg/m^3 (14.7 lb/ft^3)

(a) At atmospheric pressure (14.7 psia).

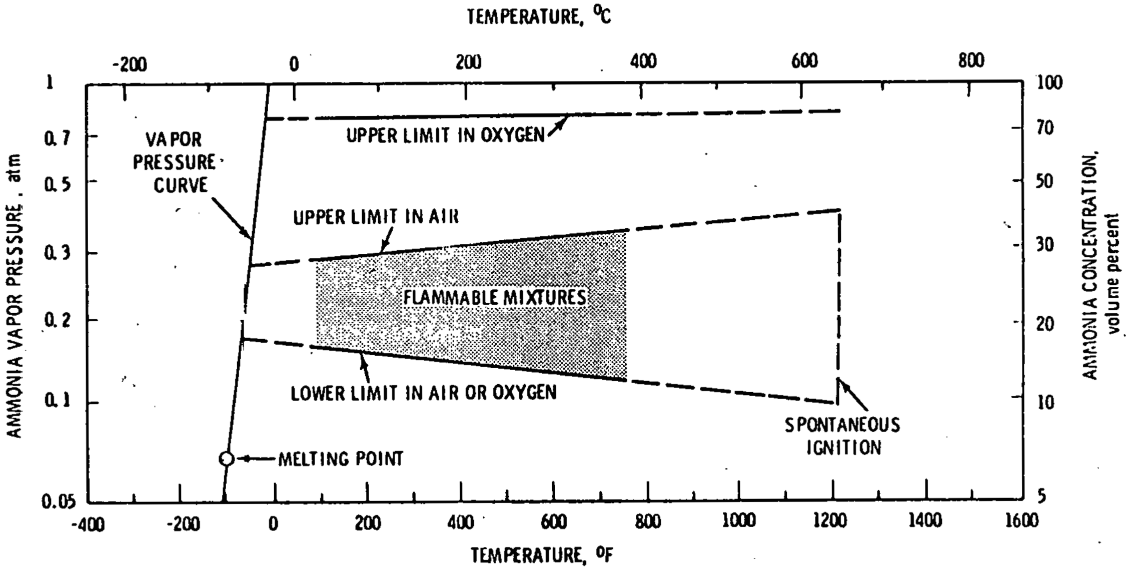

FIGURE 1. Flammability Characteristics of Ammonia in Air and Oxygen at Atmospheric Pressure (Pangborn 1974)

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3.0 SUITABILITY OF AMMONIA AS FUEL

Ammonia has been considered and used as a fuel primarily for combustion engines. This section provides an historical perspective on the use of ammonia as a fuel, a reassessment of such use under current energy and environmental constraints, and a description of its performance characteristics for various engine alternatives.

3.1 HISTORICAL BACKGROUND

The practical use of liquid anhydrous ammonia as an engine fuel dates back to the mid-30s when a Swiss-Italian company (Ammonia Casale) applied for several patents (Montagne 1938, Frejacques 1941, Ammonia Casale 1935, Ammonia Casale 1936). During World War II ammonia was occasionally used in Europe with remarkable success as fuel in buses for public transportation (Egloff and Alexander 1944). For example, a fleet of about 100 buses was operated in Brussels without a major accident during 1942-1943 (Kroch 1945). However, since ammonia is, in many respects, inferior to gasoline, and since gasoline became very cheap and abundant in the first two decades after the war, no further consideration was given to ammonia as an engine fuel. In the mid-60s the U.S. Army Material Command, as part of its "energy depot" concept, became interested in finding a synthetic fuel which could be produced with the energy from mobile nuclear reactors (Rosenthal 1964, Grimes 1964). The ultimate purpose of this concept was to increase the Army's mobility in the case of an overseas war. Studies (Pearsall 1967) indicated that ammonia would be a more suitable fuel for this purpose than alternative fuels such as hydrogen, hydrazine, and H_2O_2.(a) In that scheme, nuclear energy would be used to synthesize ammonia from air and water. Anticipating the future availability of large blocks of low-cost nuclear power, an AEC study in 1968 predicted production of ammonia from the electrolysis of water at prices competitive with those of commercial methods (Blouin 1968).

(a)Factors concerned with physical and chemical properties, handling, storage, and dispensing of the four fuels led to the choice of ammonia as the fuel with the greatest potential.

Around 1970 the Army abandoned its mobile nuclear reactor development effort and the "energy depot" project was also terminated. However, many of the research results obtained by the various contractors at that time remain valid and can be useful in evaluating the prospects of using ammonia in various types of combustion engines.

3.2 REASSESSMENT OF AMMONIA FUEL UTILIZATION

Historically, ammonia fuel utilization has been tied to actual or expected shortages in fossil fuels, particularly during political conflicts. Fossil fuel shortages may make ammonia an attractive fuel in the future because it provides a means of channeling or converting energy from large scale alternative energy developments (e.g., fusion) into a convenient fuel for small scale uses such as transportation.

Another significant factor for considering ammonia as a fuel is the reduced environmental impact. Ammonia is a non-carbonaceous fuel unlike fossil fuels such as oil, coal, and natural gas. This characteristic, along with the lack of contaminants such as sulfur oxides and trace elements, allows cleaner combustion without atmospheric emissions of CO, CO_2, sulfur oxides and trace elements. Ammonia can be produced either from water with energy from nuclear or other sources or from fossil fuel feedstocks (natural gas or coal). In either case the need to actually burn any fossil fuel would be eliminated, thus limiting atmospheric impacts.

The choice of alternative non-carbonaceous fuels is very limited with the only significant choices being hydrogen and ammonia. Hydrazine has also been considered as an alternative fuel (Schmidt 1975), but current technologies have not been able to produce it economically. Only hydrogen is presently given serious consideration and is widely promoted as the fuel of the future. Ammonia has been suggested as a source of hydrogen, (Graves et al. 1975) but as will be shown below, it has potential as fuel on its own merits (Buckley and Husa 1962; Garner 1976).

3.3 ENGINE ALTERNATIVES

Figure 2 shows the ideal case of the closed energy storage cycle that results when using ammonia as a fuel. By expending energy, ammonia can be produced from the N_2 and H_2 contained in air and water. During combustion, ammonia reverts back to N_2 and H_2 (air and water) and gives off an equivalent amount of energy. Thus ammonia can be regarded as a medium for energy storage (i.e., on balance only an exchange of energy is taking place within the cycle).

Figure 2 also shows that ammonia is a very versatile fuel, since it can be used both in internal and external combustion engines, as well as in direct and indirect fuel cells. The following will present a summary of the presently known experience with ammonia when used as a fuel in alternative combustion engines and fuel cells.

3.3.1 Otto Engines

Theoretical and experimental investigations, mainly by the University of California at Berkeley, Southwest Research Institute, and General Motors, using ammonia in a standard Otto or spark ignition engine had the following results (Hodgson 1974; Cornelius, Huellmantel and Mitchell 1964; Gray et al. 1966; Starkman et al. 1966):

- Ammonia can be used successfully at comparable gasoline engine compression ratios, if introduced as a vapor partially decomposed to hydrogen and nitrogen. Under these circumstances the hydrogen will act as a "pilot fuel" to initiate the ammonia combustion. Little engine modification is necessary other than a means for flow control of the ammonia and adjustment of the spark timing.
- Indicated engine output with ammonia is reduced to approximately 70%, but never more than 77% of that with hydrocarbon fuel. The 77% performance, a theoretical maximum, could not be accomplished if the ammonia is partially decomposed before introduction to the cylinders. Experiments with partial decomposition yielded an output of slightly over 70%.

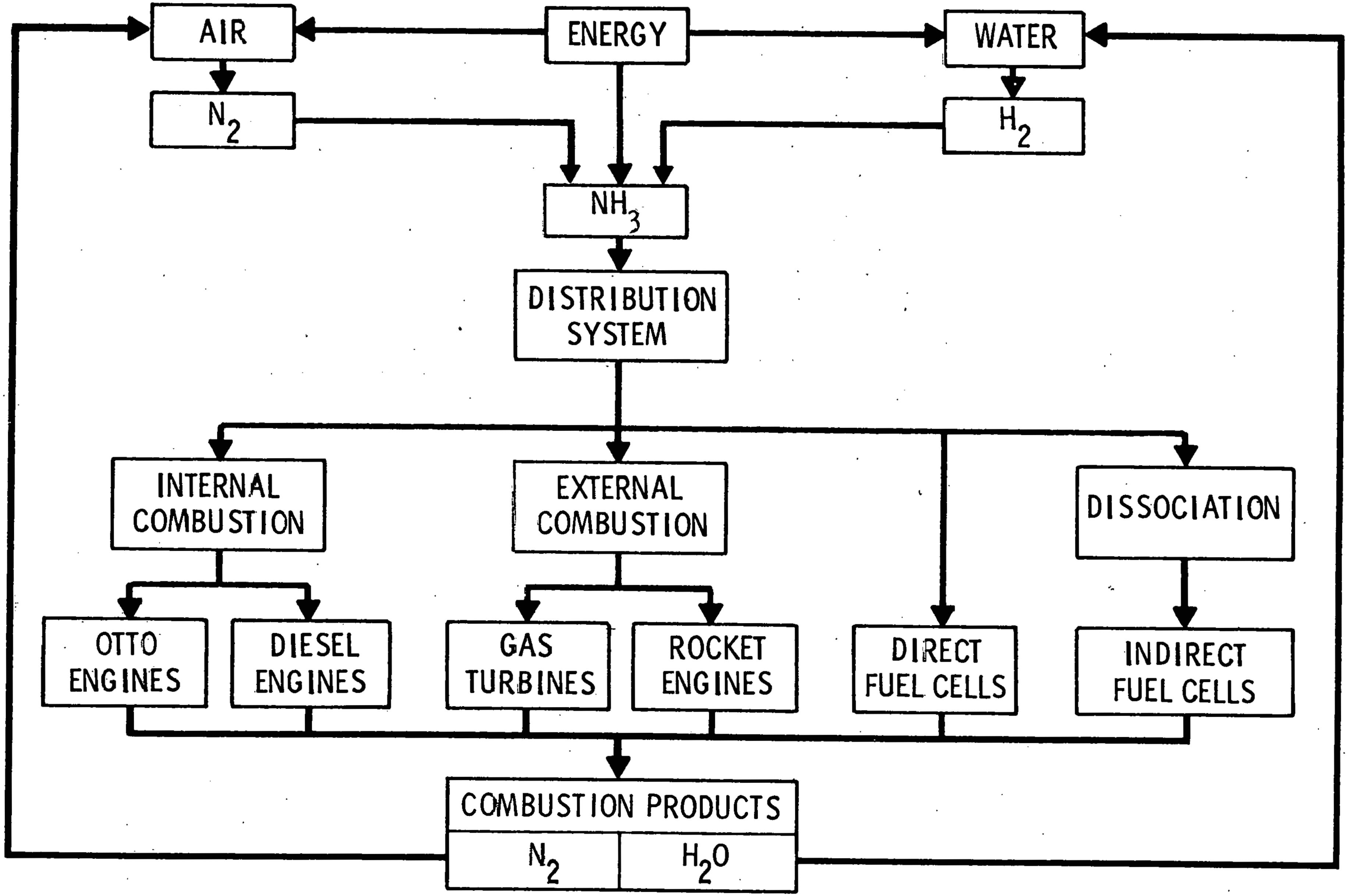

FIGURE 2. Use of Ammonia as a Fuel. (In Most Current NH_3 Manufacturing Processes, Both the Energy and the Hydrogen are Supplied by Natural Gas.)

- Specific fuel consumption[a] using ammonia is increased essentially by a factor of 2 over that of hydrocarbons.
- Ammonia is generally difficult to ignite, especially at low temperatures although the presence of hydrogen or other "pilot fuels" (e.g., gasoline) eliminates this problem. Hydrogen concentration in the fuel feed is a critical factor for successful operation on ammonia as fuel. Minimum concentrations appear to be 4 to 5% by weight at intermediate engine speeds (around 1800 rpm).
- Engine performance rapidly falls if less than minimum concentrations of hydrogen are used. This seems to relate to the self-generating character of the ammonia decomposition during the compression and combustion processes.
- Performance factors such as those influenced by engine speed, spark timing, and manifold pressure are not significantly different when using ammonia fuel rather than hydrocarbon fuel, as long as minimum amounts of hydrogen are inducted as a part of the fuel flow.
- Calculations have indicated that engine output with ammonia would exceed that with hydrocarbons if the ammonia could be introduced into the cylinder as a liquid.
- Supercharging (i.e., introduction of the combustion air at above atmospheric pressures) was demonstrated and resulted in substantially improved engine performance.
- Compatibility of ammonia and its combustion products with engineering materials and lubricants presented no substantial problems.

3.3.2 Diesel Engines

The use of ammonia in compression ignition (diesel) engines was also investigated for the "energy depot" study (Rosenthal 1964, Gray et al. 1966) and later studies (Bro and Pederson 1977). The results generally parallel those obtained for Otto engines, presented above. In particular:

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[a] "Specific fuel consumption" is defined as the fuel consumed per unit of work.

- Difficulties occur because of poor self-ignition qualities. Relative to other fuels the octane rating of ammonia is very high (about 130), but its cetane rating (i.e., ignition quality) is low.(a) Theoretically, a compression ratio of 35 would be necessary for self-ignition, but this is well beyond the current practice. (An attempt of direct injection of liquid ammonia into a specially-prepared test engine with a 30 to 1 compression ratio was not successful). Therefore, an independent source of ignition must generally be provided such as injection of a small amount of regular diesel fuel (pilot fuel) (Bro and Pederson 1977, Pearsall 1967) or use of auxiliary spark or glow coil ignition. With such modifications diesel engines have been successfully operated on ammonia at normal compression ratios (Gillis, Pangborn and Vyas 1975; Starkman, James and Newhall 1967).
- Once ignited, ammonia fuel was found to have slow flame speed (again indicated by its low cetane rating). Therefore, advanced injection timing of the fuel is required, which results in some engine power loss.
- The theoretical predictions of diesel engine performance with ammonia as a fuel have generally been confirmed by actual tests. The maximum thermal efficiency of a diesel engine with ammonia was found to be 51% versus 45% with regular diesel fuel (Pearsall 1967).
- On a weight basis, fuel consumption was found to be about 2 1/2 times higher for ammonia than for regular diesel fuel (Starkman, James and Newhall 1967), due mainly to the lower heating value of ammonia.
- Diesel engines running on fossil fuels must restrict their fuel-air ratio to about 0.7 of stoichiometric conditions because of the smoke-exhaust problems. Ammonia combustion allows smoke-free operation up to stoichiometric conditions. This provides for higher output and more efficient operation of the engine, which has been confirmed in more recent testing (Bro and Pederson 1977).

(a)Normally, as a fuel's octane rating goes up, its cetane rating goes down (Taylor 1977).

- When compared with other substitute fuels (methane, methanol, ethanol) for diesel engines, the main drawback of ammonia was considered to be the emission of unburned NH_3 because of its objectionable odor (Bro and Pederson 1977).

3.3.3 Gas Turbines

The performance of ammonia as a fuel for gas turbine applications has also been theoretically predicted (Newhall and Starkman 1966) and experimentally verified in connection with the "energy depot" study (Verkamp, Hardin and Williams 1967; Pratt and Starkman 1967). The theoretical results indicate that, on the basis of power output and efficiency, ammonia is superior to hydrocarbons by about 10%; but poorer by a factor of 2 1/2 on the basis of specific fuel consumption (Newhall and Starkman 1967). The latter facet is primarily due to the lower heat of combustion of ammonia versus hydrocarbon fuels (e.g., 8000 Btu/lb for ammonia versus 18,400 Btu/lb for JP-4 fuel). Again, as in the case of automobile and diesel engines, a much higher ignition energy is required for ammonia than for hydrocarbon fuels, but this may be easily overcome by the use of a pilot fuel or by partially decomposing the ammonia.

NH_3 flame stability limits were found to be quite low. Therefore, ammonia (either as a liquid or in vapor form) cannot serve as a direct substitute for hydrocarbons in gas turbine burners that are optimally sized for hydrocarbon fuels. However, at 28% dissociation it is quite suitable for such a purpose. Also, if the burner is optimized for ammonia combustion, ammonia can be burned in them directly (Verkamp, Hardin and Williams 1967). It has been shown that various catalysts can be used for partial ammonia dissociation. An ammonia dissociator has been tested by General Motors (Allison), which utilizes the engine exhaust heat to vaporize the liquid ammonia and simultaneously provide the thermal energy for the dissociation (Verkamp, Hardin and Williams 1967). Solar, a major U.S. gas turbine manufacturer, tested full-size ammonia-fueled gas turbine engines in connection with the U.S. Army's "energy depot" project. It was found that their combustion efficiencies were comparable to those equipped with equivalent hydrocarbon combustors (Faehn 1966).

Even though it has not been specifically verified in tests, it can be assumed that ammonia could be used as fuel in any other external combustion engine (such as Rankine and Stirling cycle engines) with similar results as in gas turbines.

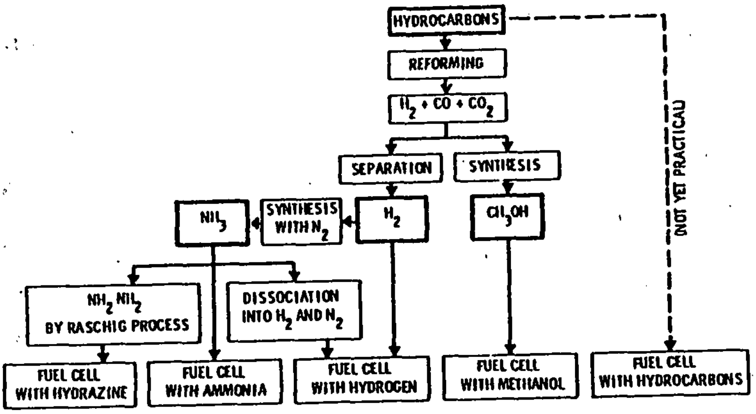
3.3.4 Rocket Engines

The theoretically high specific impulse of ammonia when reacted with liquid oxygen or liquid fluorine gives it great potential as a liquid rocket fuel. The performance of ammonia is only slightly less than that of hydrazine with the same oxidizers, and the cost and availability make it more attractive. Mixtures of ammonia and hydrazine have been proposed for use because they have physical properties superior to either fuel alone. However, since the mid-60s solid rocket fuels have generally been preferred mainly because of their simplicity and higher reliability. The North American Aviation rocket plane X-15 is the only vehicle known to have employed anhydrous ammonia as a propellant (Baumeister 1967, Gubitz 1960).

3.3.5 Fuel Cells

Since fuel cells hold the promise of very efficient (up to 90%) energy conversion, various fuels have been considered and tested for fuel cell applications (SAE J. 1968, Oniciu 1976). As is shown in Figure 3, ammonia is one of the more promising fuels. It can be used either in direct or indirect fuel cells as a source of hydrogen or hydrazine, which are both excellent fuels for fuel cells. However, published results on the use of ammonia in fuel cells are scarce.

In connection with the "energy depot" project, Allis-Chalmers built and operated 50-cell ammonia batteries but the operating data are not publicly available (Grimes 1964, Liebhafsky and Cairnes 1968). These were indirect cells which operated on hydrogen generated by the dissociation of ammonia. The resulting equipment was quite bulky and apparently uneconomical, since part of the fuel's energy had to be used for its full dissociation. At that time (1963) the direct use of ammonia in low temperature cells had not been proven successful. Later, a G.E. project (Simons and Cairnes 1968) showed that



<u>FIGURE 3</u>. Source of Principal Fuels for Use in Fuel Cells

direct ammonia-oxygen or air cells could be operated between 25°C (77°F) and 140°C (284°F). Electrodes, however, had to contain platinum (about 2.5 mg/cm^2), and power densities were limited to about 50 $milliwatt/cm^2$. A Swedish company has built and tested a 50 kW ammonia fuel cell for submarine use (<u>SAE J.</u> 1968).

Current fuel cell technology is not yet economical for most applications, and methanol fuel is generally preferred since it is (in comparison to ammonia) less toxic and liquid at ambient temperatures and pressures. Present development of fuel cell technology is directed towards direct and efficient use of fossil fuels and ammonia may not be reconsidered unless these fuels become scarce and too expensive.

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4.0 AMMONIA AND ACETYLENE - A POTENTIAL FUEL BLEND

At the same time when ammonia was used as a substitute fuel in automobiles (during World War II), the solution of acetylene (C_2H_2) in ammonia was also tested (primarily in France and Italy) for the same application (Kroch 1945, Frejacques 1941, Kufferath 1941, Claude 1941, Frejacques 1944). Such a mixture was expected to show better ignition characteristics than ammonia alone, since acetylene has a much wider ignition range in air (2.5 to 81 vol.%) than ammonia (16 to 27 vol.%) and also, acetylene has the highest heat of combustion (on a volumetric basis) of any gaseous fuel (979 $kcal/m^3$ [110 Btu/ft^3]) of stoichiometric air mixture at 18°C and atmospheric pressure, (Taylor 1977)). Acetylene could be used by itself as an automotive fuel if it were not so difficult to store. When liquefied, it can decompose and explode very violently, since its unstable molecules can split exothermally into hydrogen and carbon. However, when dissolved in a suitable liquid agent such as acetone, methanol or ammonia, it becomes much safer to handle because it cannot explode under these conditions.

Tests have shown that a liquid mixture (78% NH_3 and 22% C_2H_2 by weight) at 15°C (54°F) and 111 kPa (161 psig) produces a vapor mixture which is not explosive, and is well suited as a fuel in standard automobile engines. A Citrogen engine produced 45 hp with this fuel compared to 50 hp when it was run on gasoline (Kufferath 1941).

A recent experimental study (Hilden and Stebar 1979) by General Motors Research labs again came to the conclusion that acetylene by itself is not a suitable automobile fuel, but a mixture of ammonia and acetylene might well be. Apart from safety considerations, the technical reason given was that, with pure acetylene, knock-induced preignition occurred either with compression ratios above 6 or with fuel-air mixtures richer than 0.69 fuel/air ratio of stoichiometric. In recent tests at the Institute of Gas Technology, calcium-carbide was successfully manufactured using sunlight, as a possible future source of acetylene (Coal Research and Development 1980).

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5.0 ENVIRONMENTAL IMPACT OF AMMONIA COMBUSTION

Processing and combustion of fossil fuels continues to be the principal source of air pollution. With the anticipated greater reliance on domestic coal, it is possible that the problem will become worse. It has been suggested that ammonia be substituted on a large scale for fossil fuels (Green 1967). Since the main combustion products of ammonia are water and nitrogen, the most common atmospheric pollutants (i.e., unburned hydrocarbons, CO, NO_x, particulates, SO_2, and CO_2) could potentially be reduced. Some pollutants can be reduced by suitable, although expensive, exhaust gas scrubbing procedures, but there is little hope to diminish the vast quantities of CO_2, which are main combustion products of all carbonaceous fuels. Recently, the National Research Council has concluded, as a result of a special study, that the global carbon dioxide buildup will represent a significant problem for the future (The Energy Daily 1980). For this reason, the utilization of more noncarbonaceous fuels, such as ammonia, could provide a beneficial means of energy generation in which the fossil fuels are not burned directly, but serve as raw materials for the synthesis of the clean fuel (ammonia). This process could be made more economical by the use of nuclear energy to synthesize ammonia from water and atmospheric nitrogen. The most rewarding application of this scheme would be the use of ammonia as automotive fuel, since the cleanup of combustion gases is more inefficient on a small scale than it is in larger combustion sources.

Since the late 1960s, it has become clear that NO_x is one of the most obnoxious types of air pollution caused by automobiles. It might be suspected that the combustion of ammonia in automobile engines could also contribute to NO_x pollution, even though the combustion products of ammonia are ideally water and nitrogen. This question has been investigated in several studies (Graves and Hodgson 1975, Hodgson 1973, Hodgson 1974, Garner 1976, Starkman et al. 1970). Based on chemothermodynamic analysis, the formation of oxides of nitrogen in ammonia combustion should be much lower than that of any other known fuel (Starkman et al. 1970), except hydrogen. However, this was not fully confirmed in early experiments (Sawyer et al. 1968, Starkman et al. 1966), in which lean ammonia air mixtures produced higher NO_x concentrations than were theoretically predicted. At stoichiometric fuel/air ratios and higher, the theoretical results were substantiated and more recent, independent testing has shown a better agreement with theory (Graves and Hodgson 1975, Hodgson 1973). NO_x emissions were below 100 ppm for fuel rich ammonia-air mixtures (contrary to results of the earlier studies), concentrations were generally lower than those produced when using gasoline.

Obviously, ammonia combustion cannot generate unburned hydrocarbon pollution, but it can and does produce unburned ammonia in the exhaust gases (Graves and Hodgson 1975). Tests have indicated that ammonia concentrations of 15,000 ppm have been detected in the exhaust. Most of this ammonia could be eliminated by suitable catalytic reactors, but this would add to the complexity of the system.

Since ammonia is a relatively light gas (molecular weight 17 compared to 29 for air), it is expected to rise initially within a quiet atmosphere until concentrations become low enough that buoyant forces are balanced by turbulence. Generally, therefore, no heavy accumulations at ground level are anticipated. A serious safety problem may arise, however, in underground tunnels, where existing ventilation may be inadequate, particularly if a major spill develops (e.g., as a result of a fuel tank rupture). There is generally little concern about building up excessive ammonia levels in the atmosphere, since the oceans, the soil, the rain, and even green plant leaves absorb ammonia quite readily. Simple oxidation in the atmosphere itself removes only about 5% of the ammonia by converting it into NO (Boettger et al. 1978). For plants and soil, even a beneficial fertilizing effect has been shown. According to Hutchinson et al. (1972) the importance of such an effect "has been vastly underestimated in the past." The potential environmental hazards from atmospheric ammonia are still largely unknown (Temple et al. 1979). So far, most of the atmospheric ammonia is produced by organic means (an estimated 80% alone from animal excrements), and its level has stayed at a fairly constant equilibrium (Boettger et al. 1978, Söderlund 1976).

6.0 AMMONIA VERSUS HYDROGEN

The only significant noncarbonaceous fuels are ammonia and hydrogen. There has been a large research and development effort over the last decade to promote hydrogen as an alternative fuel (Casazza et al. 1975, Donnell et al. 1979, Hydrogen Fuel 1980, Hydrogen - Future Fuel 1979, Murray 1972, NRC 1979). Although there are many similarities in the properties of hydrogen and ammonia as fuels, very few studies have been made to promote utilization of ammonia. Differences between hydrogen and ammonia are compared below.

- Neither hydrogen nor ammonia are primary energy sources, but are synthetic fuels commonly produced from water and air (our most ample material resources) or from hydrocarbons in certain endothermic processes. Hydrogen, however, is easier to produce than ammonia.
- During combustion under ideal conditions, ammonia yields water and nitrogen; hydrogen yields water. Thus, both fuels are basically "clean" fuels ecologically. Under actual conditions, however, ammonia combustion also yields some unburned NH_3 and NO_x, while hydrogen combustion yields some NO_x (Murray 1972).
- The gravi-metric heating rate of hydrogen is the highest of all fuels, 28,728 kcal/kg (51,700 Btu/lb), whereas the gravi-metric heating rate of ammonia is only moderate, 4490 kcal/kg (8080 Btu/lb). However, the volumetric heating rate of liquid hydrogen, 0.23 x (47 kcal/m^3 [5.6 Btu/ft^3]), is lower than that of ammonia, 0.31 x (47 kcal/m^3 [5.6 Btu/ft^3]) (Hodgson 1974), and for practical purposes, a high volumetric rate is usually more important, since a large storage volume entails a large (i.e., heavy) vessel.
- Storage of hydrogen is most compact in liquid form, but this requires a temperature of -256°C (-429°F); close to absolute zero. Storage of liquid ammonia is possible at -35°C (-31°F) at atmospheric pressure and at room temperature, 21°C (70°F), at 840 kPa (129 psig). Storage of hydrogen in the form of liquid ammonia is more compact(a) than any other form of

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(a) Additionally, gaseous hydrogen can be dissolved in liquid ammonia to a limited degree (Wiebe 1934). It is not known whether this feature has ever been practically exploited for combustion improvement.

hydrogen storage. Loss from storage is practically unavoidable for liquid hydrogen (about 5% a day) even with the most elaborate insulation system, whereas, it can be kept extremely low without serious problems for ammonia.

- H_2 or NH_3 vapors escaping from the stored fuels are both unsafe. Ammonia vapors in contrast to hydrogen are toxic in large concentrations, but hydrogen vapors are far more flammable in mixtures with air. Moreover, hydrogen air mixtures are more easily detonated than ammonia which is hard to ignite and almost impossible to detonate. This makes ammonia a safer and more easily handled fuel. Also, there is a much larger practical experience available with ammonia than with hydrogen.
- It has been shown that both hydrogen and ammonia can be used in practically all types of combustion engines without major modifications. However, combustion itself is more easily accomplished with hydrogen than with ammonia. This is a result of the required ignition energy, which is 8mJ for ammonia and only 0.2mJ for hydrogen (Harris and MacDermott 1977).

Proponents of the "Hydrogen Economy" concept have listed a number of reasons why they believe that hydrogen is superior even to electricity as an energy form in many applications, perhaps for half of our energy needs (Casazza et al. 1975). Many of these are applicable to ammonia use.

1. Hydrogen is cheaper and less unsightly to transmit over long distances via underground pipelines. This should be equally true for ammonia pipelines, of which several large long distance (more than 1,000 miles) pipelines have already been used both in the USA and USSR.
2. On a large scale, hydrogen energy can be stored far more easily than electrical energy. This is still easier and safer for ammonia for reasons given above.
3. Hydrogen can be used as fuel in most domestic and industrial natural gas burning equipment with only relatively minor modifications. This would generally be true for ammonia also. A hotter flame would be available with hydrogen than with ammonia, since ammonia burners would require a catalytic ammonia cracking device of some sort. In this respect, ammonia is inferior to hydrogen.

4. Hydrogen can be produced from coal and nuclear energy, and is not necessarily dependent on imported oil or gas. This is equally true for ammonia.

5. Hydrogen, generated by nuclear power, can be used directly to replace coal or coke for steel making or to upgrade certain fossil fuels or low-Btu gases. In this respect ammonia, except as a carrier of hydrogen, would hardly be suitable.

6. Burning hydrogen and oxygen together is conceptually the simplest or most direct way of producing the huge amounts of processed steam required by industry. Obviously, this is not a strong reason for promoting the hydrogen economy, but basically the same approach could be taken with ammonia.

7. Hydrogen is an excellent fuel for all types of internal and external combustion engines because of its greater efficiency and very clean exhaust. To a large degree, this is also true for ammonia. In fact, the U.S. Army in its "energy depot" project preferred ammonia over hydrogen as the fuel for combustion engines.

Since so many reports have been written in the last few years on the potential use of hydrogen as automobile fuel, this latter point deserves some additional discussion. Even though hydrogen has been demonstrated by prototype testing to be a suitable engine fuel with highly desirable characteristics, (such as clean exhaust), it has major drawbacks (Hydrogen Fuel 1980). There are doubts about safe fueling, operation, garaging and maintenance of cars, of their susceptibility to collision damage and the consequences of substantial liquid hydrogen spills. Hydrogen leaks more readily and rapidly than any other substance and is flammable under a very wide range of hydrogen/air ratios and it also detonates quite easily. When stored in a metal hydride instead of as a liquid hydrogen, most of its advantages based on high specific energy content are lost. It has also been pointed out that a vast infra-structure for producing, transmitting and distributing liquid hydrogen would be needed, which can be expected to require high capital cost outlays and long time delays (Hydrogen Fuel 1980).

In contrast, ammonia does not possess the above drawbacks, at least, not to the same extent. It is therefore not understandable why hydrogen as a future fuel is widely promoted whereas ammonia is presently not considered at all. The most likely explanation appears to be that the potential use of ammonia as a substitute fuel is just too unknown, even within the technical community.

An additional point can be made on proposals to use ammonia as a form of hydrogen storage (Graves, Hodgson, and Tennant 1975). This appears to be preferable from an energy conservation viewpoint to storing hydrogen in liquid form. Even with the most modern liquefaction equipment (Baker and Shaw 1978) about 5kWh of energy has to be expended to liquefy 1 pound of hydrogen. To produce 1 pound of ammonia, an energy of only about 0.4kWh has to be expended (Barnett and Wilson 1960). However, since 1 pound of liquid hydrogen contains about 6 times as much energy as 1 pound of ammonia (Gregory and Rosenberg 1973), the ratio of 0.4/5 must be multiplied by 6 in order to compare the efficiencies of the two processes. Thus, the energy costs involved in liquefying hydrogen are twice the cost of producing ammonia. The capital costs of a hydrogen liquefaction plant is also considerably higher than for an ammonia manufacturing plant (both plants based on an equal energy output).

7.0 AMMONIA AVAILABILITY AND COST

Most ammonia manufactured today throughout the world is derived from natural gas, which serves both as fuel (i.e., as energy source) and feedstock (i.e., hydrogen source). This is expected to remain so unless natural gas becomes more scarce. The major oil-producing countries apparently now have more natural gas available than they can sell for direct energy use (e.g., through pipelines and as LNG). Thus, there exists a worldwide oversupply (about 10^7 tons per year) of ammonia, which is not expected to disappear until the mid-1980s (Watt 1979). This has depressed the cost of ammonia over the last years. Whereas in 1975 the price was between \$200 and \$400 per ton (Philpot and Leonard 1979), imported ammonia dropped to below \$100 per ton in mid-1979 (delivered at U.S. Gulf Coast ports). In particular, cheap ammonia supplied by the USSR was a major contributing factor in this development. As a result, a number of U.S. ammonia (fertilizer) manufacturers could no longer compete and went out of business. In October 1979, the International Trade Commission recommended, therefore, that import restrictions be placed on ammonia from the USSR. However, this recommendation was overruled by President Carter (1979). His decision still stands and has not been affected by U.S. responses to the Soviet invasion of Afghanistan. Accordingly, 10^6 tons of ammonia can be imported to the U.S. from the USSR during 1980. In the future, this limit is scheduled to rise. U.S. manufacturers can presently produce ammonia economically at about \$130 to \$140 per ton, since natural gas in the United States is no longer a surplus commodity. Under the present circumstances it might, therefore, be economically justifiable to import ammonia for use as fuel.

At a price of \$1.18 per gallon, gasoline (energy density: 19,000 Btu/lb) produces 10×10^4 Btu per dollar, whereas at a price of \$100 per ton ammonia produces 17.6×10^4 Btu per dollar. Thus, under these conditions ammonia is a less expensive fuel than gasoline.(a)

It can be expected, though, that the Soviet Union will no longer sell the ammonia at \$100 per ton, since it could easily obtain \$140 per ton and still

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(a) A factor further supporting this contention is that combustion of ammonia is more efficient than gasoline (see above).

be competitive in the U.S. In other countries, where gasoline prices range between $2 and $3 per gallon (and occasionally even higher), ammonia may still be more economical. As mentioned above, ammonia prices have been varying widely in the last decade. This has induced many companies throughout the world to make ammonia production independent of natural gas supplies and base it on domestic coal resources. Belatedly, in the U.S. the Tennessee Valley Authority (TVA) operated National Fertilizer Development Center is joining in this development (Burnett 1979). A 225 ton-per-day retrofitted ammonia plant is under construction (for completion in mid-1980), using U.S. developed technology (Texaco process) for coal gasification. As of mid-1979, the ammonia from such a plant would have to sell for $147 per ton to make its operation profitable (C & EN. 1979).

Another basic energy source, which has much appeal for ammonia production, is nuclear energy (Green 1967, Blouin 1968, Corneil et al. 1977, Cast and Percival 1977, Gregory and Rosenberg 1973). Using nuclear energy ammonia can be synthesized from water and air. These two basic resources can be truly considered inexhaustible, since upon combustion ammonia will revert back to water and air. Indeed, when fusion reactors become viable at some time in the future, and when fossil fuel supplies have essentially been exhausted, ammonia and, possibly, hydrogen might be the only practical fuels that are available for use in transportation (Isaacs et al. 1978).

Nuclear reactors have already been proposed for providing the process heat required for synthetic fuel production from coal (Pieroni et al. 1964, Weinberg 1967, Vrable 1979). For hydrocarbon fuel synthesis, however, temperatures in the range from 871°C (1600°F) to 1649°C (3000°F) are required, which is well beyond the limitations of present materials in nuclear reactors. Process temperatures for ammonia synthesis are much lower (around 540°C); therefore, high temperature gas-cooled reactors of present design could be used for this purpose. (Even standard Light Water Reactors would be suitable.) Whereas the U.S. development of High Temperature Reactor technology (by General Atomics) has been severely curtailed since 1975, the Germans are still actively pursuing it and are now unquestionably the technical leaders in this field. Ammonia production has been specifically mentioned as one of the many possible applications of such reactors (Farbman and Brecher 1975). Various biochemical processes have also been proposed which would allow the synthesis of ammonia from air and water at ambient pressures and temperatures (Kovaly 1979). A similar, but non-biochemical, process is said to generate ammonia by passing water and nitrogen over a catalyst in the presence of sunlight. Even though the yields from such processes are still quite low, there is some hope that they can be increased, thus providing means for low-cost production of ammonia from just air, water, and solar energy.

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8.0 CONCLUSIONS

Ammonia appears to provide a viable alternative fuel from several vantage points:

- Environmental Compatibility - Being a noncarbonaceous fuel, air pollutants resulting from ammonia combustion would be reduced over those from comparable fossil fuels, particularly if the ammonia was produced using water and nuclear energy. Even with fossil feed stocks, ammonia use would reduce overall pollutant emissions by allowing fossil fuels to be converted to a noncarbonaceous form in large efficient plants without combustion before use.
- Safety - Ammonia has advantages in storage and transport over hydrogen due to its lower flammability and its high density storability at near atmospheric conditions.
- Fuel Characteristics - Ammonia can replace gasoline or diesel fuels requiring only slight modifications to engines. This would provide a fuel alternative in times of hydrocarbon-fuel shortages and allow conversion of energy from other large scale alternative systems (such as fusion) into a convenient fuel for small users (i.e., transportation).
- Economics - Price fluctuations in hydrocarbons and ammonia and world instability make projections difficult, but ammonia has viability as an alternate fuel in the near future and great promise as a long-term convenience fuel available from nuclear technologies. It also appears to be more economical as a means of storing hydrogen than alternative high pressure or cryogenic hydrogen storage systems.

Ammonia does have drawbacks in its combustion performance when compared with hydrocarbon fuels (Section 3.2) but these can be overcome; perhaps through the use of acetylene/ammonia mixtures. It also is a toxic material, but extensive use would no doubt provide the necessary experience in overcoming its safety problems. Before extensive use, however, research would be required in the safety aspects of storage and handling for automotive use and in the local impacts of unburned ammonia in confined spaces such as urban street canyons.

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REPORT Y

Hydrogen Safety and Environmental Control Assessment

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Prepared for the
Environmental and Safety Engineering
Division
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under Contract W-7405-ENG-36

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REPORT Y

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EXECUTIVE SUMMARY

At the request of the Environmental Control Technology Division of the U.S. Department of Energy (DOE) the Los Alamos Scientific Laboratory (LASL) has conducted a 2-1/2 year assessment program (ending September 1979) on concerns in hydrogen safety and environmental control. This assessment produced a current status base for the areas covered by the summary report,(1) including: transmission of gaseous hydrogen by pipeline, transport of liquid hydrogen, hydrogen embrittlement of metals, safety regulations, and environmental aspects of hydrogen production and use. Details of previous work are published in the first status report (Report U, DOE/EV-0036). The assessment found that hydrogen will be used ever increasingly in closer proximity to the general public, even if hydrogen has little impact on new energy markets. Because of this, the need continues for an ongoing assessment program in hydrogen safety and environmental control. The cost of the proposed program is estimated to be one million dollars for a four year effort (an average of $250,000 per year). The summary report on the Hydrogen Assessment Program (LA-8225-PR) outlines such a coordinated program and includes in appendices a report on some of the details of the assessment program conducted by LASL.

The proposed program has been developed to provide an ongoing assessment of hydrogen safety and environmental control. As hydrogen use and its public interactions continue to expand, new concerns are identified and old ones loom larger. These are identified, together with a coordinated program for resolving them. The program contains elements of assessment and analysis in the following areas: hydrogen production methods, especially thermochemical and coal gasification processes; storage methods, including liquid, hydrides, high pressure gas, and gas in underground chambers; transport and transmission; end uses, including vehicular and space heating; and understanding the dispersion, ignition, and effects of large scale releases of gaseous or liquid hydrogen.

Regarding hydrogen production, the assessment points out that the areas of new thermochemical processes and coal gasification are ones needing further work on potential emissions and their effects on the environment, their control and disposition.

Hydrogen storage systems include cryogenic liquid, metallic or chemical hydrides, and compressed gas in cylinders at high pressure, or in underground chambers at low pressure. Safety and environmental features of these must be assessed for generic and specific locations.

Safety in the transport of increasing amounts of hydrogen as compressed gas, metal hydride, or cryogenic liquid requires continued assessment and analysis. Especially needed are relative assessments comparing hydrogen with natural gas and liquefied natural gas. As specific proposals are made for the introduction of hydrogen into natural gas pipeline systems, further detailed questions arise concerning compressors, pipes, leaks and associated hazards.

The program outlined for assessing end uses of hydrogen includes the following: pollutant emissions and novel methods of control for internal combustion engines; environmental effects of emissions of water in combination with other pollutants from high-flying, hydrogen-fueled aircraft; safety of hydrogen-fueled vehicles; and pollutant emissions and effects from hydrogen consuming equipment in homes and industry.

The final major, and most expensive, element of needed assessment is of effects of large scale spills of liquid or gas. This includes work to understand better the dispersion and ignition of combustible hydrogen mixtures.

REFERENCES

1. Edeskuty, F. J. et. al., Hydrogen Safety and Environmental Control Assessment, Los Alamos Scientific Laboratory, LA-8225-PR, March 1980.

Technical Report Documentation Page

1. Report No.
DOE/EV-0085 Vol 3 of 3

2. Government Accession No.
DOE/EV-0085 Vol 3 of 3

3. Recipient's Catalog No.

Title and Subtitle
Liquefied Gaseous Fuels Safety and Environmental
Control Assessment Program: Second Status Report

5. Report Date
October 1980

6. Performing Organization Code

7. Author(s)

8. Performing Organization Report No.

9. Performing Organization Name and Address
Pacific Northwest Laboratory
Post Office Box 999
Richland, Washington 99352

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
U.S. Department of Energy
Environmental and Safety Engineering Division
Mail Room E-201 (EV-132)
Washington, D.C. 20545

13. Type of Report and Period Covered

14. Sponsoring Agency Code

15. Supplementary Notes
This report was prepared by Dr. John G. DeSteese and staff under the cognizance of Dr. John M. Cece and Dr. Henry F. Walter. Comments about this document may be directed to the latter at the address in box 12.

16. Abstract

The DOE Assistant Secretary for Environment has responsibility for identifying, characterizing, and ameliorating the environmental, health, and safety issues and public concerns associated with commercial operation of specific energy systems. The need for developing a safety and environmental control assessment of liquefied gaseous fuels was identified as a result of discussions with various Government, industry, and academic persons having expertise with respect to particular materials. A program to address relevant issues has evolved. (Full plan contained in DOE/EV-0036, May 1979)

The goal of the Program Plan is to gather, analyze, and disseminate technical information that will aid future decisions by industry, regulators, and the public relating to facility siting, system operations, and accident prevention. (This research complements related programs supported by other Government agencies and industry.) To accomplish the goal, three objectives have been identified: verified predictive capability; verified prevention methods; verified control methods.

Volume 1 of this document outlines the DOE Liquefied Gaseous Fuels Safety and Environmental Control Assessment Program, briefly summarizes the 25 technical reports, and includes annotated bibliographies for LNG and LPG. Volume 2 contains 19 research reports focused on LNG. Volume 3 contains 6 research reports on LPG, hydrogen, and anhydrous ammonia. These reports discuss key developments between January 1979 and April 1980.

Preceding documents reporting earlier information are DOE/EV-0036 (May 1979) and DOE/EV-0002 (February 1978).

17. Key Words
liquefied gaseous fuels
scale effects experiments
vapor generation
vapor dispersion
flame propagation
flame propagation
instrumentation
release prevention

18. Distribution Statement
This document is available under catalog number DOE/EV-0085, Volume 3 of 3 from
National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
264

22. Price
Copy: $10.75
Fiche: $ 3.50

Reproduction of completed page authorized

VOLUME 3 OF 3