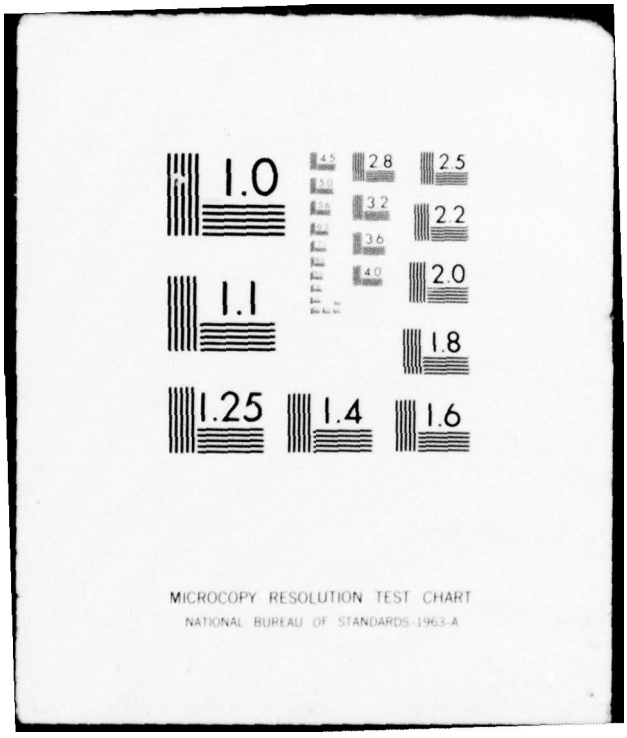
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REPORT NO. CG-D-56-77
TASK NO. 4152.3.1

FEASIBILITY STUDY OF RESPONSE TECHNIQUES FOR DISCHARGES OF HAZARDOUS CHEMICALS THAT FLOAT ON WATER

John S. Greer
MSA RESEARCH CORPORATION
Division of Mine Safety Appliances Company
Evans City, Pennsylvania 16033

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UNITED STATES COAST GUARD
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16. Abstract

An in depth evaluation was conducted of potential response techniques for ameliorating the vapor hazard from discharges of hazardous chemicals that float on water. Fifteen techniques were selected on the basis of their performance in similar situations, such as oil spills and hazardous chemical production or handling. Six of these techniques were judged to be feasible methods for achieving the objectives of this program. Vaporization rate reduction, the objective of Task I, could be achieved by using surfactant films, foams or sorbents. Vapor concentration reduction, the objective of Task II, could be achieved by encapsulation. Vapor flammability reduction, the objective of Task III, could be achieved by using foams and water aerosols. Techniques utilizing particulate cover, "foamed-in-place" urethane layer, gels and cryogenic cooling were defined as having potential for successful utilization. All techniques were judged to need some further development or assessment. Recommendations for specific programs are presented.

17. Originator's Key Words: Hazardous Chemicals, Hazardous Substances, Amelioration, Discharge Response, Spill Response, Floating Hazardous Chemicals, Toxic Substances, Vaporization Rate Reduction, Vapor Concentration Reduction, Vapor Flammability Reduction, Foams, Sorbents, Gels, Cryogens, Dilution	18. Availability Statement: This document is available to the U.S. public through the National Technical Information Service, Springfield, VA 22161		
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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
	LENGTH			
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
	AREA			
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
	MASS (weight)			
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
	VOLUME			
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
	TEMPERATURE (exact)			
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
	LENGTH			
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
	AREA			
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
	MASS (weight)			
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
	VOLUME			
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
	TEMPERATURE (exact)			
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

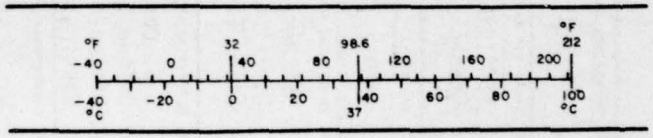


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INTRODUCTION

The Federal Water Pollution Control Act Amendments of 1972 and the National Oil and Hazardous Substances Pollution Contingency Plan (1973) which resulted from that act have given the Coast Guard the responsibility for responding to all spills of hazardous chemicals which occur into the waters of the United States. This responsibility includes the containment, removal and ultimate cleanup and disposal of many hazardous materials which have greatly different physiological, toxicological and ecological properties.

Previous pollution control measures have emphasized the reduction and removal of potential hazards to the aquatic ecosystem. The major areas of concern included petroleum and petroleum products. When the Environmental Protection Agency expanded the list of hazardous substances and the Coast Guard assembled their Chemical Hazards Response Information System (CHRIS) (1974), it became evident that modified or new developments in response techniques would be required for the protection of spill response personnel.

Hazardous chemicals that float on water are recognized to present two hazards to spill response personnel that are generally not encountered with oil spills. These are 1) toxic liquid or vapor concentrations and 2) potentially flammable vapor clouds and liquid pools.

Purpose

The primary objective of this program has been to determine the feasibility of various spill response techniques as they might apply to the amelioration of spills of hazardous chemicals which float on water.

This evaluation has been limited to those response techniques affecting the airborne vapor hazards associated with spills of these chemicals. Most spill response techniques have been developed for petroleum and petroleum products, where vapor hazards are less critical. The safety of response personnel and surrounding life becomes a primary objective, however, for spills of hazardous chemicals.

An evaluation of the feasibility of response techniques for the amelioration of spills of floating, hazardous chemicals requires data concerning the safety, efficiency and compatibility of all components. Experience and expertise must be combined in evaluating the chemical and physical aspects of a spill to assess the candidate techniques.

Candidate response techniques may be collected into three basic categories:

1. those which reduce evaporation
2. those which reduce vapor concentration
3. those which reduce vapor flammability

General Background

The major portion of spill response experience, as it pertains to aquatic ecosystems, has been obtained from confrontations with petroleum spills. Excellent reviews of the most promising techniques for treating such spills have been published by Gilmore et al. (1970), Pilie et al. (1975) and Wilder and Lafornara (1972). Three national conferences have also contributed to the development and dissemination of response techniques for the control of hazardous material spills (1972, 1974, 1976). A general listing appears in Table 1.

Gilmore, G.H.; Smith, D.D.; Rice, A.H.; Shenton, E.H. and Moser, W.H., Systems Study of Oil Spill Cleanup Procedures, Contract OS-1 (1970).

Pilie, R.J.; Baier, R.E.; Ziegler, R.C.; Leonard, R.P. Michalovic, J.G.; Pile, S.L. and Bock, D.H., Methods to Treat, Control and Monitor Spilled Hazardous Materials, Contract No. 68-01-0110, Rept. No. EPA-670/2-75-042 (1975).

Wilder, I. and Lafornara, J.P., "Control of Hazardous Materials Spills in the Water Environment", Waste and Sewage Works, January (1972).

TABLE 1 - SPILL RESPONSE TECHNIQUES

A. CONTAINMENT

1. Booms and Barriers
2. Liquid "herders"
3. Gelation
4. Flocculation

B. CLEANUP AND REMOVAL

1. Weirs
2. Vacuum collectors
3. Skimming collectors
4. Adsorption
5. Burning
6. Sinking or Precipitation
7. Neutralization
8. Solvent extraction
9. Centrifuge-separation
10. Bacteriological degradation
11. Catalytic oxidation
12. Chelation
13. Gelation
14. Ion exchange

C. VAPORIZATION REDUCTION

1. Thin films
2. Foam cover
3. Gelation
4. Cryogenic cooling
5. Adsorption

D. CONCENTRATION REDUCTION

1. Dispersion
2. Dilution
3. Adsorption
4. Cryogenic condensation
5. Encapsulation

E. FLAMMABILITY REDUCTION

1. Inert foam cover
2. Dilution
3. Liquid suppressant addition
4. Cryogenic cooling
5. Vapor suppressant addition

The variety of response techniques assessed by Gilmore et al. (1970) has been further investigated by Dawson et al. (1970), with the major conclusion being that confinement of the spill, in combination with the use of adsorbents, is the best approach towards the amelioration of aquatic oil spills. Definitions of the "best" adsorbents change periodically, as further investigations and interpretations of results are included in these assessments.

Much of the experience and technology developed for treatment and removal of petroleum spills can be used as a basis for the development of response techniques for floating, hazardous chemicals. There are four major differences between petroleum and hazardous chemicals, however, which significantly increase the risks of treating the latter. The hazardous chemicals may have:

1. A broader range of physical and chemical properties
2. Toxic and/or flammable vapors
3. Greater compatibility and corrosion problems
4. A propensity to decompose to toxic products.

1. The physical and chemical properties of oils follow a repetitive pattern. Floating, hazardous chemicals are similar to these only in that their densities are less than that of water. Melting or boiling points, toxicities, vapor pressures and chemical reactivities have few similarities.

2. Most of the floating, hazardous chemicals have vapor pressures which, under ambient conditions, will generate

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Dawson, G.W., Shuckrow, A.J. and Swift, W.H., Control of Spillage of Hazardous Polluting Substances, Contract No. 14-12-866, NTIS Rept. No. 197 596 (1970).

Gilmore, G.H.; Smith, D.D.; Rice, A.H.; Shenton, E.H. and Moser, W.H., Systems Study of Oil Spill Cleanup Procedures, Contract OS-1 (1970).

vapor cloud concentrations in excess of their threshold limit concentration values. They require the use of more intricate and sensitive instrumentation to detect and monitor, for the protection of response personnel.

3. Compatibility and corrosion are almost negligible when using the common manufacturing materials against oil spills. Many plastics are attacked by the floating, hazardous chemicals, but even the metal equipment is subject to greater corrosion.

4. Both hazardous chemicals and petroleums are flammable. The greater vapor pressures and reactivities of the hazardous chemicals increase the risks of fire or explosive reactions. In addition, many of these chemicals decompose at flame temperatures to form toxic byproducts or react to form toxic products.

The selection and development of spill response techniques for floating, hazardous chemicals considered these areas to choose candidates compatible with their physical and chemical properties. Modifying each technique to be applicable in all situations creates an unwieldy variety, whereas some response techniques for oil products are easily adaptable. Response technologies are being continually expanded, creating a broader background of information and experience from which decisions can be made.

Recent emphasis has been upon the removal and recovery of petroleum and petroleum products from moving waters. Ayers et al. (1975) and Beach and March (1975) have published results on petroleum-retrieval-systems which appear feasible for removing these chemicals where currents are present.

Ayers, R.R.; Bickham, K.L.; Fraser, J.P. and Titus, P.E., A Zero-Relative-Velocity Belt Skimmer, Report No. CG-D-116-75 (April, 1975).

Beach, R.L. and March, F.A., Development of a Streaming-Fiber Oil Spill Control Concept, Report No. G-D-35-75 (March, 1975).

Spill response techniques having general applicability towards the broader scope of hazardous, floating chemicals, have been outlined by Sinclair and Bauer (1976). A listing of containment and recovery devices which appeared to be applicable for floating hazardous chemicals is reproduced as Table 2.

Sinclair, J.R. and Bauer, W.H., "Containment and Removal of Floating Hazardous Chemicals with Commercially Available Devices", Nat'l. Conf. on Control of Hazardous Material Spills (1976).

TABLE 2 - TYPICAL CONTAINMENT AND RECOVERY DEVICES (Sinclair and Bauer [1976])

Most Advantageous Containment Devices'

OFF-THE-SHELF

1. VIKOMA SEAPACK, The British Petroleum Co., Ltd.
2. OFFSHORE BOOM, Clean Water, Inc.
3. BOA-BOOM I, and BOA-BOOM II, Environetics, Inc.
4. "SEA SENTRY" IM, The Goodyear Tire and Rubber Co.
5. HIGH SEAS BARRIER, Offshore Devices, Inc.
6. POLLUTION BOOM, A. G. Peterson & Sons, Inc.
7. MINI SEALDBOOM and STANDARD SEALDBOOM, Uniroyal, Inc.
8. BOOM, TYPES E, T-8, and T-16, William Warne & Co., Inc.
9. STANDARD OIL BOOM and HEAVY DUTY BOOM, Gamlen Chemical Co.

EASILY MODIFIED

1. ACME "O.K. CORRAL", Acme Products Co.
2. OPTIMAX and SIMPLEX, American Marine, Inc.
3. INSHORE and OFFSHORE BOOMS, Bennett Pollution Control Ltd.
4. CWI HARBOUR BOOM, Clean Water, Inc.
5. COASTAL OIL BOOM, Coastal Services, Inc.
6. ANTI-POLLUTION BOOM, Gamlen Chemical Co.
7. STANDARD BOOM, Hurum Enterprises, Inc.
8. TYPE I and TYPE II OIL BARRIER, The Marsan Corporation
9. CALM-WATERS SEA CURTAIN and FAST & CHOPPY WATER CURTAIN, Kepner Plastics Fabricators, Inc.
10. MP BOOM, Metropolitan Petroleum Petrochemicals Co., Inc.
11. HARBOUR CONTAINMENT BARRIER, Ocean Systems, Inc.
12. MEGATOR MINI-BOOM, Megator Corporation
13. ALUMINUM BOOM, Kepkan, Inc.
14. AQUA FENCE, Pacific Pollution Control, Inc.
15. MARK V and MARK VI HARBOR & RIVER BOOMS, Slickbar, Inc.
16. SEA BOOM 3PF, Submarine Engineering Assoc., Inc.

Most Advantageous Recovery Devices'

INFLEXIBLE PLANE SKIMMERS

1. VIKOMA SEASKIMMER, B. P. North America, Inc.
2. CLEAN SWEEP, Lockheed Missiles and Space Co., Inc.

MOVING BELT SKIMMERS

1. BELT OIL SKIMMER, Aerodyne Development Co.
2. INSHORE-OFFSHORE SKIMMER, Bennett Pollution Control Ltd.
3. REX BELT SKIMMER, Envirex, Inc.
4. DIP SKIMMERS, JBF Scientific Corp.
5. MARCO SKIMMERS, CLASS I, II, III, Marco Pollution Control Corp.
6. OIL MOP, Oil Mop, Inc.
7. RECLAIMATOR SKIMMER, Peabody Welles, Inc.
8. SLICKLICKER, R. B. M. Cybernetics (1970) Ltd.

SUCTION HEAD SKIMMERS

1. ACME MODELS FSV5 and FSV40, Acme Products Co.
2. MEGATOR DELTA MARK II, BETA MARK II and PUDDLE MOP, Megator Corp.
3. OILHAWG, Parker System, Inc.
4. SLICKSKIM, Slickbar, Inc.

WEIR SKIMMERS

1. ACME MODELS SK-39T and SK-51T, Acme Products Co.
2. SLURP SKIMMER, Coastal Services, Inc.
3. CRISAFULLI AQUA-SWEEPER and MINI-SWEEPER, Crisafulli Pump Co.
4. OELA-III, Industrial Municipal Engineering
5. SEA BOOM, Sunshine Chemical Corp.
6. ORS MODELS 125, 1000, and 2000, Ocean Systems, Inc.

FLOATING SORBENT MOVING BELT SKIMMER

1. "SOP" SYSTEM, Ocean Design Engineering Corp.

Sinclair, J.R. and Bauer, W.H., "Containment and Removal of Floating Hazardous Chemicals with Commercially Available Devices", Nat'l. Conf. on Control of Hazardous Material Spills (1976).

RESPONSE TECHNIQUE SELECTION CRITERIA

Study Approach

Spills of floating, hazardous chemicals usually involve smaller quantities than those of oils and petroleum products. Potential hazards are greater, however, in that these chemicals combine vapor toxicity with flammability hazards and are more difficult to detect and monitor. Most of the floating, hazardous chemicals are colorless, and therefore present a difficult problem for visual detection, compared to the opaque oils.

Consequently, response techniques involving confinement and immobilization must be modified to meet these different properties, when being transferred from oil spill to hazardous chemical response technology. Providing "absolute" safety protection against spills of all hazardous chemicals is probably impossible, but at best would involve a complex system which would be expensive and unwieldy for rapid responses.

The objective of this investigation has been to select those response techniques providing adequate protection against the greatest variety of chemicals. This selection involved the consideration and evaluation of response techniques designed to ameliorate spills of any chemical on water.

A review of chemical properties and the accumulation of pertinent literature on response techniques was initiated early in the program and continued to interface with individual tasks as new data or different correlations were required for evaluation.

Candidate Evaluation

A pragmatic evaluation of this program reveals the primary objective to be the protection of Coast Guard personnel responding to spills of floating, hazardous chemicals. The evaluation of candidate response techniques followed three general areas in which hazard amelioration was possible. The investigation was separated into three tasks, which treated these three areas independently:

Task I - Vaporization Rate Reduction
Task II - Vapor Concentration Reduction
Task III - Vapor Flammability Reduction

The evaluations of all candidate response techniques followed a general pattern of approximately six steps:

1. Definition of the response technique and its technology
2. Selection and elaboration of high potential candidates
3. Practical and theoretical evaluation of specifications
4. Calculations and estimations of performance
5. Ranking of techniques
6. Research and development recommendations

A graphical presentation of the logical pattern is presented in the diagram of Figure 1.

In this program, immobilization or confinement of the floating chemical was considered necessary to prevent dispersion. Immobilization or confinement will alleviate the problems of detecting and monitoring a proliferation of liquid or vapor phases.

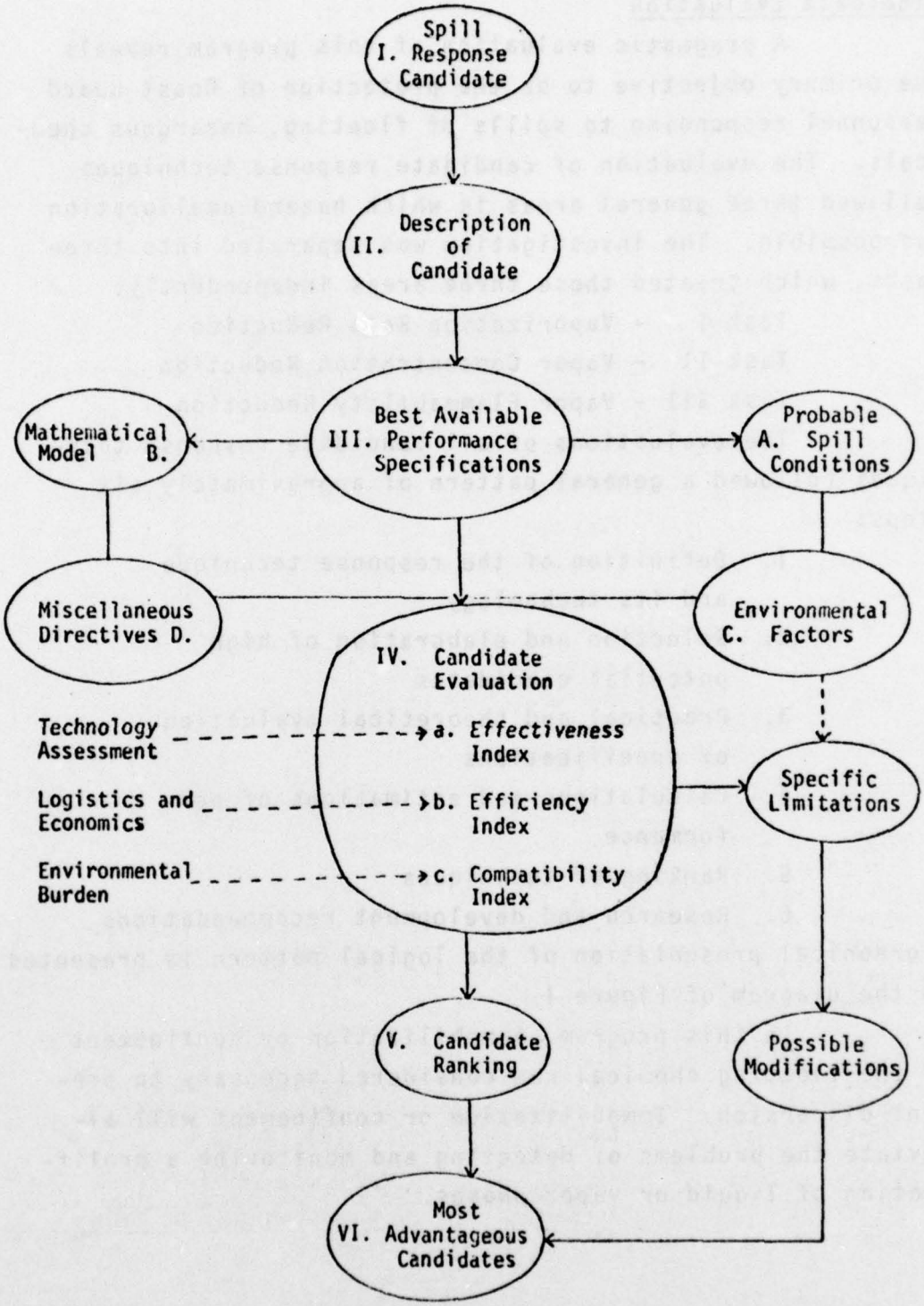


FIGURE 1 - ANALYTICAL EVALUATION PROCEDURE FOR CANDIDATE SPILL RESPONSE TECHNIQUES

Some chemical and physical similarities of oils and floating, hazardous chemicals aid the assimilation of confinement technology into response techniques. This aspect of hazardous chemical spill amelioration has been investigated by Bauer et al. (1976), Freestone et al. (1976), Sinclair and Bauer (1976), Pilie et al. (1975) and Bauer et al. (1974).

Vaporization Rate Reduction - Task I

The objective of this task was to assess the capabilities of candidate spill response techniques for reducing evaporation from the surface of a spill of floating, hazardous chemical. Techniques were ranked according to their ability to ameliorate toxicity and/or fire hazards associated with these vapors, for the protection of response personnel and also the general environment.

Bauer, W.; Borton, D.N.; Bulloff, J.J. and Sinclair, J.R., "Agents and Methods for Amelioration of Discharges of Hazardous Chemicals on Water", National Conference on Control of Hazardous Material Spills (New Orleans, 1976).

Freestone, F.J.; Lafornara, J.P.; Sinclair, J.R. and McCracken, W.E., "Performance Testing of Several Oil Spill Control Devices on Selected Floatable Hazardous Materials", National Conference on Control of Hazardous Material Spills, (New Orleans, 1976).

Sinclair, J.R. and Bauer, W.H., "Containment and Recovery of Floating Hazardous Chemicals with Commercially Available Devices", National Conference on Control of Hazardous Materials Spills, (New Orleans, 1976).

Pilie, R.J.; Baier, R.E.; Ziegler, R.C.; Leonard, R.P., Michalovik, J.G.; Pile, S.L. and Bock, D.H., "Methods to Treat, Control and Monitor Spilled Hazardous Materials", Report No. EPA-670/2-75-042, Contract No. 68-01-0110, (June, 1975).

Bauer, W.; Bulloff, J. and Borton, D., Agents, Methods and Devices for Amelioration of Discharges of Hazardous Chemicals on Water, Contract No. DOT-CG-52759-A (1974).

The approach toward this objective involved identification of the factors influencing evaporation rates, investigation of response techniques having some effect on these factors, evaluation of their efficiencies and selection of "the best response technique". Evaporation rates are controlled by five major factors:

1. Heat transfer
2. Surface area
3. Surface turbulence
4. Surface cleanliness
5. Vapor-saturated interfacial film

Evaporation is the process by which molecules of a liquid are transferred into a gas phase. The transport of molecules across the phase boundary requires energy and therefore evaporation is an endothermic process. Vaporization is controlled by heat transfer, an interfacial film and surface cleanliness.

Heat transfer and insulation are properties which have been thoroughly studied. A considerable body of literature was available for theoretical evaluation and practical application. It was sufficient for this evaluation to recognize that anything promoting heat transfer into the spilled chemical would aid vaporization while anything reducing heat transfer or removing thermal energy would inhibit it.

Surface area and surface turbulence are contributing factors in heat transfer. The total heat transferred is directly proportional to both, increasing their significance in determining evaporation.

Surface turbulence aids evaporation by minimizing the effects of the interfacial film. Surface convection, induced by either thermal gradients or gas turbulence, provides the natural means of increasing evaporation. The

surface is cooled by vaporization and any disruption can provide a source of energy to offset evaporative cooling effects.

The influence of surface cleanliness is of considerable interest in this program since it reflects many of the parameters desired in the methods to be applied for vaporization rate reduction. The presence of surface contaminants disrupts the interfacial film, interferes with heat transfer and can also influence surface convection currents.

Vaporization rate reductions may be obtained by five candidate spill response techniques:

1. Surfactant films
2. Foams
3. Sorbents
4. Gelling agents
5. Cryogens

Vapor Concentration Reduction - Task II

The objective of this task was to evaluate candidate spill response techniques concerning their capabilities for reducing vapor concentrations released from spills of floating, hazardous chemicals. The criteria used to evaluate the various techniques were similar to those of Task I: ranking them according to their ability to reduce hazardous chemical vapor concentrations below the threshold limit value or lower flammability limit.

The approach used to attain this objective was to identify the controlling factors, codify the techniques affecting these factors and select the ones having the best capabilities for reducing vapor concentrations.

Vapor concentrations are controlled by temperature, vapor pressure, diffusion and dispersion. The influence of evaporation, and its component factors, was investigated in

Task I. Eliminating the control of evaporation, vapor concentrations above spills of hazardous chemicals may be reduced by five general operations:

1. Dilution
2. Sorption
3. Condensation
4. Encapsulation
5. Reaction

Vapor Flammability Reduction - Task III

The objective of this task was a critical evaluation of methods which could be used to ameliorate the fire hazards associated with floating, hazardous chemicals. Potential techniques for reducing flammability were assessed on the basis of published, measured and estimated data for the pertinent controlling factors.

The approach used to evaluate vapor flammability reduction techniques was the preparation of a theoretical description of flammability hazards and the factors influencing their generation, the selection of response techniques having desirable effects on these factors and the consideration of their efficiency, effectiveness and ultimate fate (consequences) to prepare an estimate of potential applicability.

Vapor flammability is controlled by four factors:

1. Fuel concentration
2. Oxidizer concentration
3. Activation or initiation energy
4. Reaction energy

Fuel concentrations are determined by the vapor pressure of the spilled chemical and environmental conditions at the scene of the spill. The concentration is limited to the partial pressure at equilibrium of the individual chemicals, but for many hazardous chemicals this exceeds the lower flammability limit.

Oxygen concentrations of the gas mixtures generated by chemical spills are set by the ambient atmosphere. Both the fuel and oxidizer concentrations may be reduced by the addition of inert gases, but this has limited applicability for some hazardous chemicals (e.g., tert-butyl hydroperoxide) which do not require additional oxidizer.

Activation or initiation energies demonstrate the broad range of properties exhibited by the floating, hazardous chemicals. The amount of energy required to initiate a combustion reaction may be increased by the addition of energy-absorbing or reactive-intermediate-absorbing materials. Any response technique which operates within this area should create an essentially inert gas mixture.

The reaction energies available from combustion of floating, hazardous chemicals are frequently sufficient to make these reactions self-propagating. The amount of energy, or strength of the reaction, will depend upon the components and their relative concentrations in the reacting mixture. The energy released from combustion reactions may be controlled by dilution with inert materials or various reaction mechanism inhibitors. The method available to ameliorate combustion reactions all require the expenditure of a considerable amount of energy to prepare homogeneous gas mixtures. Flames propagating through heterogeneous mixtures, even containing suppressants, have greater strength than those of equivalent, homogeneous mixtures.

Amelioration of flammability hazards around spills of hazardous chemicals may be accomplished by five techniques:

1. Flame Inhibitors
2. Dilution
3. Cryogens
4. Foams
5. Aerosols

Definitions and Terminology

Vaporization rate, the main term used in Task I, may be defined by several combinations of units, which reflect the experimental method used in measurement. The common terminology used in this program defined vaporization rates in units of mass per unit time (g/sec or lb/sec). This vaporization rate is assumed to be the result of random, uninhibited, molecular motion.

The term permeation is used to describe vaporization losses when an attempt has been made to reduce evaporation. The units for this term may reflect both the method used for reducing evaporation and the method used to measure it. The units most commonly reported are length per unit time (cm/sec or in /sec).

A reciprocal unit, resistivity, has been defined to measure the efficiency of methods used to reduce the vaporization rate. It is commonly reported as the reciprocal of time times distance (cm^{-1} sec^{-1} or in^{-1} sec^{-1}).

Terminology in Task II resolves into that used to signify vapor concentrations. Common units are percentages or parts per hundred parts and parts per million parts, expressed as volumes. Some uncertainties may be generated by evaluating vapor concentration reductions in terms of percentages of either percentages or parts per million (parts). This has been common usage, however, and does offer a rapid means of comparison.

The terms used in measuring or defining flammability are somewhat more vague. This reflects the complex physical and chemical phenomena occurring during deflagrations and also some of the bewilderment of investigators attempting

to define and measure these phenomena by empirical knowledge or inadequate theoretical information.

The lower flammability limit is defined as that fuel concentration below which no self-propagating flame can be initiated. Variations occur with temperature and pressure but it is usually defined for air at ambient temperatures and pressures.

There is a plethora of terms used in describing the reduction of flammability hazards. The term, retardant, is generally used as a categorical term to signify any compound having a negative effect on the propagation of a flame.

The term inhibitor is used in this report to describe those compounds which increase the amount of energy required to initiate a flame, reduce the rate of reaction or reduce the range of concentrations which will support a self-propagating flame. Although inhibitors may be further divided according to the chemical or physical means or mechanisms involved, these separations were not considered necessary for the objective of this program.

Three indices were used to assess the feasibility of response techniques: 1) effectiveness, 2) efficiency and 3) compatibility. The effectiveness index was a technological assessment of the protection provided by each technique in terms of vaporization, concentration or flammability reduction. The efficiency index assessed the techniques in terms of their availability, economical and logistical factors. The compatibility index assessed the techniques in terms of their environmental compatibility and factors regarding their ultimate disposal. The diverse nature of spills and response techniques made these assessments rather general in nature and the indices were described as acceptable, conditionally acceptable with modifications or unacceptable.

The primary assessment in the effectiveness index was whether the technology and materials used in a candidate response technique were capable of fulfilling the objectives of the task. Data from areas such as experience, development and maintenance were the more concrete means for developing this assessment. Estimates and extrapolations had to be made in some areas, such as the difficulties of incorporating equipment and procedures developed for oil (or another hazardous material category) into a scheme for responding to many different chemicals.

Other such areas included: the definition of typical spill conditions, longevity or working lifetimes of response techniques and mathematical descriptions of vaporization, dispersion and flammability phenomena.

The final evaluation had to be made in rather general terms because many of the final comparisons and correlations were made between experimental data or practical experience and theoretically defined circumstances.

The primary criterion used in determining the efficiency index was how well the candidate technique could be installed aboard a ship and operate in the marine environment. Secondary considerations within this area included such things as availability, stability, economics and the logistics of treating a typical marine spill.

The compatibility index was determined by assessing the compatibility of candidate techniques with the environment and the hazardous chemicals. Logical estimates or data available for other criteria, such as personnel safety hazards and removal or possible reclamation of the hazardous chemical and response materials were also included in this evaluation.

Vapor Dispersion Model

A mathematical model, describing the natural dispersion of vapors from a spill, was an important tool in evaluating the efficiency of spill response techniques. The standard Sutton or Pasquill model has been well documented by Turner (1969). Variations have been developed and used by Eckert (1959), Murad et al. (1970) and Srinivasan et al. (1975).

The standard approach was found to have the following faults, when applied to the special needs of this investigation:

1. The steady state equations do not permit diffusion in the downwind direction.
2. The instantaneous source equation does not have the property that at time zero the concentration is zero if x, y or z is not zero.

The model for this study used an instantaneous scattering kernel that was consistent with the prior literature but corrected the defects in the standard dispersion equations, thereby allowing more accurate calculations when concentration gradients were large. By using a scattering kernel of the same general form, but with the coefficients dependent on time rather than x distance (specifically time raised to a power), internally consistent results are obtained and the overall results approach the steady state values.

Turner, D.B., Workbook of Atmospheric Dispersion Estimates, PHS Publication No. 999-AP-26 (1969).

Eckert, E.R.G., Introduction to the Transfer of Heat and Mass, I Edition, McGraw-Hill (1959).

Murad, R.J.; Lamendola, H.I. and Summerfield, M., "A Study of Some Factors Influencing the Ignition of a Liquid Fuel Pool", Combustion and Flame 15, 289 (1970).

Srinivasan, S.; Thomas T.; Geyer, A.; Coyle, A. and Kimm, C., Influence of Environmental Factors on Selected Amelioration Techniques for Discharges of Hazardous Chemicals, Contract No. DOT-CG-23223-A-18, Report No. CG-D-81-75 (1975).

Dispersion from point sources depends upon atmospheric conditions, physical properties of the spilled chemical and the distance separating the sampling point and the source point. The concentration of the hazardous vapor species at any location was considered as the sum of the contributions of all the points. In order to decrease computer time, integration in the crosswind direction was represented in closed form, and the summation done only in the direction of wind flow. The program for the Digital PDP-8/L computer is presented in Appendix B.

The following set of parameters has been used in preparing a typical spill situation for evaluating candidate spill response techniques:

Spill volume	3800 to 38,000 liters	100 to 10,000 gal
Spill thickness	∿1 centimeter	∿0.4 inch
Spill area	380 to 3800 square meters	4070 to 40,700 sq ft
Spill temperature	27° Celsius	80° Fahrenheit
Wind speed	16.1 kilometers per hr	10 miles per hr

A more detailed description of the spill conditions, used for evaluating candidate response techniques within the three separate tasks of this program, was developed through the use of the mathematical model of vapor dispersion. The model predicts that an area of approximately 7.4×10^5 m^2 (8×10^6 ft^2) would be exposed to benzene vapor concentrations of 10 ppm or more, ten minutes after a spill of 38 m^3 (10,000 gal). The volume of the vapor cloud would be approximately 5×10^6 m^3 (1.8×10^8 ft^3), much more than could be practically confined or diluted to remove toxicity problems. Similar results have been obtained for aniline and toluene 2,4-diisocyanate in which the combination of vapor pressures, diffusivities and threshold limit values compensate one another.

The computer model of vapor dispersion was also capable of describing upwind diffusion of hazardous, chemical vapors. Using conditions of 27°C (80°F) and a 16.1 km/hr (10 mi/hr) wind for a simulated spill of benzene, it was found that upwind diffusion would not create a hazard for response personnel.

A graphical representation of the vapor cloud resulting from a typical spill is depicted in Figure 2. Vapor rise above the spill has been deleted, for ease of presentation, but would be as much as a hundred feet above the surface. These data were calculated for a spill of 38 m^3 (10^4 gal) covering a 3.8 x 10^3 m^2 (4 x 10^4 ft^2 or ~115 x 350 ft) at 27°C (80°F) in a16.1 kph (10 mph) wind.

The total volumes to be treated have also been considered, as a function of the source, assuming the "effective vapor pressure" or evaporation rate could be controlled by a separate means. The resulting vapor cloud volumes are shown in Figure 3, as calculated from the vapor dispersion model.

A similar correlation is shown in Figure 4, where the vapor cloud volume is plotted against pool length. Our calculations have assumed a rectangular pool for which the ratio of crosswind and downwind measurements remain at 0.75.

The model does, however, predict dramatic changes in concentration near the spill boundaries. Isopleths have been calculated for a typical spill, also. The area of the vapor cloud containing 325 ppm or more vapor has been inset into Figure 2 for comparison. High vapor concentrations, especially those close to the lower flammability limit, would be confined to the immediate spill area, for most weather conditions.

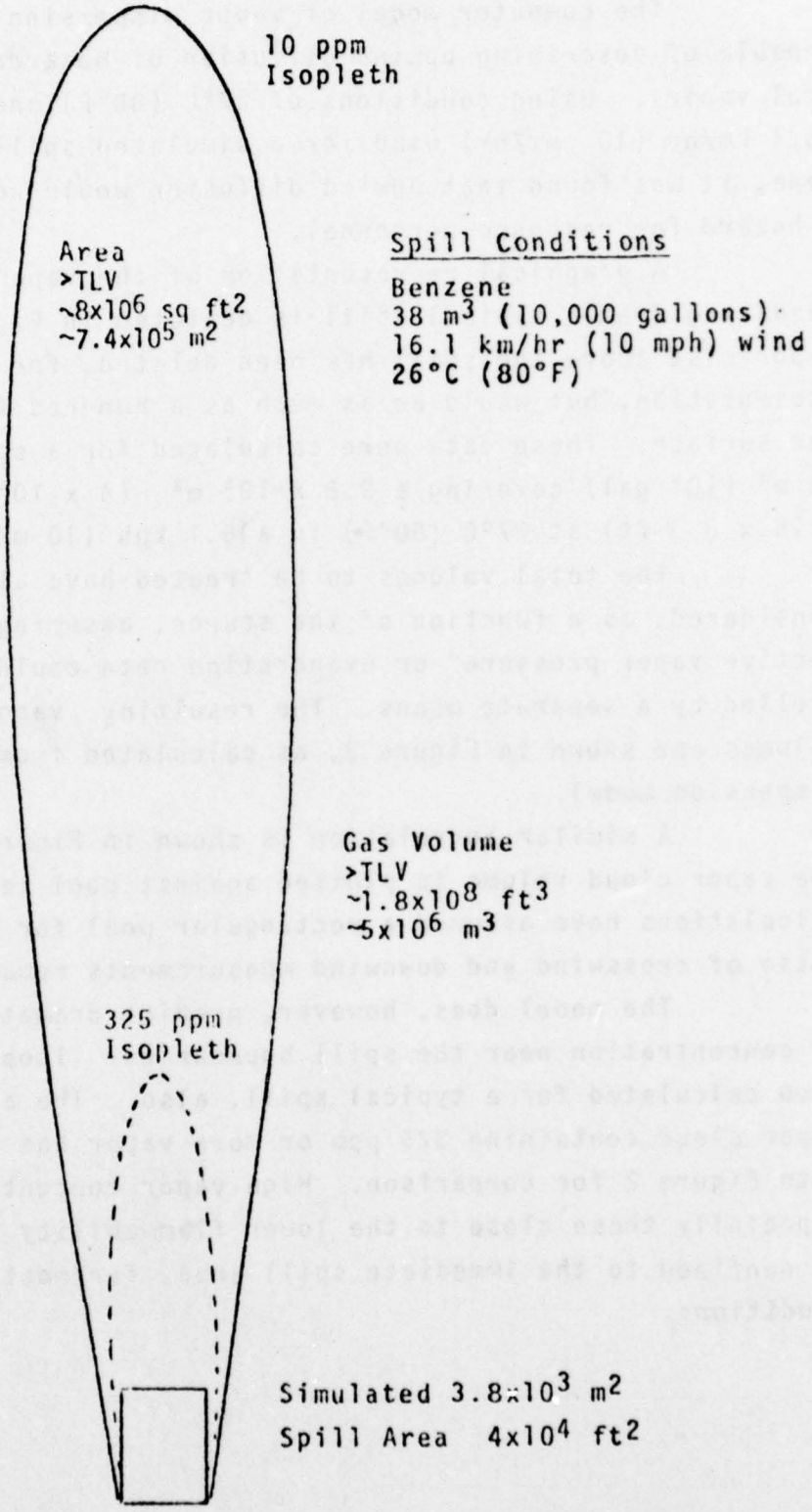


FIGURE 2 - MATHEMATICAL DESCRIPTION OF VAPOR CLOUD RESULTING FROM A SPILL OF BENZENE

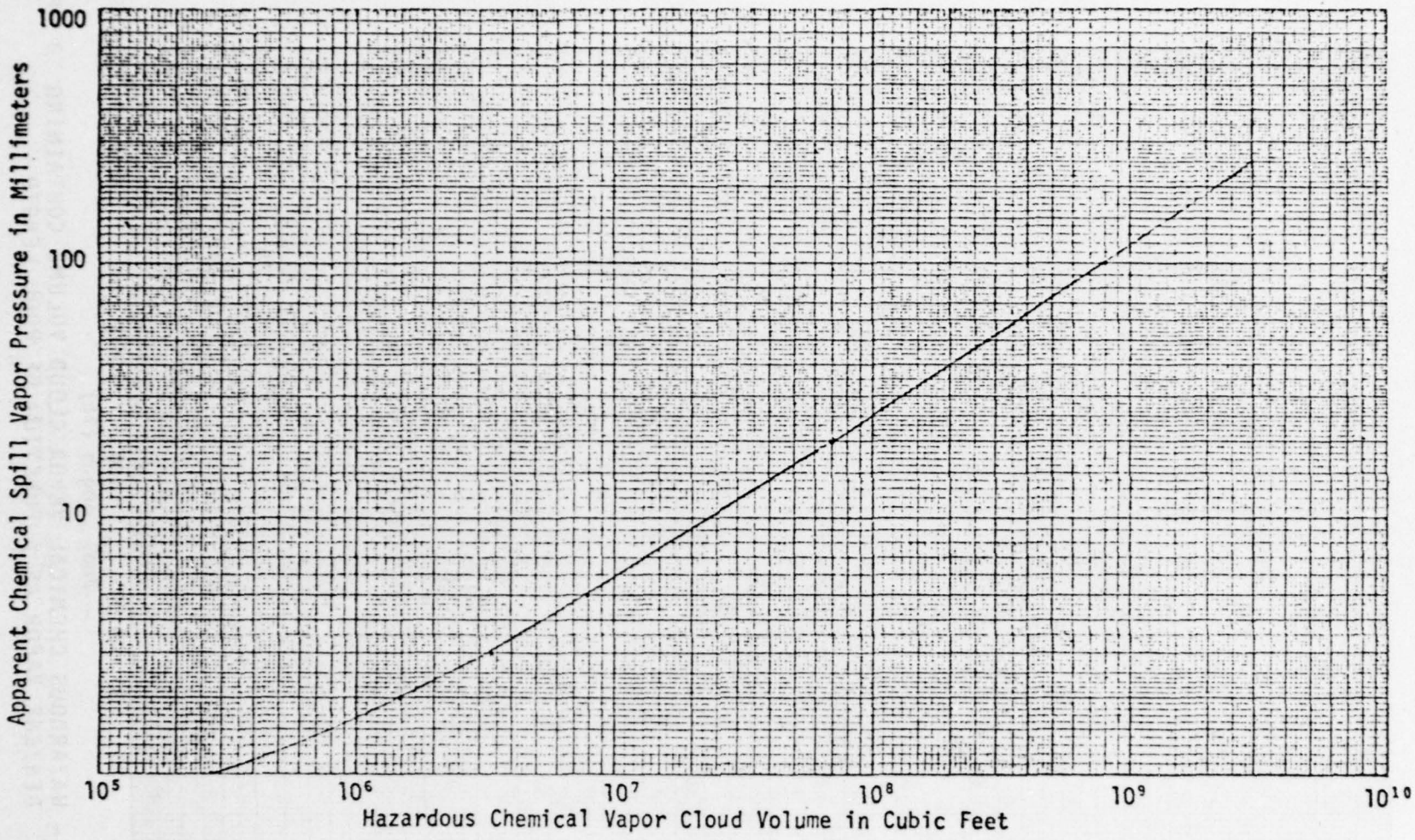


FIGURE 3 - VAPOR HAZARD ASSESSMENT FOR VARIOUS "APPARENT" VAPOR PRESSURES OF BENZENE

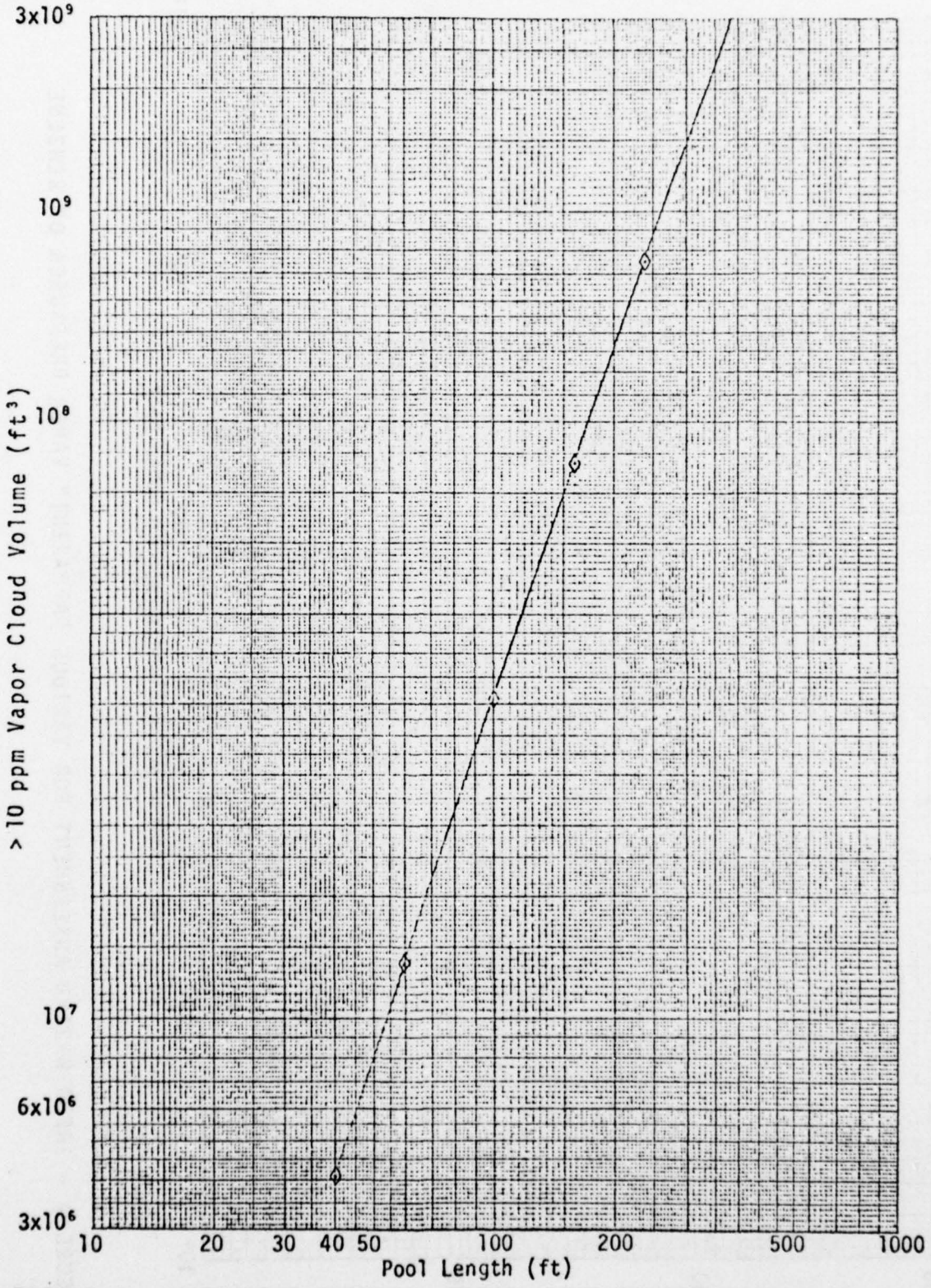


FIGURE 4 - HAZARDOUS CHEMICAL VAPOR CLOUD VOLUME CONTAINING 10 PPM BENZENE VAPOR AS A FUNCTION OF POOL LENGTH

Discussion of Flammability Hazards

Flammability, or the ability to participate in self-propagating oxidation reactions, is a hazard commonly associated with organic materials. These reactions may proceed regularly, as normal combustion, or uncontrolled, as explosions. Experimental investigations of flammability have revealed that these reactions depend upon the individual chemical and its concentration, relative to that of available oxygen.

At standard temperature and pressure, flammable limits of vapor-air mixtures are generally expressed in terms of the lower and upper fuel concentration limits or lower (LFL) and upper (UFL) flammability limits. These limits depend upon such variables as the ignition source, direction of propagation, temperature and pressure, but the differences may be considered negligible for field conditions.

The flammability limits of mixtures may be calculated from their composition and the limits of the individual components by the modified Le Chatelier expression:

$$L_m = \frac{100}{C_1/L_1 + C_2/L_2 \ldots C_n/L_n} \qquad (1)$$

where L_m is the flammable limit (either upper or lower) of the mixture in percent by volume; $C_1 \ldots C_n$ are the concentrations of the individual species in the mixture and $L_1 \ldots L_n$ are the flammable limits for the individual components.

A general relationship has also been reported by Zabetakis et al. (1965) which showed the lower flammability limit, expressed in terms of the weight of fuel per unit volume of air, is relatively constant for a variety of organic substances. With the exception of some low molecular weight substances, such as methane and acetylene, the lower flammability limit falls generally in the range from 45 to 50 mg of combustible per liter of air.

Experimental values of flammability limits for pure hydrocarbons have been reported by a number of investigators (e.g., Coward and Jones [1952]). Flammability limits for a large number of pure substances and mixtures have been compiled by the National Fire Protection Association (NFPA, 1969). When experimental data are non-existent, flammability limits may be estimated by means of various empirical correlations, as reviewed by Affens (1966).

The relationship of flammability limits with other hydrocarbon properties, such as heat of combustion, flash points, vapor pressure, and molecular weight, have been explored by other investigators, also. Flash points of hydrocarbons are often defined in terms of an empirical test procedure, but a more meaningful definition is that suggested by van Dolah (1963). Flashpoint is defined as "the minimum temperature at which sufficient vapor is released by a liquid or solid to form a flammable vapor-air mixture at one atmosphere

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Zabetakis, M.G., Flammability Characteristics of Combustible Gases and Vapors, Bulletin 627, Bureau of Mines (1965).

Coward, H.F. and Jones, G.W., Limits of Flammability of Gases and Vapors, Bulletin 503, Bureau of Mines (1952).

Affens, N.A., "Flammability Properties of Hydrocarbon Fuels", J. Chem. Eng. Data 11(2), 197, (1966)

van Dolah, R.; Zabetakis, M.; Burgess, D. and Scott, G., Review of Fire and Explosion Hazards of Flight Vehicle Combustibles, Bureau of Mines Report 8137, (1963).

pressure. Thus, flash point, vapor pressure and flammability limit are directly related.

Liquid flammability hazards have been classified according to the degree of safety precaution required by the U.S. Coast Guard (1964). The term, inflammable liquids, is used for those liquids which evaporate to form flammable vapor mixtures below 27°C (80°F). The term, combustible liquids, is used for those liquids requiring temperatures in excess of 27°C (80°F) to form flammable vapor mixtures.

Ignition of a pool of inflammable liquid is possible (in principle) at 27°C (80°F) by introducing sufficient energy in close proximity to the pool. Ignition of combustible liquids requires not only the minimum ignition energy, but sufficient excess to bring a portion of the liquid to its flashpoint.

The flammability hazard rising from the spill of a floating, hazardous chemical can be ameliorated by actions to bring about changes in two areas:

1. the concentration of the vapor (fuel) above the spill or the relative concentrations of vapor and oxygen, and
2. energy requirements for heating, ignition or continuous reaction.

The desired changes would be obtained by actions resulting in a significant increase or decrease in the rate of evaporation, the addition of cryogenic or other energy absorbing materials, or the addition of inert materials to hinder reaction and heat transfer.

United States Coast Guard, A Manual for the Safe Handling of Inflammable and Combustible Liquids, Rept. No. CG-174 (March, 1964).

Discussion of Toxicity Hazards

Toxicity, or the adverse effects resulting from exposure to various chemicals, is another hazard associated with many organic chemicals. This property is measured according to various biological effects occurring in humans or other living species.

The most common classifications of toxicity hazards include: threshold limit values (TLV), short-term inhalation limits, odor thresholds and ingestion toxicity (LD_{50}). Threshold limit values are most commonly used in defining or estimating the toxicity hazards for humans in eight-hour work day exposure or related work room assessments.

The relative hazards associated with exposures to the floating, hazardous chemicals may be correlated in terms of the threshold limit values published by the American Conference of Governmental and Industrial Hygienists for 1974. The Environmental Protection Agency is another source for toxicity data, publishing results from various classifications according to the Occupational Safety and Health Act of 1970.

These data were used for assessing the relative hazards resulting from spills of hazardous chemicals and evaluating the possibilities for reduction and/or control of these hazards by the use of candidate spill response techniques.

The toxicological hazards arising from spills of floating, hazardous chemicals can be ameliorated by actions which would cause changes in these spills in two areas:

1. concentration of the vapor above the spill
2. chemical and physiological activity of the vapor

Only those actions affecting concentrations have been considered a part of this investigation.

Vapor concentrations must be reduced to ameliorate their toxicity. These reductions may be obtained using three general approaches:

1. suppressing evaporation
2. diluting the vapors with nontoxic gases or mixtures
3. removing the vapors from the mixture over the spill

Response techniques involving evaporation barriers, energy absorbing materials or vapor absorption are potential candidates to ameliorate the toxicological hazards of spills of hazardous chemicals.

The threshold limit value concentration for allowable exposure places a much more stringent criterion on the effectiveness of a given response technique than does the fire hazard criterion. For most flammable substances, the LFL concentrations are of the order of one percent by volume while TLV values for toxic vapors are of the order of a few parts per million (ppm). Many of the response techniques for control of airborne vapor hazards are effective for control of flammability hazard but not for toxic vapor control.

DEFINITION OF HAZARDS AND HAZARDOUS MATERIALS

Organic compounds are the primary source for hazardous chemicals which float on water. Toxicity hazards for this class of chemicals range from common foodstuffs through carcinogens and lethal poisons. Most are flammable, with the rate of decomposition varying between self-propagation and detonation. Approximately one hundred sixty-seven of the four hundred chemical species contained in the Chemical Hazards Response Information System (CHRIS), are categorized as floating, hazardous chemicals, and were of primary interest in this study. The chemicals considered in this program are listed in Table 3.

Evaluating the hazards surrounding the accidental discharge of these chemicals involves determining the potential impact upon human health from initial exposure, detrimental environmental reactions or slow erosion from residual activity. The hazardous situations created by such diverse chemicals present such a variety that reasonable comparisons are difficult. The toxicity of vapors, both from compounds and decomposition products, and their flammability were the primary hazards used in ranking floating, hazardous chemicals.

Recent experience with pesticides, insecticides and carcinogenic chemicals has accentuated the necessity of determining benefit/risk potentials for hazardous chemicals. Similar evaluations have been made concerning the transport of chemicals, where spillage and accidents are responsible for the generation of potential hazards.

Dawson, et al (1970) developed an overall risk factor for a broad spectrum of hazardous chemicals which included data concerning threshold limits, quantities

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Dawson, G.W.; Shuckrow, A.J. and Swift, W.H., Control of Spillage of Hazardous Polluting Substances, PB 197-596 (1970).

TABLE 3 - HAZARDOUS CHEMICALS THAT FLOAT

Acrylonitrile
Adiponitrile
Aldrin
Allyl Alcohol
Amyl Acetate
n-Amyl alcohol
Aniline
Asphalt
Asphalt Blending Stocks:
  -Roofers flux
  -Straight run residue
Benzaldehyde
Benzene
Butadiene, inhibited
n-Butyl acetate
sec-Butyl acetate
n-Butyl acrylate
iso-Butyl acrylate
n-Butyl alcohol
tert-Butyl hydroperoxide
n-Butyraldehyde
Camphor oil
Cresols
Cumene
Cyclohexane
Cyclohexanone
Decaldehyde
1-Decene
n-Decyl alcohol
Dibutyl phthalate
Dicyclopentadiene
Diethylbenzene
Diethyl carbonate
Diisobutyl carbinol
Diisobutylene
Dioctyl adipate
Dioctyl phthalate
Distillates:
  -Straight run
  -Flashed feed stocks
Dodecanol
Dodecene
Dowtherm
Epoxidized vegetable oils
Ethyl acetate
Ethyl acrylate
Ethylbenzene
Ethyl butanol
Ethyl ether
2-Ethyl hexanol
Ethyl hexyl tallate
2-Ethyl-3-propylacrolein
Gas oil: Cracked
Gasolines:
  -Automotive (4.23 g lead/dal)
  -Aviation (<4.86 g lead/gal)
  -Casinghead
  -Polymer
  -Straight run
Gasoline blending stocks:
  -Alkylates
  -Reformates
Heptane
Heptanol
1-Heptene
Hexane
Hexanol
1-Hexene
Isoamyl alcohol
Isobutyl acetate
Isobutyl alcohol
Isodecaldehyde
Isodecyl alcohol
Isohexane
Isooctyl alcohol
Isooctaldehyde
Isopentane
Isoprene
Isopropyl acetate
Jet fuels:
  -JP-1 (Kerosene)
  -JP-3
  -JP-4
  -JP-5 (Kerosene, heavy)
Kerosene
Lauryl mercaptan
Linear alcohols
Methyl acrylate
Methyl amyl acetate
Methyl amyl alcohol
Methyl ethyl ketone
Methylethylpyridine
Methyl isobutyl carbinol
Methyl isobutyl ketone
Methyl methacrylate

TABLE 3 - HAZARDOUS CHEMICALS THAT FLOAT (Con't.)

Mineral spirits
Naphtha:
  -Coal tar
  -Solvent
  -Stoddard solvent
  -VM&P(75% naphtha)
Nonanol
Nonene
1-Nonene
Nonylphenol
Octanol
1-Octene
Oils:
  -Clarified
  -Crude
  -Diesel
Oils, edible:
  -Castor
  -Cottonseed
  -Fish
  -Olive
  -Peanut
  -Soya bean
  -Vegetable
Oils, fuel:
  -No. 1 (Kerosene)
  -No. 1-D
  -No. 2
  -No. 2-D
  -No. 4
  -No. 5
  -No. 6
Oils, miscellaneous:
  -Absorption
  -Coal tar
  -Lubricating
  -Mineral
  -Motor
  -Neatsfoot
  -Penetrating
  -Range
  -Resin
  -Rosin
  -Sperm
  -Spindle
  -Spray
  -Tall
  -Tanner's
  -Transformer
Pentadacanol
Pentane
1-Pentene
Petrolatum
Petroleum naptha
Phenol
Polybutene
n-Propyl acetate
Propylene butylene polymer
Propylene tetramer
Styrene
Tallow
Tetradecanol
1-Tetradecene
Tetrahydronaphthalene
Toluene
Toluene 2,4-Diisocyanate
Tridecanol
1-Tridecene
Triethylamine
Triethylbenzene
Turpentine
Undecanol
1-Undecene
Valeraldehyde
Vinyl acetate
Vinyl chloride
Vinyltoluene
Waxes:
  -Carnauba
  -Paraffin
o-Xylene
m-Xylene
p-Xylene

transported and spill probabilities. Their indices represented a critical review of potential pollution hazard problems. This was the first effort to systematically analyze spill problems and define spill parameters.

The data of Lyman et al. (1974) were used predominantly in the selection of representative chemicals for evaluating candidate response techniques. Their work involved the compilation of hazardous chemicals and evaluation of chemical and physical behavior, in conjunction with risk indices, to select representative chemicals for the rapid assessment of response techniques and equipment.

Lyman et al (1974) divided the major category of floating spills into eight subdivisions, each with a representative compound. These representatives and a brief description are presented in Table 4.

All candidate response techniques evaluated in this program were assessed in terms of their reported, extrapolated or estimated capabilities in treating spills of these eight chemicals. Benzene was added to this list since it is lighter than water and its vapors are both toxic and flammable. Benzene is also transported in very large volumes.

Comparison and correlation of potential hazards for the purpose of ranking required some estimation and extrapolation. The basic assumption used in this assessment was that toxic vapors, no matter how they were generated, present a greater risk to response personnel than flammable vapors.

Data for the hazardous chemicals have been compiled from sources such as CHRIS Hazardous Chemical Data (1974),

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Lyman, W.; Nelson, L.; Partridge, L.; Kalelkar, A.; Everett, J.; Allan, D.; Goodier, J.L. and Pollack, G., Survey Study to Select a Limited Number of Hazardous Materials to Define Amelioration Requirements, AD/A-004311, Contract No. DOT-CG-29655A (1974).

Coast Guard, Hazardous Chemical Data, CG-446-2 (January, 1974).

TABLE 4 - FLOATING SPILL TYPES AND REPRESENTATIVE CHEMICALS*

Amelioration Category	Representative Chemical
A Floats: Solids	Pentadecanol
B Floats: Liquids, high flammability	Ethyl ether
C Floats: Liquids, low flammability	Kerosene
D Floats: Liquids that spread	n-Amyl alcohol
E Floats: Liquids that do not spread	Naphtha: solvent
F Floats: Liquids, esters	Ethyl acetate
G Floats: Liquids, simple hydrocarbons	Hexane
H Floats: Liquids, oxygen containing: other	n-Butyraldehyde

*Lyman, W.; Nelson, L.; Partridge, L.; Kalelkar, A.; Everett, J.; Allan, D.; Goodier, J.W. and Pollack, G., Survey Study to Select a Limited Number of Hazardous Materials to Define Amelioration Requirements, AD/A-004311, Contract No. DOT-CG-29655A (1974).

Lyman et al. (1974), Dawson et al. (1970), Srinivasan et al. (1975) and reports by the Manufacturing Chemists Association, the American Chemical Society and the American Conference of Governmental and Industrial Hygienists.

Chemical vapor hazards can be measured by several criteria, including threshold limits, 50% lethal dosage, short-term inhalation limits, nuisance concentrations, flash points and flammability limits.

The environmental conditions and chemical and physical properties of the hazardous chemicals, at the time of the spill, combine to determine the feasibility of a candidate response technique. Assessing the feasibility of individual response techniques often involved the extrapolation or estimation of some properties, due to the differences in the response techniques. Correlating and ranking these techniques involves the evaluation and assessment of data from several different areas.

The results of this review of chemical properties are presented in Table 5. This tabulation provided the basic data for correlating the potential hazards of individual chemicals with chemical and physical properties which could be used for their containment and removal.

Hazardous chemicals were ranked according to several individual and composite sets of data. The five most appropriate compilations are presented in Table 6. These

Lyman, W.; Nelson, L.; Partridge, L.; Kalelkar, A.; Everett, J.; Allan, D.; Goodier, J.W. and Pollack, G., Survey Study to Select a Limited Number of Hazardous Materials to Define Amelioration Requirements, AD/A-004311, Contract No. DOT-CG-29655A (1974).

Dawson, G.W.; Shuckrow, A.J. and Swift, W.H.; Control of Spillage of Hazardous Polluting Substances, PB 197-596 (1970).

Srinivasan, S.; Thomas, T.; Geyer, A.; Coyle, A. and Kimm, C., Influence of Environmental Factors on Selected Amelioration Techniques for Discharges of Hazardous Chemicals, Contract No. DOT-CG-23223-A-18, Rept. No. CG-D-81-75, (February, 1975).

TABLE 5 - PHYSICAL AND TOXICOLOGICAL DATA FOR HAZARDOUS CHEMICALS THAT FLOAT

Compound	TLV (ppm)	Dielectric Constant	Flash Point (°F)	LFL (%)	Evaporation Rate [1]	Vapor Pressure 0°C (mm)	Vapor Pressure 27°C (mm)	Water Solubility (g/100 ml)	Surface Tension [2] (dyne/cm)
Acrylonitrile	20	33.0	30	3.05	5.2	28	125	7.3	
Adiponitrile	50		199						
Aldrin								~0.01	
Allyl alcohol	2		70	2.5	8.5	4	26	8.5	25.8
Amyl acetate	100	4.75	77	1.1	11.6	~1	~6	0.1	25.68
n-Amyl alcohol	100		91	1.1	38.1	~1	5	2.4	25.6
Aniline	5	6.89	158	1.3	200	<1	~1	3.65	45.50
Asphalt				1.0					
Asphalt roofers flux									(10)
Asphalt straight run residue									
Benzaldehyde		17.8	148		85		1	0.33	40.04
Benzene	10	2.28	12	1.3	2.8		100	0.03	28.88
Butadiene, inhibited	1000			2.0		~950	~1900	0.001	13.41
n-Butyl acetate	150	5.01	72	1.7	7.8	3	10	0.5	24.0
sec-Butyl acetate	200	5.29	88	1.7		6			23.3
n-Butyl acrylate			120	1.4		~1	7	0.16	(20)
i-Butyl acrylate				1.0			9		2.47
n-Butyl alcohol	50	17.1	95	1.4	19.6	~1	5	7.9	24.5
Tert-butyl hydroperoxide			100			~2	5	0.1	(30)
n-Butyraldehyde	1.7	13.4	30	2.5	30	50	90	3.7	24.6
Camphor oil	2	11.35	117					0.1	(20)
Cresols	5	11.5	178-202		>400	<1	~1	2	37
Cumene	50	2.38	111	0.9	13.9	0.5	6		28.2
Cyclohexanone	50	18.3	111	1.1	22.2	~30	5	2.4	34
Decaldehyde			185				~1		(20)
1-Decene			(130)			1.6	~5		22.68
n-Decyl alcohol		8.1	180				<1	2.3	(15)
Dibutyl phthalate		6.44	322	0.5	200		<1	0.10	34
Dicyclopentadiene			90	0.8			~5		(20)
Diethylbenzene		2.23	135	0.8			~1		30
Diethyl carbonate		2.82	77		14	~1	~5	1.4	26.31
Diisobutyl carbinol			165	0.8		~1			(40)
Diisobutylene			20	0.9		~10	47		20.7
Dioctyl adipate			400						(15)
Dioctyl phthalate			425					0.001	(15)

[1] Ratio of evaporation rates as $\frac{\text{time to evaporate one mol chemical}}{\text{time to evaporate one mol ethyl ether}}$ where time for ethyl ether = 1

[2] Surface tension at 20°C

Numbers in parentheses are estimated values.

TABLE 5 - PHYSICAL AND TOXICOLOGICAL DATA FOR HAZARDOUS CHEMICALS THAT FLOAT (continued)

Compound	TLV (ppm)	Dielectric Constant	Flash Point (°F)	LFL (%)	Evaporation Rate	Vapor Pressure 0°C (mm)	Vapor Pressure 27°C (mm)	Water Solubility (g/100 ml)	Surface Tension (dyne/cm)
Distillate, straight run			104	1.1		~13			19-23
Distillate, flashed feed stocks						~13			19-23
Dodecanol			212						(15)
Dodecene	200	2.01	191			<1			23.99
Dowtherm			235	0.5					40.1
Epoxidized vegetable oils									(40)
Ethyl acetate	400	6.02	24	2.2	2.7	≈20	~100	8.0	23.9
Ethyl acrylate	25		60	1.8		~10	40	2.0	25
Ethyl benzene	100	2.41	59	1.0	9.4	≈1	10	0.014	29.2
2-Ethyl butanol		4.34	135	1.9		~1	~2	0.4	24.3
Ethyl ether	400	4.41	-49	1.8	1	180	550	7.5	17.01
2-Ethyl hexanol			178				~5	0.1	27.6
Ethyl hexyl tallate			395						(25)
2-Ethyl-3-propyl acrolein			155			≈1	~1	0.07	28.2
Gas oil, cracked				6.0					(25)
Gasolines	500		<0	1.1			25		20.5
Heptane	400	1.924	25	1.0	2.7	~10	~50	>0.005	19.8
Heptanol			160			<1		0.1	26.2
1-Heptene		2.07	(20)	1.0		15	~40		19.52
Hexane	100	1.89		1.2	1.9	45	940	>0.013	18.43
Hexanol		1.33	145	1.2		≈5	~1	0.6	24.5
1-Hexene	500	2.05		1.2		~55	215	0.001	17.87
Isoamyl alcohol	100	14.7	109	1.2	30.7	~1	5	2.67	23.8
Isobutyl acetate	150	5.29	64	2.4	5.8	~5	20	0.63	23.7
Isobutyl alcohol	50	5.01		1.6	16.3	<1	15	9.5	23.0
Isodecaldehyde			185						(20)
Isodecyl alcohol			220					>0.01	(20)
Isohexane		1.92	<-20	1.2			260		17.38
Isooctyl alcohol			180	0.9				7	29.5
Isooctaldehyde			104				0.5		26.9
Isopentane		1.88	<-60	1.4		~260	700	0.000001	13.72
Isoprene		2.02	-65	2.0		~210	275	0.00001	16.9
Isopropyl acetate	250		40	1.8	3.0	~15	65	3.09	26
JP-1	200		95	0.7		≈1	3		23-32
JP-3	200		110			~100	250		(25)

TABLE 5 - PHYSICAL AND TOXICOLOGICAL DATA FOR HAZARDOUS CHEMICALS THAT FLOAT (continued)

Compound	TLV (ppm)	Dielectric Constant	Flash Point (°F)	LFL (%)	Evaporation Rate	Vapor Pressure 0°C (mm)	Vapor Pressure 27°C (mm)	Water Solubility (g/100 ml)	Surface Tension (dyne/cm)
JP-4	200		<-10	1.3		~35	95		22.6
JP-5	200		140	0.6		< 1			25.7
Kerosene	200		~100	0.7		~1	~ 3		23-32
Lauryl mercaptan						0.25	~1		(30)
Linear alcohols			180			<1			(30)
Methyl acrylate	10		27	2.8	2.2	20	90		24.2
Methyl amyl acetate	50		110	0.9	3.6	~1	5	0.13	(25)
Methyl amyl alcohol	25	6.19	106	1.0	3 6	~1	~ 5	1.7	22.8
Methylethyl pyridine	(1700)		165	1.1		~1	~3	1.22	(25)
Methyl isobutyl carbinol	25	5.82		1.0		~10		1.7	22.8
Methyl isobutyl ketone	100	13.11	73	1.4	5.6	~5	7	1.7	23.6
Methyl methacrylate	100	2.9	50	2.1		~10	40		28
Mineral spirits			104	0.8		< 1	~3		(20)
Coal tar naphtha	100		100		29	~1	~3		20.6
Naphtha solvent	100			0.8		~1	~3		19-23
Naphtha stoddard solvent	200			0.8		~1	~3		19-23
VM&P naphtha			20	0.9		~1	~3		19-23
Nonanol	(500)		170	0.8				0.1	(25)
Nonene			78	0.7		~1	~6		21.83
1-Nonene				0.8				0.0001	21.83
Nonylphenol			285	1.0			15	0.001	(30)
Octanol		10.34	178			~0.2		0.03	27.53
1-Octene		2.08	70	0.9		~5	20		20.79
Pentadecanol									(25)
Pentane	500	1.84		1.4	0.97	180	150	0.05	16.00
1-Pentene		2.02	0	1.4		235	680		15.57
Petrolatum									(45)
Petroleum naphtha	500					~1	3		19-23
Phenol	5		175	1.7			<1	8.5	40.9
Polybutene	~4000		~ 215						(25)
n-Propyl acetate	200	6.00	58	2.0	4.4	~8	35	1.89	24.3
Propylene butylene polymer						~1			(25)
Propylene tetramer	200		120			~1	2		16.7
Styrene	100	2.43	88	1.1	12.4	~2	~5	0.1	32.14
Tallow			492						(30)

TABLE 5 - PHYSICAL AND TOXICOLOGICAL DATA FOR HAZARDOUS CHEMICALS THAT FLOAT (continued)

Compound	TLV (ppm)	Dielectric Constant	Flash Point (°F)	LFL (%)	Evaporation Rate	Vapor Pressure 0°C (mm)	Vapor Pressure 27°C (mm)	Water Solubility (g/100 ml)	Surface Tension (dyne/cm)
Tetradecanol			285					0.02	(25)
1-Tetradecene			230				<1		24.99
Tetrahydronaphthalene	25	2.77	176	0.8	100	0.1	0.5	0.1	(45)
Toluene	100	2.38	40	1.3	4.5	7	35	0.047	28.43
Toluene-2,4-diisocyanate	0.02	2.44	275	0.9		<0.05	0.08		(25)
Tridecanol			250						(30)
1-Tridecene			(175)				<1		24.52
Triethylamine	25	2.42	20	1.2	2.7	15	57	1.5	20.7
Triethylbenzene			181			~1	<1		(25)
Turpentine	100	2.29	95	0.8	375	≈1	~5	0.1	(20)
Undecanol								<0.02	25.5
1-Undecene			160			<1			23.39
Valeraldehyde			54			7	37		(30)
Vinyl acetate	10		18	2.6	3.3	31	130	2.5	23.95
Vinyl chloride	1		-110	4.0		595		0.1	16
Vinyl toluene	100	2.56	125	0.8		0.25	~2		31.35
Wax, Carnuba		2.75	540						(30)
Wax, Paraffin		2.25	390						30.6
Xylenes, o-,m-,p-	100	2.27	65	1.1	9.2	~2	~10	0.01	28-30
Oils									
Clarified							~45		(25)
Crude	(500)		20-90	(0.9-1.3)		(10-20)	(40-45)		24-38
Diesel	(300)		100-125	1.3			(40-60)		(<50)
Castor			445				~45		(25)
Cottonseed			486				~45		(25)
Fish			420				~45		(25)
Olive			437				~45		(25)
Peanut			540				30		(25)
Soya Bean			540				30		(25)
Vegetable			610				25		(50)
No. 1-D	(300)		~100	1.3			(50-70)		47-49
No. 2	(500)		136				(50-70)		(>20)
No. 2-D	(500)		125	1.3			(50-70)		(>20)
No. 4	(500)		130	1.0			(50-70)		(>20)
No. 5	(500)		130	1.0			(30-50)		(>20)
No. 6	(500)		>150	1.0					(>20)
Absorption	(500)		255				~45		(>20)
Lubricating	(500)		300-450				~45		36-37
Mineral			380				~45		(25)
Mineral Seal	200		170				~45		(25)

TABLE 5 - PHYSICAL AND TOXICOLOGICAL DATA FOR HAZARDOUS CHEMICALS THAT FLOAT (continued)

Compound	TLV (ppm)	Dielectric Constant	Flash Point (°F)	LFL (%)	Evaporation Rate	Vapor Pressure 0°C (mm)	Vapor Pressure 27°C (mm)	Water Solubility (g/100 ml)	Surface Tension (dyne/cm)
Neatsfoot			430				<45		(>25)
Penetrating	(300)		295				<45		(>25)
Resin			255				<45		(>25)
Rosin			266				<45		(50)
Sperm			428-450				<45		(>25)
Spray	200		140	0.6			<45		(25)
Tall			380				<45		(>25)
Tanner's							<45		(25)
Road	(300)						<45		(50)
Transformer			295				<45		(25)

TABLE 6 - RANKING CHEMICAL SPILL HAZARDS[1]

A. D. Little	Evaporation Rates[2]	Threshold Limit Value	Vapor Pressure[2]	Flash Point
Acrylonitrile	Pentane	Isoprene	Butadiene	Butadiene
Benzene	Ethyl ether	Toluene-2,4-diisocyanate	Vinyl chloride	Isoprene
Ethyl benzene	Hexane	Vinyl chloride	Hexane	Ethyl ether
2-Ethyl hexanol	Methyl acrylate	Allyl alcohol	Isopentane	Gasoline
Hexane	Triethyl amine	Camphor oil	I-Pentene	Isohexane
Isopropanol	Heptane	Cresols	Ethyl ether	JP-4
Methyl ethyl ketone	Ethyl acetate	Aniline	Isoprene	Hexane
Phenol	Benzene	Dicyclopentadiene	Isohexane	Petroleum naphtha
Styrene	i-Propyl acetate	Phenol	1-Hexene	1-Pentene
Toluene	Vinyl acetate	Dioctylphthalate	Pentane	Benzene
Vinyl acetate	Methyl amyl acetate	Dibutyl phthalate	Vinyl acetate	1-Hexene
Vinyl chloride	n-Propyl acetate	Methyl acrylate	Acrylonitrile	n-Butyraldehyde
Xylenes	Toluene	Vinyl acetate	Ethyl acetate	Ethyl acetate
Butadiene	Acrylonitrile	Benzene	n-Butyraldehyde	Heptane
Pentadecanol	Methyl-i-Butyl ketone	Acrylonitrile	Methyl acrylate	Methyl acrylate
Ethyl ethers	i-Butyl acetate	Ethyl acrylate	Isopropyl acetate	Acrylonitrile
Kerosene	n-Butyl acetate	Triethylamine	Heptane	Methyl methacrylate
n-Amyl alcohol	Allyl alcohol	Methyl amyl alcohol	Methyl methacrylate	Pentane
Solvent naphtha	Xylenes	Isobutanol	1-Heptene	n-Propyl acetate
Ethyl acetate	Ethyl benzene	Methyl amyl acetate	Toluene	Ethyl benzene
n-Butyraldehyde	Amyl acetate	Adiponitrile	n-Propyl acetate	Ethyl acrylate
Valeraldehyde	Styrene	Amyl acetate	Allyl alcohol	Isobutyl acetate
Butyl acetates	Cumene	Amyl alcohols	Gasolines	Allyl alcohol
Hexanol	Diethyl carbonate	Ethyl benzene	Valeraldehyde	1-Octene
Octanol	n-Butyl alcohol	Hexane	Isobutyl acetate	n-Butyl acetate
Turpentine	Cyclohexanone	Methyl isobutyl ketone	Diethyl carbonate	Methyl isobutyl ketone
Gasoline	Coal tar naphthas	Methyl methacrylate	Butyl acetate	Amyl acetate
	n-Butyraldehyde	Hexane	Xylenes	Diethyl carbonate
	i-Amyl alcohol	Coal tar naphthas	Methyl isobutyl ketone	Asphalt
	Methyl amyl alcohol	Solvent naphthas	Butyl acrylate	Isobutyl alcohol
	n-amyl alcohol	Styrene	Amyl acetate	Isobutyl acetate
	Benzaldehyde	Toluene	Amyl alcohol	Styrene
	Tetrahydronaphthalene	Turpentine	Cumene	Dicyclopentadiene
		Vinyl toluene	1-Decene	n-Amyl alcohol
		Xylenes	Methyl amyl alcohol	Kerosene
		Butyl acetates		

[1]Listing in order of decreasing risk assessment (top to bottom) of floating, hazardous chemicals only.
[2]Ambient temperature

chemicals were compiled early in the program using all available sources. They are used throughout the investigation to evaluate the effectiveness of candidate, spill response technologies against hazardous, floating chemicals.

Spill amelioration techniques were assessed in terms of their flexibility toward, or applicability for, a broad spectrum of hazardous chemicals, the amount of protection or control they provided and their compatibility with the environment for ultimate disposal. Data from three general areas, (1) chemical constitution and compatibility, (2) system engineering design capabilities, and (3) general past performance, were used in developing this assessment outline.

TASK I - VAPORIZATION RATE REDUCTION

The objective of this task was to assess the capabilities of candidate spill response techniques for reducing evaporation from the surface of a spill of floating, hazardous chemical. Techniques were ranked according to their ability to ameliorate toxicity and/or fire hazards associated with these vapors, for the protection of response personnel and also the general environment.

The five factors influencing evaporation rates were presented in the "General Discussion" section of this report. A selection of the "best response technique" in this task required quantitative data for evaporative losses which were compared with the task criteria. Task criteria were established in the primary objective, to ameliorate toxicity and flammability.

The average lower flammability limit for the floating, hazardous chemicals is approximately 1%. This translates into a vapor pressure of approximately 7.6 mm (0.30 in. Hg) under static conditions. Natural dispersion will reduce the field concentrations, but the equilibrium condition was used as a reproducible datum point for comparison.

Individual chemical toxicities cover a wide range of concentrations and commensurate vapor pressures. If a threshold limit value of 10 ppm is selected as a typical value, vaporization rate reductions must be three orders of magnitude greater to permit a safe eight hour working day.

Candidate techniques for vaporization rate reduction of floating, hazardous chemicals included foams, surfactant films, sorbents, gels, and cryogens. Foams reduce the vaporization rate of floating, hazardous chemicals by forming a continuous bubble wall which resists vapor release and also by a "capacitance factor", as the vapor phase approaches an

equilibrium composition. Surfactant films reduce evaporation by the generation of a spatially oriented film which is insoluble in the liquid and forms a barrier against the transfer of liquid molecules into the vapor phase. For sorbents, evaporation rate reduction is achieved by the preferential wetting and absorption of the spilled chemical into a material with high surface area and surface activity. Gels reduce evaporation by forming a continuous cover of gelled material on the surface of the spill, held together by the chemical and physical interactions. Cryogens operate by absorbing heat energy from the spill and removing the energy available to transfer molecules into the vapor phase.

Surfactant Films Technology

Monomolecular films were used to reduce the evaporation rates of water and aqueous solutions by Hedestrand (1924), Rideal (1925), and Langmuir and Langmuir (1927). More recent developments and applications were reviewed by LaMer (1962) and the use of fluorinated surfactants for the suppression of fuel evaporation has been studied by Tuve et al. (1966), Bernett et al. (1970)and Moran et al. (1971).

Hedestrand, G., "Influence of Thin Surface Films on the Evaporation of Water", Jour. Phys. Chem. 28, 1245 (1924).

Rideal, E.K., "Influence of Thin Surface Films on the Evaporation of Water", Jour. Phys. Chem. 29, 1585 (1925).

Langmuir, I. and Langmuir, D.B., "The Effect of Monomolecular Films on the Evaporation of Ether Solutions", J. Phys. Chem. 31, 1719 (1927).

LaMer, V.K., Retardation of Evaporation by Monolayers, Symposium on Transport Properties, 1960 Academic Press (1962).

Tuve, R.L. and Jablonski, E.J., Compositions and Methods for Fire Extinguishment and Prevention of Flammable Vapor Release, U.S. Patent No. 3,258,423 (June, 1966).

Bernett, M.K.; Halper, L.W.; Jarvis, N.L. and Thomas, T.M., "Effect of Adsorbed Monomolecular Films on the Evaporation of Volatile Organic Liquids", Ind. Eng. Chem. Fundamentals 9, 150 (1970).

Moran, H.E.; Bernett, J.C. and Leonard, J.T. Suppression of Fuel Evaporation by Aqueous Films of Fluorocarbon Surfactant Solutions, NRL Report No. 7247 AD 723 189 (April, 1971).

The initial investigations were made with films of long-chain, aliphatic acids or alcohols on only one substrate, water. The surface films were shown to consist of a close-packed array of molecules, vertically oriented so that the acid or alcohol groupings interfaced with the water. Vaporization reductions were attributed to the formation of a nearly impermeable film or membrane on the surface, and extinction of surface waves and convection currents and diffusion barriers at both interfaces.

Two mechanisms contribute to vaporization rate reductions obtained from monomolecular films, film resistance and surface quiescence. Langmuir and Langmuir (1927), Sebba and Rideal (1941), Archer and LaMer (1955) and Rosano and LaMer (1956) have investigated the factors contributing to film resistance. They have found that organic chain length and both the chemical and stereochemical nature of the surfactant affected the rate of evaporation of liquids through monomolecular films.

Surface turbulence and convection currents are considerably reduced when a monomolecular film is placed on the surface of a pool of liquid. This has been attributed to the generation of a film pressure when the monomolecular film is being established.

Langmuir, I. and Langmuir, D.B., "The Effect of Monomolecular Films on the Evaporation of Ether Solutions", J. Phys. Chem. 31, 1719 (1927).

Sebba, F. and Rideal, E.K., "Permeability in Monolayers", Trans. Faraday Soc. 37, 273 (1941).

Archer, R.J. and LaMer, V.K., "The Rate of Evaporation of Water Through Fatty Acid Monolayers", J. Phys. Chem. 59, 200 (1955).

Rosano, H. and LaMer, V.K., "The Rate of Evaporation of Water Through Monolayers of Esters, Acids and Alcohols", J. Phys. Chem. 60, 348 (1956).

The operating parameters, established through the investigations referenced above, for monomolecular films include: 1) the film must be monomolecular and spatially oriented; 2) the surfactant must have very limited solubility in the liquid; 3) the film must be uniform and continuous, as a 1% breakage was shown to reduce the film resistance by 90-99%.

Vaporization rate reductions were measured in terms of a "specific resistance to evaporation", which was influenced by four factors:

1. length of the molecular chain
2. temperature
3. diffusion energy
4. continuity of the film

1. Archer and LaMer (1955) reported the influence of molecular chain length on vaporization rate reduction. They found that the vaporization rate decreased progressively with increasing chain length, when saturated fatty acids of C_{16} to C_{20} were used to form these films.

2. Temperature influences the vaporization rate because it is a contributing factor to kinetic energy.

3. Diffusion energy may be a misnomer for permeation through thin films. Diffusion through monolayers does not obey Fick's Law, but progresses in accordance with the Arrhenius Law for the velocity of a chemical reaction. Vaporization through monomolecular films can be described as being comparable to a monomolecular gas reaction.

4. The influence of film continuity was shown by Archer and LaMer (1955) where they reported a 1% film area breakage (holes) reduced the efficiency of the vaporization suppression by more than 90%.

Archer, R.J. and LaMer, V.K., "The Rate of Evaporation of Water Through Fatty Acid Monolayers", J. Phys. Chem. 59, 200 (1955).

Tuve et al. (1964) proposed a unique method of forming this thin layer, i.e., the use of fluorochemical surfactant foams, which collapsed to form a thin film. Bernett et al. (1970) and Moran et al. (1971) showed the feasibility of this method for hydrocarbon fuels.

Fluorochemical surfactant films were found to reduce vaporization of fuels when present at a thickness of about 10μ. This technique works best for hydrocarbon fuels having relatively low vapor pressures, but may be applied to most chemicals having a surface tension equal to, or greater than, 20 dyne/cm (1.4×10^{-3} lb/ft).

Evaporation rates were reduced 90 to 98% when the hydrocarbon liquids were covered with fluorochemical surfactant films. This work was primarily directed towards proving the evaporation suppression capabilities of aqueous-film-forming-foams. Fine sprays or fog nozzles should also produce these films when directed over a floating hazardous chemical spill, with the additional safety factors of vapor dilution and the addition of a vapor phase flame suppressing mixture.

Vapor permeabilities through the various monomolecular films will vary, depending upon the characterization of the film according to the four factors presented at the beginning of this section. For some materials vaporization reductions will be the result of forming a diffusion barrier, while others will reduce evaporation primarily by their ability to stop surface convection currents.

Tuve, R.L.; Peterson, H.B.; Jablonski, E.J. and Neill, R.R., "A New Vapor-Securing Agent for Flammable-Liquid Fire Extinguishment", NRL Report No. 6057 (March, 1964).

Bernett, M.K.; Halper, L.W.; Jarvis, J.L. and Thomas, T.M., "Effect of Adsorbed Monomolecular Films on the Evaporation of Volatile Organic Liquids", Ind. Eng. Chem. Fundamentals 9, 150 (1970).

Moran, H.E.; Bernett, J.C. and Leonard, J.T., Suppression of Fuel Evaporation by Aqueous Films of Fluorochemical Surfactant Solutions, NRL Report No. 7247 AD 723 189 (4/71).

Surfactant Films as a Candidate Spill Response Technique

This technique, as developed by Moran et al (1971), utilizes fluorochemical surfactants in water solution to form a thin film over the surface of a spilled chemical. The surfactant/water film should be between 10 and 20 μ (3.3×10^{-5} and 6.6×10^{-5} in.) thick to seal the surface of the hazardous chemical and reduce evaporation.

Two distinct methods may be used to form the surfactant/water film. An aerosol or mist of the surfactant/water solution may be formed to settle out over the surface of the spill and spread to form the thin film. An alternative procedure is to use the fluorochemical surfactant in a special foam formulation (aqueous film-forming foam) to be generated and spread over the surface of the spill. The foam is formulated for rapid collapse, to form the surfactant/water film.

The amount of solution required for this response technique can be calculated from the typical size and volume estimates established for spills of floating, hazardous chemicals and the film thickness. The volume of solution required for responding to the typical spill of 100 to 10,000 gallons would be between 4 and 76 liters (1 to 20 gal.).

In the alternative method for preparing surfactant/water films the fluorochemical is incorporated into the foam. This aqueous solution may be used with low expansion foam generators, to form a foam having a nominal expansion ratio of 10 to 1. The foam has been formulated to collapse rapidly and form an aqueous film, which seals the spilled chemical.

Some assumptions must be used in calculating application rates for aqueous film-forming foams. The amount of surfactant/water solution required to form the film is constant. The film should be only slightly affected by the presence of foaming agents, extenders and stabilizers, since they are also present at low concentrations. Fire-fighting experience with foams will

influence the actual use of spill response techniques, however, and significantly increase the amount of foam used.

Normal fire-fighting applications require between one hundred twenty and two hundred times as much foam as theoretically necessary to form the surfactant/water film. The excess liquid would form "lenses"in the film and increase the probability for securing film to drop through the spilled chemical layer. Using approximately one hundred times the minimum surfactant/water solution required for film formation should permit visual verification of the foam cover and a realistic safety factor for establishing the film upon collapse of the foam.

Either hydraulic or pneumatic equipment could be used to deploy the surfactant/water solution over the surface of the spill. The small volume required for sealing these spills favors hydraulic equipment, but pneumatic systems could cover equal or larger areas without relying on prevailing winds to obtain particulate drift.

Typical hydraulic equipment might be a Model FFF Fog FOAM nozzle, manufactured by Rockwood Manufacturing. This nozzle could be used to generate either aerosol or foam. Its operating parameters are described in Appendix C. Such a system would consist of spray nozzle, pump, holding tank and ancillary equipment such as pipes, valves, hoses and mounting platform. A special system for spill response could easily be prepared from the components, purchased from individual suppliers.

Hydraulic equipment for preparing the surfactant/water films would require a minimum of deck space. These units are approximately 1.75 m^2 (19 ft^2) and may be attached to the ship's water system. Total equipment costs would be approximately $10,000 installed and a maximum of approximately 2.64/l ($10/gal.) for the surfactant/water solution.

The "Eagle" model blower, manufactured by Finn Equipment Company, is a typical pneumatic dispersing system. This equipment would deploy the surfactant/water solution as a mist, using misting nozzles and other optional equipment for this operation.

This system would occupy approximately 10 m^2 (109 ft^2). It could also be attached to the ship's water supply or have a separate hydraulic pump to supply the water solution. Pneumatic equipment costs would be approximately $10,000, with options and installation added.

Either hydraulic and pneumatic equipment would provide a long service life (10-20 yrs). Normal operation and maintenance would be similar also for these marine installations. It is estimated that either hydraulic or pneumatic systems could be operated by one man in response to spills of hazardous chemicals.

Total cost of hydraulic equipment and materials required to respond to a spill of 38 m^3 (10,000 gal.) of a floating, hazardous chemical, covering approximately 3800 m^2 (40,700 ft^2) would be $11,000. The total cost of pneumatic equipment and materials to respond to this spill would be approximately $15,000.

The foam generators used in the alternative method of preparing surfactant films would use between 400 and 7,570 l (100 to 2000 gal.)of the foam solution to cover a typical hazardous chemical spill. This foam would have a nominal 10/1 expansion ratio to give a maximum cover of approximately 0.7 cm (0.27 in.). A foam generator, similar to the Model FFF Fog FOAM turret nozzle, manufactured by Rockwood Systems Corporation, would be used to generate the foam.

The equipment for this response technique would include a storage tank, pumping unit and auxiliary hardware for transporting and metering, in addition to the foam generating nozzle. Such a system would have a capacity for generating approximately 380 l/min (100 gal/min) of low expansion (10/1

volume ratio) foam and dispersing it up to 30.5 m (100 ft). It would weigh approximately 818 kg (1800 lb), occupy 2.8 m^2 (30 ft^2) of deck space and cost approximately $10,000, installed. The total cost of foam equipment and materials required for the surfactant film technique as a response to a typical spill of 38 m^3 (10,000 gal) of hazardous chemical would be approximately $30,000.

Foam Technology

The overall efficiency of spill amelioration techniques is controlled by their physical and chemical compatibilities with the hazardous chemicals. This compatibility can be selected, or modified to some extent, by the formulation of the foam. Soft foam systems may utilize one of two foaming agents: 1) protein extracts or natural surfactants, and 2) synthetic surfactants.

1. Protein foams have been developed for many different applications in recent years. Special alcohol foams have been developed for fire extinguishment, but as yet they will not provide a useful life when placed upon polar solvents and reactive chemicals.

2. Synthetic foams have somewhat greater flexibility in that there are different classes. Anionic, cationic, non-ionic and amphoteric properties are used to denote the major classes in this formulation system. There is a separate class of synthetic foam formulations which employ fluorocarbon or silicone surfactants as a means of forming a surface film. These formulations (aqueous film-forming foams) offer an alternative approach to ameliorate spills. They are not considered within the scope of this section since they are nonpersistent foams.

The Foaming Process

The production of foam is facilitated by lowering the surface tension (γ) of a foaming solution. This reduces the work (W) required to produce the foam according to the equation $W = \gamma A$; where A is the total surface area of the bubbles. The initial height of the foam may be correlated with the surface tension of the foaming solution; greater initial foam height produced by foaming solutions will lower surface tension.

However, for foam to have any stability, the foam film produced must have some elasticity, i.e., as the film thins and stretches, there must be some restoring force generated by the stretching process which opposes this effect and prevents the stretching from continuing with eventual rupture of the film. It is for this reason that pure liquids, even with low surface tension, do not foam. In solutions of surface-active agents, this restoring force is believed to be due to the higher surface tension which a newly increased surface shows. According to this mechanism, when a portion of a foam film is stretched, the local concentration of surfactant is decreased momentarily and the surface tension at the stretched spot becomes momentarily greater than the tension in the surrounding areas. This causes a surface tension gradient, radiating out from the stretched spot, which draws liquid in from the surrounding areas, countering the stretching of the film and thickening it.

For this mechanism to act effectively, it is essential that the surface tension at the stretched portion not be reduced too rapidly; i.e., the reduction of the surface tension to its equilibrium value by surfactant

migrating to the surface from the interior should not take place before sufficient material from the perimeter has been moved in to thicken the film under the influence of the surface tension gradient. Therefore, a surfactant which is a good wetting agent, i.e., rapidly reduces the surface tension at an extended interface, can act as a defoamer by preventing the operation of this film-healing mechanism.

The general concensus concerning foam collapse is that the prelude to breakage is drainage from the cell walls that leaves the bubble in a delicate or friable condition. Subsequent rupture invariably results in the generation of a mist of foam fragments. This behavior is considered similar to that observed with distorted liquid droplets in an air stream. Foams begin to collapse as soon as they are generated.

Foam Generation

At the present time three mechanisms are used to generate foam. These are mechanical agitation, impaction of a spray against a screen or bubble formation through controlled orifices. Mechanical agitation normally results in a low expansion foam less than 80:1. It is characterized by small bubble size and good stability.

The impaction of a spray against a screen is the most common method of generating medium to high expandion foam from 100:1 to as high as 1500:1. The air velocity required to generate high expansion foam is usually provided by a fan. However, air can be induced to obtain a good foam by using high pressure water sprays. This eliminates the need for a fan or an external power supply. Aspirating generators have limitations. Expansion

is restricted to a maximum of 400:1 and individual units are restricted in size.

The generation of foam through controlled orifices has seen limited commercial utilization. These use a system termed a flooded plate generator. This is a compartmentalized unit in the form of a box. A horizontal perforated plate separates it into two halves. Foam solution flows over the top of the perforated plate and the flowing air is introduced below the plate. Bubble size (expansion) is controlled by the size and spacing of the perforations. This system has the advantage of insuring complete containment of all air in the foam with no leakage.

At present, its use has been limited to the generation of foam from solutions too viscous to be handled in other types of generators. Expansions have usually not gone above 200:1, but higher expansions appear possible.

Foam Collapse

Surfactant foams begin to collapse as soon as they are generated. The rate varies with the surfactant used. Drainage is a controlling factor; the faster the water drains the more rapid the natural collapse and the more susceptible the foam is to chemical or mechanical influences.

Without outside influences surfactant foams exhibit linear collapse rates in the range of 0.2 to 2 m/hr (8 in. to 80 in./hr).

The effects of drainage occurring in foam masses can be illustrated in Table 7 which shows the apparent or initial density of foams blown at various expansion rates. Thus, the higher expanded foams, blown

to an expansion of 1000 to 1 or better, yield a density of slightly less than twice the density of air.

TABLE 7 - FOAM PROPERTIES AS A FUNCTION OF EXPANSION RATIO

Volume Expansion Ratio gas/liquid	gas phase (g/10ℓ@30°C)	liquid phase (g/10ℓ@30°C)	Density (g/ℓ@30°C)	Density (lb/ft³)
10	0.9	1,000	100.1	6.25
100	9.0	100	10.9	0.68
500	9.98	20	2.99	0.19
1000	9.99	10	1.99	0.12
1500	9.99	6.67	1.67	0.10
moist air at 30°C			1.12	0.07

Published drainage ranges for stable, aqueous foams which are commercially available indicate as much as 30-50% loss of the liquid phase in 15-20 minutes. As was observed earlier, loss of the liquid in foam blown initially at an expansion of 500/1 will, after a short period of standing, undergo a decrease in density and in effect become a foam mass equivalent of about 2000/1. Since foamed masses drain from top to bottom under gravity, the uppermost layer becomes the most delicate.

The parameters influencing surfactant foam formation, stabilization, drainage and bubble size and distribution, have been examined by several investigators in relation to countercurrent foam extraction processes (e.g., Haas and Johnson, 1967; Shih and Lemlich, 1971).

These authors present models and mechanisms for foam interaction after initial generation and also provide considerable information in techniques of observation and measurement of foam behavior. Drainage and interaction models show the interrelationship of such parameters as surfactant type, surface tension, gas-liquid ratio (or foam density) and height of foam column.

Collapse can be slowed down in anionic foams and the best of the current fire fighting foams show rates in the 20 to 30.5 cm (8 in. to 12 in.) per hour range. This is accomplished by balancing the chemistry in the bubble wall. Further reductions are possible by the incorporation of water soluble polymers. Mecca et al (1971) report a foam formulation which collapsed at the rate of only 0.25 cm (0.1 in.) per hour.

Haas, P.H., and Johnson, H.F., "A Model and Experimental Results for Drainage of Solution Between Foam Bubbles", Ind. Eng. Chem. Fundam. 6(2), 225 (1967).

Shih, F., and Lemlich, R., "Continuous Foam Drainage and Overflow", Ind. Eng. Chem. Fundam. 10(2), 254 (1971).

Mecca, J.E., Jensen, H.F., and Ludwick, J.D., "Noble Gas Confinement Study. I. Development of a Long-Lived, High-Expansion Foam for Entrapping Air-Bearing Noble Gases", U.S.A.E.C. DUN-7221 (1971).

Foam Limitations

Destruction or retardation of the formation of foams, is of considerable importance. The technical literature contains hundreds of examples of compositions which are claimed to inhibit or destroy foams. These substances must, in general, possess properties which are the opposite of those needed for foam stabilization or production. It seems likely that reductions in surface elasticity are achieved by the anti-foaming agent displacing the foaming agent from the interface. In order to do this, the anti-foaming agent, if it is a liquid, must have a low intrinsic surface tension and must be able to spread when it is applied to the foam lamellae.

Not all types of foam can be destroyed or prevented by one single type of anti-foaming agent, and many of these agents work on quite different principles. Ross and Haak (1958) have shown, for example, that tributyl phosphate and methylisobutyl carbinol have an anti-foaming action on "nacconol NRSF" (an alkylated aromatic sulphonate) foam by increasing the rate of drainage of liquid from the foam lamellae. Although at higher concentrations methylisobutyl carbinol destroys the film-stabilizing action of the foaming agent, the tributyl phosphate acts only by increasing the drainage from the lamellae.

Aqueous Foams as a Candidate Spill Response Technique

A foam consists of an array of gas bubbles dispersed throughout a liquid phase in such a way as to partition off the gas into a myriad of tiny, inter-connected cells.

Ross, S., and Haak, R.M., "Inhibition of Foaming. IX Changes in the Rate of Attaining Surface Tension Equilibrium in Solutions of Surface-active Agents on Addition of Foam Inhibitors and Foam Stabilizers" J. Chem. Phys. 62, 1260 (1958).

The walls or windows of each cell are nearly identical to the monomolecular films described previously. Their thickness depends upon the expansion ratio at which the foam was generated and the extent of drainage.

Vapors released from the spill are immediately incorporated into this array of bubbles. Foam permeability becomes a two-fold entity, comprised of diffusion resistance through the cell walls and a capacity for assimilation of vapor into the gas phase. The net effect of these two phenomena is to increase the thickness of the saturated vapor layer over the liquid surface and to immobilize the vapor phase.

The efficiency with which foams reduce evaporation from a simulated pool was found to depend upon seven factors:

1. Chemical compatibility
2. Foam layer thickness
3. Surfactant concentration
4. Water solubility of vapors
5. Expansion ratio
6. Thermal insulating capability
7. Environmental factors

Without a foam cover, factors such as wind, surface turbulence, liquid convection currents and spreading coefficients would have greater cumulative effects on the rate of evaporation.

The chemical compatibility of foams with floating, hazardous materials is the most important factor influencing the formation of a foam cover. Foams are generally compatible with nonpolar compounds and with those having a pH close to water (neutral).

Recent developments in foam formulations have expanded their compatibility with polar compounds, but the extended lives necessary for controlling vaporization and vapor hazards limit their use to compounds having a dielectric constant less than 3. Each formulation offers

slight variations of chemical compatibility which may be used to extend the number of compounds which may be treated.

"Type L foam", manufactured by Mine Safety Appliances Company, and "Universal Foam", manufactured by National Foam Systems, Incorporated, were the only formulations found to be generally compatible with the floating, hazardous chemicals. "Type L foam" would be used as a 30% solution of the foam concentrate and "Universal Foam" would be used as a 10% solution of the foam concentrate in water. "Type L foam" is the more stable, having a collapse rate of 1.27 cm/day (0.5 in./day), and was more impermeable to the chemicals used in the experimental tests done in this investigation.

Some experimental tests were performed during this investigation to measure the vapor permeability of these foams. These tests showed that a 40 cm (16 in.) layer of high expansion foam (~200/1 volume ratio) would be sufficient to reduce vaporization and ameliorate flammability hazards. A 15 cm (6 in.) layer of low expansion foam (~10/1 volume ratio) would provide similar protection.

A high expansion (~200/1) foam cover for the largest typical spill would require the generation of approximately 1520 m^3 (53,700 ft^3) of foam. This approach would include handling approximately 7.6 m^3 (270 ft^3) or 7600 ℓ (2000 gal) of liquid in the high-expansion foam generating equipment.

Most commercial foam generators produce foams of higher expansion ratios than the 200/1 recommended for vaporization suppression. This lower expansion is the preferable compromise for vaporization rate reduction, foam life and foam resiliency.

Foam generators may be powered by electricity, gasoline or water. Each of these generators has the flexibility to generate the desired foam requirements. The water-powered units would provide the desired flexibility while being free of any flame initiating hazards.

The MSA "Model 6000 Foamaker" is a typical example of high-expansion foam generating equipment applicable for hazardous spill response. This unit weighs approximately 102 Kg (225 lb) and would require 2.5 m^2 (27 ft^2) of deck space. It normally operates at water pressures between 2.8×10^4 and 7×10^4 Kg/m^2 (40 to 100 lb/in^2) with water flows between 235 and 390 ℓ/min (62 to 103 gal/min).

Some modifications would be required to make the MSA Model 6000 standard foam generator produce foams with a nominal 200/1 expansion ratio. This unit is designed to deliver foam at a rate of 557 m^3/min (6000 ft^3/min) with a nominal expansion ratio of 600/1. Changing the ratios of gears driving the fan would be one method of obtaining the desired foam. Similar, minor changes might also be required for skid or cart-mounted units which would make them amenable to service on ship decks. Similar modifications would be required on the other foam generating equipment referenced in this report.

This equipment would require approximately 30 min to generate the 1520 m^2(53,700 ft^3) foam layer. Multiples of this typical unit or some of the larger units described in Appendix C could be used to decrease the total response time. Using multiples of smaller generators could also aid the production of a uniform foam layer.

The foam generating system would include a water supply, holding tank and ancillary equipment for transporting, metering and mixing, in addition to the foam generator.

The entire system would weigh approximately 4500 Kg (9700 lb), require approximately 3 m^2 (32 ft^2) of deck space, and cost approximately $40,000, installed.

Foam generating systems would have an estimated life of approximately 10 to 20 years. It would be possible to operate several foam generator units from one large pumping station and reduce the amount of control required while increasing total foam output. The foam generating technique is considered a one-man operation for the systems described. Regular maintenance would be required to preserve the design capabilities of the equipment against the rigors of shipboard exposure. Total cost of equipment and materials required to place the 40 cm (16 in.) layer of high-expansion foam over a spill of 38 m^3 (10,000 gal) of floating, hazardous chemical would be approximately $50,000.

Low expansion foams (10/1 volume ratio) may also be considered as a method to achieve evaporation rate reductions. The volume of foam required in response to the largest typical spill investigated in this program can be calculated from the minimum layer required (0.15 m or 6 in.) and total area 3800 m^2 (40,700 ft^2). The amount of foam solution required to form this 620 m^3 (21,900 ft^3) of low expansion foam would be between 6,200 and 18,700 ℓ (1,600 and 4,800 gal).

This layer of low expansion foam would not completely stop the evaporation of a floating, hazardous chemical. However, a layer between 7.6 and 10 cm (3 to 4 in.) would be sufficient to inhibit flammability or arrest combustion reactions from flashing back into the pool of floating chemical.

Low expansion foams are considered as candidates to fulfill the objectives of Task III. This response technique and its application are described in greater detail in the section concerning vapor flammability reduction.

Sorption Technology

Sorption has been a basic tool in water treatment processes for many years. The objectives of these processes, to reduce contaminant concentrations and remove nuisance vapors, are similar to those of this investigation.

Sorption is a surface process and is controlled by the physical and chemical properties of the sorbing surface. It is usually expressed as a capacity, mass of sorbate per unit mass of sorbent, which is determined for a dilute solution under equilibrium conditions. Since there is no way to completely separate the phases for this investigation, this term indicates both liquid and vapor sorption for a hazardous chemical spill. The value may be used to indicate the relative effectiveness of a sorbent to ameliorate chemical spills.

Normal sorbent capacities are in the range of 10% by weight, which places a severe limit on the efficiency of the sorption technique. This lack of capacity is balanced by their flexibility. With the proper selection of compatibilities, sorbent materials may be used without modifications or serious corrosion with all the floating, hazardous chemicals.

Activated carbons, which would provide the greatest flexibility of response, normally have densities greater than water and present difficulties for treating those chemicals which float. Floating, activated carbons are in the process of development but have no immediate application and appear only marginally applicable with further research.

The sorption technique, to ameliorate spills of floating, hazardous chemicals, is influenced by five factors:

1. Physical and chemical attraction
2. Surface geometry or morphology
3. Surface area
4. Contact time
5. Density ratio of sorbent/sorbate

Physical and chemical attraction are the binding powers of adsorption and chemisorption, with varying degrees of interplay between the two. These binding forces influence both the initial pickup of the hazardous material and its subsequent removal for recycle or disposal.

Surface geometry is a general term used to cover pore conformation, surface activity and surface cleanliness. Correlations between molecular and surface pore geometry indicate the degree of sorption possible. Surface activity and surface cleanliness affect sorption processes insofar as they relate to surface contact. The viscosity of the hazardous chemical also influences this contact as to whether it "wets" the sorbent.

Surface area is a controlling factor in sorption processes since sorption is directly affected by the total area available. The surface area of the sorbent depends upon the surface geometry but is primarily controlled by the type and amount of material.

Contact time is an indication of the time available for the physical and chemical interactions of the sorption process. Greater contact times permit more flexible response towards those chemicals where interactions are the slowest.

The ratio of sorbent and sorbate densities is a factor affecting sorption as used in spill response techniques. These two densities must be similar to obtain an adequate contact time for the sorption process and must be less than the density of water, if recovery of hazardous chemicals spills is to be practical.

Several environmental factors also affect the sorption process. Ambient temperature affects both the rate of reaction and sorbent capacity. The pH and salinity of the water affect the chemical and physical interactions and may also influence the sorbent capacity.

Combining normal sorption and sponge-like entrapment offers a means of increasing the efficiency of sorption processes. This combination increases the total capacity of the sorbent to a point where it may hold nearly its own weight of spilled chemical. This has been developed into the "imbiber" beads and other macroreticular resins used as sorbents.

Dispersing sorbent materials over the surface of a spill is a difficult procedure interrelated with several complex variables. The amount of sorbent material required to ameliorate a given volume of spilled chemical may be easily determined. The rate of coverage required in real spill situations becomes quite complex, however, when wind, waves and spreading actions combine to change the spill dimensions. This interrelationship of complex variables makes modeling and calculating design specifications almost impossible.

Morris and Weber (1964), Gilmore et al (1970) and Bauer et al (1975 and 1976) have evaluated the applicability of general sorption processes for ameliorating spills of

Morris, J.C. and Weber, W.J., Adsorption of Biochemically Resistant Materials from Solution Contract No. SA pH 76295 HEW Report No. AWTR-9 (1964).

Gilmore, M.A.; Smith, D.D.; Rice, A.H.; Shenton, E.H. and Moser, W.H. Systems Study of Oil Spill Cleanup Procedures Vol I Analysis of Oil Spills and Control Materials Contract No.OS-1 API Marine Management Service (1970).

Bauer, W.H.; Borton, D.N.; Bulloff, J.J. and Sinclair, J.R. "Agents for Amelioration of Discharges of Hazardous Chemicals on Water" 1976 Nat'l Conf. on Control of Hazardous Materials Spills.

Bauer, W.H.; Borton, D.N. and Bulloff, J.J. Agents, Methods and Devices for Amelioration of Discharges of Hazardous Chemicals on Water, Contract No. DOT-CG-42759-A (August 1975).

various chemicals. Pilie et al (1975) and Dawson et al (1976) have investigated the applicability of carbon sorbents for spills of hazardous chemicals.

Bauer et al (1975) identified the advantages of using sorbent materials to ameliorate spills of hazardous chemicals. Their tabulation of "good sorbents" included: activated carbons, polyurethane foam, macroreticular resins, propylene fibers, zeolite molecular sieves, sorbent clays, polyolefins, polymethyl-methacrylates and polystyrene sulfonates.

Direct cost and other economic factors have been the criteria used for selecting sorbent materials to ameliorate oil spills, creating favorable circumstances for using straw, seaweed, leaves, corncobs and similar materials. None of these have the capacity or efficiency required to reduce the health and flammability hazards associated with the floating hazardous chemicals.

Activated carbons provide the most versatile approach to the sorption of hazardous chemicals, but the density of carbon is a most serious drawback. Carbons must be treated to retain hydrophobic character throughout the exposure to water while retaining their capacity. Floating activated carbons are being produced in experimental quantities at the present time, but there are no plans to produce the large amounts necessary for spill response techniques. Alternative application methods to circumvent the problem of density are the "tea bag container" advocated by Pilie et al (1975), or the "Dynactor" manufactured by R.P. Industries, which combines vapor and liquid removal in venturi-scrubber-type equipment.

Pilie, R.J., Baier, R.E.; Ziegler, R.C.; Leonard, R.P.; Michalovic, J.G.; Pek, S.T. and Bock, D.H. Methods to Treat, Control and Monitor Spilled Hazardous Materials EPA-670/2-75-042 (June, 1975).

Dawson, G.W.; Shuckrow, A.J. and Swift, W.H.; Control of Spillage of Hazardous Pollution Substances, PB 197-596 (1970).

Bauer, W.H.; Borton, D.N. and Bulloff. J.J. Agents, Methods and Devices for Amelioration of Discharges of Hazardous Chemicals on Water, Contract No. DOT-CG-42759-A (August 1975).

Molecular sieves offer good capacities, but must be treated the same as carbons to maintain a low density and prohibit sinking. These materials are also more selective sorbents and would require maintaining a larger stockpile to permit responses to the wide variety of hazardous chemicals.

Polyurethane foams provide a combination of physical and chemical properties which are a definite advantage for hazardous chemical spills. Owens-Corning Fiberglas Corporation has developed the "Glasorb" blanket and several manufacturers market systems to utilize small pieces of urethane for continuous recycling sorption processes. Another approach would be to foam the urethane "in situ" as a container and cover for the spill.

The macroreticular resins, ion exchangers and various foamed plastics would provide alternative sorbent characteristics which would benefit spill response techniques. Most of these do not have the versatility of activated carbons but could have greater capacities for individual chemicals and all have lower densities.

Sorbents as a Candidate Spill Response Technique

This candidate spill response technique would include a commercially available sorbent material and the equipment for dispersing it over the surface of the spill. The best sorbents would interact with both the liquid and vapor phases of the spilled chemical to reduce the vapor hazards resulting from the spill.

The volume of sorbent used would range from one to ten times the volume of the spilled chemical. Calculated from the typical spill characteristics used for this investigation, the maximum amount of sorbent material could be as much as 380 m^3 (1.34×10^4 ft^3) spread over an area as large

as 3800 m^2 (40,700 ft^2). The average distribution rate would be approximately 0.1 m^3 sorbent per m^2 of spill (0.33 ft^3/ft^2).

The sorbent material must have a good capacity, buoyancy and compatibility with spill removal equipment. Polyurethane foams, macroreticular resins and ion exchange resins have the desired characteristics. A combination of buoyancy (to maintain the excess sorbent in the gas phase) and particle geometry (to aid close packing) influence the ability of the sorbents to reduce evaporation. If they become completely saturated or sink beneath the layer of floating, hazardous chemicals, their effectiveness is lost.

Pneumatic equipment appears to be the best means for dispersing sorbent materials. Hydraulic systems are similar in all respects, but the presence of water disrupts the spill layer (as well as the sorbent cover) permitting vapor losses.

Snow blowers, forage blowers and mulch spreading equipment could be used to deploy the sorbent materials. Capacities are in the range of 1.4×10^4 to 4.5×10^5 Kg/hr (15 to 500 tons/hr). Sizing the equipment or number of units to be used would be predicated upon the characteristics of the sorbent and amount of cover required.

American Snowblast Corporation manufactures a typical snow thrower unit which would be capable of handling sorbent materials. Their model RHS-300-76 is capable of dispersing 2.7×10^5 Kg/hr (300 tons/hr) of snow. This unit weighs approximately 730 Kg (1600 lb) and occupies approximately 21 m^2 (23 ft^2) of deck space. A 37 hp gasoline motor is used to give a range of 3 to 18.3 m (10 to 60 ft). Total cost for this unit would be approximately $7000.

Kool Brothers Corporation manufactures a typical forage blower unit. Their model KB-1000 is capable of dispersing approximately 1.4×10^5 Kg/hr (150 tons/hr) by using

a 90 hp power take-off. Electric motors have also been used as a power source to make an independent system. This unit weighs slightly less than 450 Kg (1000 lb) and occupies approximately 3.8 m^2 (41 ft^2) of deck space. Sorbents could be deployed a distance of 15 to 30 m (50 to 100 ft) from the blower. Total cost for this system would be approximately $1350.

Finn Equipment Company manufactures an "Eagle" model, typical of mulch spreaders, which could be used to deploy sorbent materials. This unit is capable of handling 1.4×10^4 Kg/hr (15 ton/hr) with either 110 hp gasoline or 104 hp diesel power. It weighs 2360 Kg (5200 lb) and would occupy approximately 10 m^2 (109 ft^2) of deck space. Sorbents could be blown up to 26 m (85 ft) from this system in standard form, and over 46 m (150 ft) with optional extensions. Total cost for this system would be slightly in excess of $10,000.

Storage and transfer systems would be additional accessories required for any of the pneumatic systems used for deploying sorbents. Storing up to 380 m^3 (13,400 ft^3) of sorbent materials would require barges or separate cargo holds and either mechanical or pneumatic systems to transfer the sorbent to the disperser unit. The cost for the accessory equipment, and installation, would be in the same range as the blower units (i.e., $5000 to $10,000).

Total costs for this response technique would depend upon the sorbent as well as the equipment used to deploy it. Common oil sorbing materials are available for approximately $21.50 per m^3 ($2/ft^3). Ion exchange resins are sold for approximately $753.50 per m^3 ($50/ft^3) while prices of urethane foam are available for about $5.38 per m^3 ($0.50/ft^3).

The total cost of equipment used to deploy the sorbent would be approximately $25,000, installed. Total

cost of sorbent material would be as little as $7,000 for urethane foam pieces, or about $27,000 for macroreticular resins. Total costs would range between $32,000 and $52,000 for responding to a spill of 38 m^3 (10,000 gal) of a floating hazardous chemical.

Gel Technology

The formation of gels, in which a spilled chemical is the dispersed phase, is a potential means for reducing the vapor hazards from spills of floating hazardous chemicals. The gelation process selectively reacts the spilled chemical with a gelling agent, to form a less mobile product. These reactions are usually limited to pairs of reactants, but a more versatile mixture has been developed in recent research.

Gels are members of a class of colloidal systems which may be defined in terms of dispersed phase, particulate sizes, and other characteristics, but which, for this program, encompassed any colloidal system undergoing viscosity increases upon mixing. Although classes such as resins, sols, gels and emulsions all fit this description, no efforts were made to distinguish the individual classes' effects on vaporization rate.

Gel formation is usually the result of the interaction between a high molecular weight molecule (macromolecule) and a liquid. The gel structure is a combination of physical and chemical interaction that generally results in the formation of a two- or three-dimensional network of macromolecular cages, which entrap the liquid phase. Irzhak (1975) has reported experimental work and theoretical interpretations of gelation reactions.

Irzhak, V.I., "Statistical Theory of Gelatinization Sol Fraction" Vysokomol Soedin, Series A 17 (3), 535 (1975).

The formation of a gel does influence the evaporation rate and therefore the vapor concentration of a spilled chemical. This influence is not great, however, and the primary benefit obtained from gelation is immobilization or confinement. This technique also has good flexibility, due to a great variety of gelling agents, good shelf-life and low toxicity.

The time required for the gelling reactions to be completed is a limiting factor for this technique. There are a few gels which may be formed within minutes, but most gelling reactions are measured in terms of hours.

The "Universal Gelling Agent", developed by Calspan Corporation, has a specific blend of gelling agents combining the flexibility and rapid reaction rates required for treating spills of floating, hazardous chemicals.

Gelation or emulsification techniques affect spills of hazardous chemicals within five distinct areas:

1. Detection and monitoring
2. Vaporization rate reductions
3. Recoverable forms
4. Recycle or reclamation
5. A base for the application of other amelioration techniques

Detection of spilled chemicals and monitoring of the surface spread is an important part of responding to spills of floating, hazardous chemicals. Immobilization and containment, by the formation of the gel or emulsion, significantly reduces the problems of distinguishing surface phases. There is little effect on the detection and monitoring of vapor concentrations, however.

Evaporation rate reduction is achieved by forming a continuous cover of gelled material to encapsulate the more volatile spilled liquid. Gelling techniques which

result in the formation of a thin, surface barrier are more efficient for reducing evaporation than those gelling a thick mass of material. The ability to limit or stop the spread of hazardous chemicals over the water surface also reduces evaporation since the amount of vapor released is proportional to the surface area.

Recovery or removal of spilled chemicals often presents a problem even after steps are taken to decrease the hazards. Gelling agents interact with the chemical to form a mobile phase, which is more easily removed by mechanical means.

There is a possibility for reclamation and recycle of the hazardous chemicals after the gelling technique has been used. The toxicity of some compounds is not diminished by common disposal techniques (i.e., landfill or incineration). The combination of expensive materials, ready markets and harmful waste products for these chemicals increases the desirability for a method of reclamation.

The gel produced by this technique provides a stable base of immobilized material, which could be used in conjunction with other response techniques, to provide additional protection.

This compatibility with other response techniques is an asset which has not been utilized in the development of combination response techniques.

The major factors influencing the rate of evaporation from gelled masses are:

1. extent of physical and chemical interaction
2. homogeneity of gel
3. environmental factors

Gelling agents interact with the spilled chemical to considerably increase viscosity and form a semi-solid

(gel). These polymerization type reactions are often quite exothermic, however, and the reactants must be critically chosen to avoid excessive heat release while forming stable gels. The extent to which this compromise can be attained governs the release of spill vapors and eventual reclamation.

A homogeneous layer of gelling material (and the gel formed) also promotes the formation of a stable gel. Particle size and distribution equipment influence this parameter and must be chosen to compliment each other.

Environmental factors, such as ambient temperatures and wind, influence the effectiveness of gelation. Both affect the gelling reaction and final integrity of the gelled layer as it is formed on the surface of a body of water.

A considerable amount of development has been reported for gelling reactions during recent years. Fuller (1971) and Goldstein et al (1973) have reported on gelling techniques developed specifically for oil spills, in addition to the development work at Calspan Corp.

Research and development programs have been reported by Bannister, Pennace, Reynolds and Curby (1974) and Weaver, Bagley, Fanta and Doane (1974) which have potential applications in the gelation of spills on water. These are given further consideration in the section on research recommendations.

Fuller, H.L., "Use of Floating Absorbents and Gelling Techniques for Combating Oil Spills on Water", Journ. Inst. Petrol. (London) 57 (553, 35 [1971]).

Goldstein, A.M., Koros, R.M., and Tarmy, B.L., "Engineering Study of an Oil Gelation Technique to Control Spills from Distressed Tankers", Paper presented at the Joint Conference on Prevention and Control of Oil Spills, 4th, Washington, D.C. (1973).

Bannister, W.W.; Pennace, J.R.; Reynolds, H.H. and Curby, W.A., "Gelation of Oil by Amine Carbamates as a Means of Removal and Recovery", Paper presented at ACS Meeting (Southeastern Regional), Norfolk, Virginia (October, 1974).

Weaver, M.O.; Bagley, E.B.; Fanta, G.F. and Doane, W.M. "Gel Sheets Produced by Hydration of Films from the Potassium Salt of Hydrolyzed Starch-Polyacrylonitrile Graft Polymer" Appl. Polymer Symp. No. 25, pp 97-102 (1974).

Gelling Agents as a Candidate Spill Response Technique

Gelling hydrocarbon cargoes and other commercial organic chemicals to prevent flow or surface spread has been possible for some time. The specific use of gelling agents to ameliorate the hazards resulting from spills of floating hazardous chemicals has been developed by Calspan Corporation (1974). Their work resulted in the formulation of a "Universal Gelling Agent" mixture which will congeal all floating hazardous chemicals, according to Calspan Corporation.

The "Universal Gelling Agent" mixture contains four or five commercial gelling agents as components. The composition and performance specifications have been prepared by Calspan Corporation under government contracts. The four gelling agents listed in their report include:

(1) Dow Chemical Corporation, Gelgard, to combat spills of aqueous liquids,

(2) Dow Chemical Corporation, Imbiber Beads, for spills of the inert spirits-type liquids (typified by cyclohexane),

(3) BF Goodrich Corporation, Hycar 1422, to combat the polar organic chemical spills including the chlorinated hydrocarbons, and

(4) BF Goodrich Corporation, Carbopol (and in some cases, Union Carbide, Polyox) to selectively thicken and control alcohol spills.

In addition, a one-fifth portion of Cabot Corporation "Cabosil" was used to increase the fluidity of the mixture.

A listing of the hazardous chemicals used to test the performance of the "Universal Gelling Agent" is presented in Table 8 from the report of Pilie et al (1975).

Baier, R.; Michalovic, J.; DePalma, V. and Pilie, R., Universal Gelling Agent for the Control of Hazardous Liquid Spills, Calspan Corp., (August, 1974, reprint).

Pilie, R.; Baier, J.; Ziegler, R.; Leonard, R.; Michalovic, J.; Pile, S. and Bock, D., Methods to Treat, Control and Monitor Spilled Hazardous Materials, Contract No. 68-01-0110, EPA Report No. EPA-670/2-75-042 (June, 1975).

TABLE 8 - COMPOUNDS TESTED WITH UNIVERSAL GELLING AGENT

ACETONE	FORMALDEHYDE
ACETONE CYANOHYDRIN	GASOLINE*
ACRYLONITRILE*	ISOPRENE*
AMMONIUM HYDROXIDE	ISOPROPYL ALCOHOL
ANILINE*	KEROSENE*
BENZALDEHYDE*	METHANOL
BENZENE*	METHYL ETHYL KETONE*
BUTANOL	OCTANE (2,2,4 TRIMETHYL PENTANE)*
CARBON DISULFIDE	
CARBON TETRACHLORIDE	ORTHO-DICHLOROBENZENE
CHLORINE WATER (SATURATED)	PETROLEUM ETHER*
CHLOROFORM	PHENOL (89%)*
CYCLOHEXANE*	PYRIDINE
CYCLOHEXANONE*	SULFURIC ACID
ETHANOL	TETRAHYDROFURAN*
ETHYLACETATE*	TRICHLOROETHYLENE
ETHYLENE DICHLORIDE	WATER
ETHYLENE GLYCOL	XYLENE*

*Chemicals considered in this study

The "Universal Gelling Agent" should be dispersed to form a homogeneous layer at a rate of approximately 0.12 Kg/ℓ (1 lb/gal) of the spilled chemical. This provides sufficient material to gel all hazardous chemicals and insure a stiffer hydrolysis-resistant gel.

Approximately 4536 Kg (10,000 lb) of the "Universal Gelling Agent" would be dispersed in response to the largest typical spill (38 m^3 or 10,000 gal). The developers have recommended the MSA Model 400 "Bantam" rockduster for dispersing the gelling mixture. This unit and several others, with optional equipment for modifying them to meet special requirements, are described in Appendix C.

The "Bantam" model weighs 318 Kg (700 lb), would occupy approximately 8.9 m^2 (96 ft^2) of deck space, and cost approximately $5000. Normal operation of this equipment requires either 1 or 2 people in attendance. An estimated life for this equipment would be approximately 20 years, with proper maintenance, under the sporadic usage against chemical spills. The "Universal Gelling Agent" can be prepared for approximately $6.61 per Kg ($3.00 per lb). Total cost of equipment and materials necessary for the gelation of a spill of floating, hazardous chemical would be approximately $35,000.

Cryogenic Cooling Technology

Cryogenic cooling of floating, hazardous chemicals is a direct route to vaporization rate reduction. This response technique, although simple in application, encompasses a variety of theoretical aspects which span the three major tasks of this program. The evaluation of cryogenic cooling as a candidate spill response technique can, therefore, be considered within the scope of each task.

Any stable compound which could be easily cooled and stored below normal, ambient temperatures would be

adequate for simply cooling a spill of hazardous chemical. A selection of the "best cryogen" would be made on the basis of individual spill conditions and capability of the individual spill response team. Liquid air, liquid nitrogen, refrigerants, solid carbon dioxide or common ice are possible candidates.

Selection of the cryogen becomes more of a logistics problem when the theoretical aspects of cooling are considered. Some general trends may be predicted from Trouton's Rule: $\ln \rho/\rho_o = 20.7/R(1-T_o/T)$, or the integrated form of the Clausius-Clapeyron equation: $\ln \rho/\rho_o = \lambda/R(1/T_o-1/T)$ where ρ_o and ρ are vapor pressures at T_o and T absolute temperatures, R is the gas constant and λ, the molal heat of vaporization.

Using these theoretical descriptions, vapor pressures (equilibrium vapor concentrations) could be reduced between 40 and 95%, if the final temperature is limited to the ice point. The vapor pressures tabulated in Table 5 indicate reductions in the range 50 to 80% would be possible for the majority of hazardous, floating chemicals. Data obtained with benzene in equilibrium with ice at 0°C, 32°F showed a 74% reduction.

The efficiency of cryogenic cooling to ameliorate spills of floating, hazardous chemicals is controlled by four factors:

1. Delivery
2. Physical Properties
3. Freezing Point of Water and Spilled Chemical
4. Environmental Factors

Delivery of the cryogenic material affects the ultimate efficiency of this technique much the same as the other techniques. It is imperative that the cryogen be spread evenly, over as large an area as possible, very quickly. Vaporization rate reductions will be directly

proportional to the efficiency with which a homogeneous cooling blanket of cryogen is placed over the spill.

Physical properties such as melting point, freezing point, vapor pressure, specific heat, viscosity, surface tension and heat of fusion, for both the spilled material and the cryogen, determine the theoretical efficiency of this response technique.

The presence of a tremendous excess of water limits the equilibrium temperature to 0°C (32°F). Although the evaporation rate reductions are favored by lower temperatures, the freezing point of water is a more realistic temperature limit.

Environmental factors, such as rain, wind and water turbulence, are just as important in this spill response technique as the others. Warm days with bright sunshine will impose a higher, surface heat load, while rain, wind and waves will increase the heat load by mixing.

Cryogenic Cooling as a Response Technique

Cooling a volatile spill material to near the ice point (0°C [32°F]) will reduce its vapor pressure and evaporation rate correspondingly. Heat removal requirements are conservatively estimated at 136 KCal/m^2 (50 Btu/ft^2) for initial spill material cooling, plus 41 KCal/m^2-hr (15 Btu/ft^2-hr) heat losses to surrounding air and water for the duration of the spill. A maximum size spill (3780 m^2, 40,670 ft^2) will require .51 x 10^6 KCal (2 x 10^6 Btu) initial cooling, plus 1.6 x 10^5 KCal/hr (6 x 10^5 Btu/hr) continuous cooling.

Cryogenic materials offer a portable heat sink for such spill cooling service. They can be applied directly, or in combination with water (ice) or other heat transfer agents, as required for ease of disposal. Theoretical refrigeration values and costs of some common coolants are typically as shown in Table 9.

TABLE 9 - THEORETICAL REFRIGERATION VALUES AND COSTS OF COOLANTS

COOLANT	STATE	NET REFRIGERATION		COST		
		Cal/gm	Btu/lb	$/lb	$/ton	$/$10^6$ Btu
Air	ℓ, 78.8°K (-317.8°F)	98	176	.07 (~2 x LN_2, Special Order Only)	140	400
Nitrogen (N_2)	ℓ, 77.4°K (-320.4°F)	97	176	.033	66	190
Carbon Dioxide (CO_2)	ℓ+g, 274°K (300 psi, 1.7°F)	71	127	.04	80	315
	S, 194.7°K (-109.3°F)	153	275	.095	190	346
Water Ice	S, 273°K (0°C, 32°F)	80	144	.015	30	104

Cryogenic material selection for spill cooling may well be limited to liquid CO_2, as indicated by Dr. S.M. Mathews of AIRCO.* Liquid CO_2 was recommended over LN_2 based on:

- Loss-free storage, since CO_2 tanks are equipped with refrigeration cycles to reliquefy boil off.
- CO_2 storage tanks are single wall, in contrast to the vacuum tanks used for LN_2. This makes CO_2 tanks less costly and more resistant to the "high-g" stresses experienced aboard ships.
- CO_2 costs less than LN_2 based on equivalent "effective" refrigeration effects expected during spill disposal. Spraying would vaporize all LN_2 within a few feet from the nozzle. Pouring LN_2 on the spill surface may spread slowly by flowing over local ice plates, initially formed. The LN_2 would lay and boil off these plates with excessive cooling at the point of application.
- CO_2 dispersal is easier to visualize since "snow horns"** are available for local application. Modifications for large application areas may be feasible using such methods as: Positioning booms for standard snow-horns; a snow lance at the perimeter to create a snowstorm at some loss in transfer efficiency; blowers to broadcast the snow horn feed directly, or intermediately using a water spray heat transfer media to broadcast a mixture of wet/dry ice.

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*Private communication from Dr. S.M. Mathews, AIRCO Industrial Gases, Division of AIRCO, Inc.

**AIRCO CO_2 "Snow Horns" are expansion nozzles used to convert liquid CO_2 to the solid form at conversion rates between 42 and 45% by weight.

Liquid CO_2 stored at 300 psi will yield about 43 Cal/gm (77 Btu/lb) of cooling in the spill material, after allowing for transfer inefficiencies using snow horns directed over the spill area. To meet the cooling requirements of a maximum size spill, 12,000 Kg (13 tons) are needed for initial cooling, followed by 3,600 Kg/hr (3.9 ton/hr) for maintaining the lower temperature.

Liquid carbon dioxide storage facilities would be similar to those recently prepared by Airco Industrial Gases Company for use on barges. This facility consisted of a 27,000 Kg (30 ton) capacity tank, fitted with a heat loss refrigerator installed on an ISO frame, occupying 77 m^3 (2770 ft^3), weighing 18,000 Kg (20 tons) empty, and costing $30,000 each.

Snow horns are available from AIRCO converting the liquid CO_2 to solid CO_2 snow at high (42-45% by weight) efficiencies. Largest standard horns cost ~$1000 and have a capacity of 19 Kg/min (42 lb/min) of snow, using 45 Kg/min (100 lb/min) of liquid CO_2 supply. To apply initial cooling within 1/2 hr, about 10 snow horns are required at a total cost of $10,000. Equipment required for dispersing the snow over the spill area as discussed, can easily add $30,000 to the system cost. This could be a conventional snow blower, modified for cryogenic service, using stainless steel contacting parts. Operation would require 2-3 men. Electrical power (20 hp) is required for storage refrigeration. Standby maintenance is minimal. A 10-year useful life would be expected for hazardous spill response service.

Total cost of a typical 45,000 Kg (50 ton) liquid CO_2 system would be approximately $170,000.

Alternative spill refrigerant systems could be based on using either solid CO_2 (dry) ice or solid water (wet) ice. The solids would be crushed and pneumatically broadcast over the spill using a snow thrower or mulch spreader. Shipboard storage of ice would include high losses

and considerable labor and mechanical handling equipment. Special materials of construction would be required for the cryogenic temperature of dry ice. Offsetting advantages would include higher "effective" refrigeration effects, smaller quantities of refrigerant required, and lower cost/Btu content. Use of water-ice system could prove particularly attractive, since it can be generated "in situ" for maintaining an adequate supply.

Solid carbon dioxide would absorb approximately 153 cal/g (275 Btu/lb) when dispersed over a spill of floating hazardous chemical. Therefore, the quantity of solid carbon dioxide required to be dispersed in response to the largest typical spill would be about 3.3×10^4 Kg (37 ton) for the initial cooling and 6×10^2 Kg/hr (6.6 ton/hr) to maintain the low temperature.

Solid water (ice) would absorb about 80 cal/g (144 Btu/lb) when dispersed over a hazardous chemical spill. The quantity of ice necessary to respond to the largest typical spill could be approximately 64,000 kg (65 tons) for the initial cooling and 2×10^3 kg/hr (2.2 ton/hr) dispersed throughout the time for removing the spill, to maintain the low temperature.

Both these coolants could be dispersed by equipment similar to the model R-300-76 snow blower, manufactured by American Snowblast Corporation. The special helical feed cutter would need some modification for supplying the coolant from a separate storage. This equipment would weigh about 680 kg (1500 lb) and occupy about 2.1 m^2 (23 ft^2) of deck space. The storage unit would be large and rather cumbersome unless incorporated into the response vessel.

The total cost for equipment and materials necessary for the cryogen response technique would be approximately

$80,000 for the solid carbon dioxide response technique and approximately $55,000 for the water ice response technique.

Evaluation of Candidate Techniques for Task I

Films - The surfactant film technique for ameliorating spills of hazardous chemicals can only be used if the ambient temperature is less than ~33°C (~91.5°F), there is little wind and there is no rain, wave action or current to disrupt the film. It is applicable against most chemicals having a surface tension greater than 20 dyne/cm (1.4×10^{-3} lb/ft).

Either foam or aerosol application could be used to generate the surfactant/water film. While each method offers some advantages, the aerosol method is preferred. The surfactant/water solution must be dispersed over the surface of the spill for rapid production of the film. The foam application involves throwing a low expansion (heavier) foam over a large range, with commensurately greater chances of disrupting the floating chemical layer.

There is some uncertainty whether the 90 to 98% reduction in evaporation measured in the laboratory would be possible with a hazardous chemical spill. The forces generated by the action of swells and waves may cause the film to penetrate through the floating chemical layer and lose its control of evaporation.

The effectiveness index for the surfactant film technique is conditionally acceptable.

The small volumes of surfactant/water solution required and general characteristics of the films produced are assets for this candidate spill response technique. The efficiency index is rated as acceptable.

After many years of being considered innocuous, fluorinated compounds are being reexamined for detrimental

effects to the environment. Even the small concentrations of fluorinated surfactants used in aqueous film forming foams are considerably greater than those in the environment. The fate and consequences of fluorinated compounds in the environment are in the process of evaluation by governmental and industrial health agencies. The compatibility index is conditionally acceptable.

Foams - A 40 cm (16 in.) layer of high expansion foam would reduce the rate of evaporation from a spill of floating, hazardous chemical as long as the foam remained in place. The foam would not confine the spreading layer of chemical and one of the standard boom enclosures would significantly aid the homogeneity and life of the foam layer. This technique would perform best when the air was cool, calm and there was no rain.

The two high expansion foams evaluated are compatible with approximately 75% of the floating, hazardous chemicals. They will reduce evaporation losses to the atmosphere, but retain these vapors within the foam mass, where they may be ignited. Combustion reactions are less active than the unconfined gas mixtures, but are self-propagating. The effectiveness index of the high expansion foam technique is conditionally acceptable.

This technique can be applied by commercial equipment which can be assembled into a system by a single supplier or the components may be assembled by the Coast Guard. The few modifications which could be required for spill response applications would be easily obtained and inexpensive. The amount of foam solution required to cover typical spills would not create a storage problem unless wind and rain dissipated the foam too rapidly. Booming the spill would be a definite asset for the high expansion foam technique. The efficiency index for this technique is acceptable.

Commercial foams are formulated to meet standards for environmental compatibility. The amount of foam required to ameliorate hazardous chemical spills would not affect this. The compatibility index of this technique is acceptable.

Sorbents - Vaporization rate reductions are possible with sorbent materials only when an excess sorptive capacity is available. The best conditions for using this technique would include cool, calm weather with no rain or water turbulence to break the sorbent layer. This technique is rated as conditionally acceptable for its effectiveness index.

Commercial equipment is available to disperse the sorptive materials over a hazardous chemical spill. The volumes of sorbent required place stringent requirements on shipboard storage and handling capabilities, however. The presence of sorbent materials may also interfere with the removal of the hazard with commercial equipment for removing spilled liquids. This technique is rated as conditionally acceptable for its efficiency index also.

Most sorbent materials will not pose any environmental difficulty in themselves. After exposure to and sorption of the hazardous chemicals they may present a more concentrated hazard. Inefficiencies in retrieval or a density change from exposure which permits the sorbent to sink and avoid removal will increase the potential hazards from chemical spills. Small percentage losses of the large volumes of sorbent required to ameliorate a chemical spill will leave significant amounts of material to be assimilated into the environment. This technique is rated as conditionally acceptable for its compatibility index.

Gels - Vaporization rate reduction by gels is the result of the formation of a continuous layer of chemically and physically bonded material and the reduction of convection currents and heat transfer within the spilled chemical. Experimental measurements in this investigation showed only 40% reduction of the evaporation rate of benzene.

The flammability hazard was another part of the evaluation of gelling agents as a response technique for spills of floating hazardous chemicals. Glassman et al (1969) have reported that convective flow is an important parameter in determining the flammability of pools of liquid fuels. They concluded that "thickening fuels decreases the flame-spreading rate, but increases the ignitability". Therefore, gelling agents would need to have an inhibitor included in their formulation to reduce flammability hazards.

The gelling agent technique for response to hazardous chemicals spills has been rated as unacceptable for the effectiveness index.

The amounts of material and rates of application are within the compatibilities of existing equipment. Costs, although significant, are not unreasonable and could possibly be reduced by judicious selections of gelling agents and dispersal equipment. The efficiency index rating of this technique is acceptable.

A major attribute of the gelling agent technique is its ability to control the spread of a hazardous chemical spill and significantly aid confinement methods. This is particularly applicable in assessing the burden to the environment. The semisolids produced by gelation are more easily removed and reclaimed from aquatic environments.

Glassman, I., Hansel, J. and Eklund, T., "Hydrodynamic Effects in the Flame Spreading, Ignitability and Steady Burning of Liquid Fuels", Combustion and Flame 13, 99 (1969).

The only negative aspect found during the development testing program was when the gelled material was mistaken for food by fish. This was attributed to the feeding habits developed in laboratory fish. This technique is evaluated as acceptable for the compatibility index.

Cryogens - Cryogens can be used to reduce the vaporization rate of all floating hazardous chemicals. Vapor pressure or equilibrium vapor concentrations can be reduced by 40 to 95% if the final temperature is maintained at the ice point. The vaporization rate of benzene was reduced approximately 74% in an experimental test conducted in this program. This response technique is rated as conditionally acceptable for the effectiveness index.

The quantities of cryogen and rates of dispersal required for adequate securing of a hazardous chemical spill create problems for both storage and delivery. These will require some modifications to presently available equipment or to the ships carrying them to respond to a spill. This response technique is rated as conditionally acceptable in terms of the efficiency index.

Selection of the cryogenic material determines the environmental burden of this response technique and the compatibility index. Most refrigerants must be excluded on the basis of their toxicity and carbon dioxide would change the pH of water, when used in these quantities. Liquid nitrogen and solid water (ice) are considered to be the only materials which can be used in this response technique to give an acceptable rating for the compatibility index.

Summary of Ranking Within Task I

This evaluation concentrated on five candidate techniques to achieve vaporization rate reductions on discharges of floating, hazardous chemicals. Only three of these appear adequate for fulfilling the goals of this task. These three have been ranked in the order surfactant films, foams and sorbents.

The surfactant film technique is ranked first because of the small amounts required, relative ease of application and its applicability on a wide variety of hazardous chemicals.

These general attributes must be balanced by the environmental pollution problems of fluorinated chemicals, by the limiting surface tension value for which this technique may be used and by recognized limits for reducing vapor release, except under optimum conditions.

Foam covers are an alternative approach to vaporization rate reductions of floating, hazardous chemicals. Both high and low expansion foams may be used, with cost factors favoring the use of high expansion and production and foam life factors favoring low expansion.

A judicious selection of foaming agent is required to obtain the best flexibility in treating floating, hazardous chemicals. Foaming agents lack compatibility with chemicals having a dielectric constant greater than three (3) and must be selected to avoid exposure to chemicals which are solvents for the foam constituents.

The use of sorbent materials to achieve vaporization rate reduction requires both sorptive capacity and buoyancy. Any combination of overloading or loss of buoyancy will nullify their effectiveness. When the sorbent material becomes saturated with water and/or hazardous chemical, it provides a greater surface area for evaporation.

All of the recovery devices listed in Table 2 may be used with these response techniques. Moving belt skimmers would present the most problems when used with these techniques for ameliorating vapor hazards. Weir, suction head, and inflexible plane skimmers may be used after the candidate ameliorating techniques. Further measurements would be necessary to determine which combinations would maintain the best protection for response personnel.

TASK II - VAPOR CONCENTRATION REDUCTION

The objective of this task was to evaluate candidate spill response techniques concerning their capabilities for reducing vapor concentrations released from spills of floating, hazardous chemicals. The criteria used to evaluate the various techniques were similar to those of Task I. Techniques were ranked according to their ability to reduce hazardous chemical vapors below their threshold limit value or flammability limits.

Attaining this objective required the identification and definition of factors controlling the removal of hazardous chemical vapors by dilution, condensation or sorption. The investigation of candidate techniques consisted of selecting a minimum number of methods involving concentration reduction capabilities for a maximum number of hazardous chemicals.

The response techniques which might provide some capabilities for reducing vapor concentrations include:

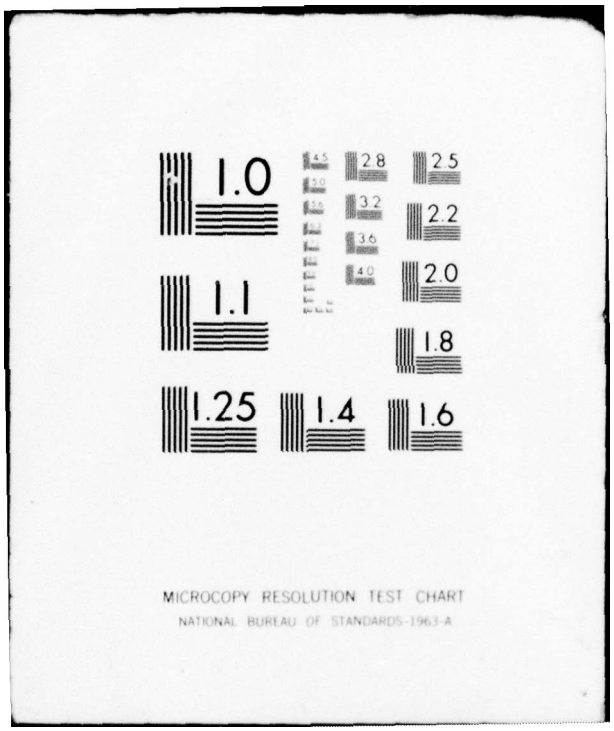
1. Dilution or dispersion
2. Condensation
3. Sorption
4. Reaction
5. Encapsulation

Each of these techniques is applicable toward a majority of the floating hazardous chemicals. They were evaluated on the basis of rapid response and application to the immediate vicinity of the spilled chemical for the effectiveness and efficiency ratings in this program.

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FEASIBILITY STUDY OF RESPONSE TECHNIQUES FOR DISCHARGES OF HAZA--ETC(U)
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Vapor Dilution as a Candidate Spill Response Technique

Simple dilution provides a direct approach toward vapor concentration reduction. This approach can be considered a spill response technique since the performance specifications can be calculated and equipment is available for achieving these specifications.

The dilution technique involves the transport and mixing of uncontaminated air with the vapors released from a chemical spill. The volume of uncontaminated air must be large enough to maintain the concentration of hazardous chemical vapors below their threshold limit value or lower flammability limit.

Performance specifications can be calculated from data generated with the natural dispersion model described previously. This model predicts the evaporation rates for spills of floating, hazardous chemicals to be in the range of 1 to 3.5 cubic meters of vapor released per hour per square meter of spill surface (3.3 to 11.5 $ft^3/hr \times ft^2$).

Typical spills are anticipated to cover between 378 and 3780 square meters (4,069 to 40,690 square feet) and release between 378 and 13,230 cubic meters of vapor per hour (13,350 and 467,200 ft^3/hr). If an average threshold limit value of 10 parts per million is assumed, then between 3.78×10^7 and 1.3×10^9 cubic meters of uncontaminated air must be added each hour (1.3×10^9 to 4.7×10^{10} ft^3/hr) to keep the concentration of the hazardous chemical vapor at this limit. If an average lower flammability limit of 1% by volume is assumed, then between 3.78×10^4 and 1.3×10^6 cubic meters of uncontamined air must be delivered each hour (1.3×10^6 to 4.7×10^7 ft^3/hr) to keep the vapor concconcentration at this limit.

These maximum estimates, approximately 10^9 cubic meters of "clean" air per hour ($\sim 5 \times 10^{10}$ cubic feet per hour) to achieve the threshold limit and approximately 10^6 cubic meters of "clean" air per hour (5×10^7 cubic feet per hour) to achieve the lower flammability limit concentrations, indicate the necessity of very large equipment. The dilution technique for responding to spills of hazardous chemicals may be considered to be a man-made wind. Such large gas volumes can be handled by blower equipment incorporating surplus jet engines. Such blowers are currently used by railroads to remove snow, and by airports to remove fog.

Some typical examples of this equipment are manufactured by Railway Maintenance Corporation, Pittsburgh, Pennsylvania. Their equipment is designed to remove snow from the road beds and switches to permit smooth operation in winter. An example of particular interest to this application is their "Hurricane" model blower, which is based upon an Allison J-35 jet engine. This blower can generate a 650 MPH air blast, which would deliver approximately 2.9×10^5 m^3/hr ($\sim 10^7$ ft^3/hr) of diluting air over the spill.

The "Hurricane" model jet blower is presently fabricated as a self-propelled railway car assembly, complete with the accessories necessary for 5 to 6 hours' independent operation. It occupies a space of approximately 10 m^2 (~ 108 ft^2), weighs 12,250 kg (27,000 lb) and costs approximately $75,000. Modifications, such as flat-bed mounting or a skid assembly, for shipboard operation are conceived as resulting in reductions of >50% in weight and cost.

Sporadic use against hazardous chemical spills, coupled with proper maintenance and storage precautions, can be expected to yield a long (10-20 yr) useful system

life, with occasional (2-5 yr) major overhaul programs. Operation would involve 1-2 men for start-up, followed by occasional adjustments and periodic refueling during long-term spill response applications.

Assuming the spill conditions are calm to stagnant, as many as 5000 jet blowers would be required to ameliorate the toxic properties of chemical vapors released from a large spill. If it were required only that the lower flammability limit not be exceeded, then up to 5 jet blowers would be required. In either case, any natural wind would reduce the number of blowers required.

The performance of this response technique is controlled by two factors:

1. the temperature of the exhaust gases, and
2. the sensitivity of concentration monitoring methods.

The jet exhaust is cooled by the eduction of excess air in the blower assembly, but will require that the blower be removed somewhat from the spill edge. This will permit additional mixing and cooling of the exhaust gases and minimize the heat input to the spilled material. Remote positioning also assures that there will be a minimum amount of the spill vapor picked up with the diluting air.

Not all floating, hazardous chemicals are easily detected and/or monitored. Monitoring the concentration of the hazardous vapor throughout the areas where response personnel would be working would place a significant burden upon the analytical instruments available and significantly increase the number of people required for a spill response team.

Cryogenic Condensation as a Candidate Spill Response Technique

Condensation, the inverse of evaporation, uses heat absorption by a second material to cool and coalesce the chemical vapors. Heat transfer in the vapor phase is inefficient because of spill conditions and the fact that most cryogens are used as solids or liquids. It is difficult to obtain good contact and mixing when such large surfaces and volumes are included in the operating conditions.

The cryogenic condensation technique involves the cooling, transport and dispersal of cryogenic materials over the spill. Performance specifications for this technique have been obtained from physical property data for the floating hazardous chemicals and the mathematical model for natural dispersion.

Only a vague estimate is possible for the heat absorption required to cool the vapors over these hazardous chemical spills. A value approximately ten times that required to cool the spill alone may be used to establish an order of magnitude but the effectiveness of the response technique would ultimately depend upon mixing or contact of the vapor with the coolant.

The amount of heat to be absorbed for vapor condensation over a spill of 38 m^3 (10,000 gal) would be approximately 5.1×10^5 Kcal (2×10^7 Btu), using these assumptions. This corresponds to the dispersal of approximately 33,000 Kg (37 ton) of solid carbon dioxide, or approximately 52,600 Kg (58 ton) of liquid nitrogen, over the spill.

Several dispersing systems would be necessary to deploy the cryogens as quickly and evenly as possible over the surface of the spill. One or more would be necessary to maintain the reduced temperature and stop the recurrence

of the maximum vapor concentration. This equipment would be similar to that described within Task I, with multiple units being required, to provide rapid cooling of the vapor phase. Total costs of this response technique would be estimated in terms of multiples of the basic units described in Task I.

Sorption as Spill Response Technique

A spill response technique, incorporating sorption or reaction of the spilled chemical, has been developed by R.P. Industries. The "Dynactor" they manufacture utilizes the sorption capabilities of activated carbon, while avoiding the problems of sinking and loss by using it in an enclosed system.

A "Dynactor" was fabricated and tested by R.P. Industries under contract to the Environmental Protection Agency (Contract No. 68-01-0123). The unit was designed for use as a self-contained response vehicle, mounted in a highway trailer. This system aspirated 1.4×10^4 m^3/min (5×10^4 ft^3/min) air while pumping and treating approximately 950 ℓ/min (250 gal/min) water. The basic design has been used for fabricating systems handling 7.0×10^3 m^3/min (2.5×10^5 ft^3/min) and appears feasible for larger units.

The operation of these systems is similar to venturi scrubbers or vapor diffusion pumps and they provide exceptional solid/vapor or solid/liquid contact. This permits high efficiency operation for sorption or reaction of unwanted chemicals.

Absorption would provide the most versatile approach for responding to hazardous chemical spills. Specific reactants or sorbents could be stored, however, for ameliorating special chemicals or particular classes of common chemicals.

The mobile unit designed for incorporation into a highway trailer occupies approximately 33.5 m^2 (360 ft^2) of floor space. This includes a diesel powered electric generator and walkways for operating personnel to move within the trailer. R.P. Industries estimated that approximately one third of the area within the trailer is used for these purposes. The system weighs approximately 18,000 Kg (40,000 lb) and can be purchased as prepared for this trailer mounting. The approximate cost of a unit handling 950 ℓ/min (2500 gal/min) water and 1.4 x 10^3 m^3/min (5 x 10^4 ft^3/min) air would be approximately $400,000. The cost of smaller or larger units prepared for this basic design would vary almost linearly with the air aspirating capabilities of the proposed unit (i.e., a system handling 7 x 10^3 m^3/min [2.5 x 10^5 ft^3/min] would cost somewhat less than $2,000,000).

Encapsulation as a Candidate Spill Response Technique

The basic encapsulation concept can be visualized as a floating boom enclosure, fitted with an elastomeric membrane cover (lid). Putting this lid over a floating hazardous chemical is a direct approach for containing the toxic vapors with nearly 100% efficiency. Accomplishing this feat quickly and safely over a typical chemical spill will severely test engineering acumen.

Floating cover assemblies are presently being fabricated by a number of suppliers for such purposes as protecting drinking water reservoirs, collecting methane gas from sewage waste lagoons, and sealing a broad range of liquid chemicals for atmospheric isolation. Minimal modifications to existing designs are anticipated for sealing floating, hazardous chemicals.

A typical example of this technique is performed by Globe Linings, Inc. (Long Beach, CA) which manufactures

a Hypalon membrane (0.8 to 1.1 mm [30-45 mil] thick) fitted with polyurethane floats for varied chemical service, including off-gas collection. Normal installation is by using 7.6 m (25 ft) wide sections, supplied in rolls, to build up the full area required. Covers up to 9750 m^2 (105,000 ft^2) have been installed, typically by 2 men within 2 days. Cover cost is approximately \$38.75/m^2 (\$3.60/ft^2). Skirting, similar to containment booms, is being currently evaluated for reservoir repair access service. Application potential for floating spill service is excellent.

Another producer, Gulf Seal Corp. (Houston, Texas) provides a continuous polyethylene foam underlay to float the sealing membrane for water service. This supports heavy snow, ice, or personnel, including polyethylene work platforms. Normal installation is by floating 3 to 30.5 m (10-100 ft) wide sections and tying them together at grommet provisions. Sizes in excess of 4.05×10^3 m^2 (1 acre) pose no problem. Material compatibility can be attained by substituting resistant foams and membranes. Portability and rapid deployment provisions need development since their continuous float arrangement may merely push the spill material ahead of the cover as it is pulled over the spill.

Polyethylene, vinyl and other common plastics are used as cover materials. Their light weight, availability and prices are major factors contributing to their use on these large installations. Polyurethane is an alternative cover material and composite or layered materials could also be considered.

The selection of encapsulating material and method of deployment must be made using factors such as:

1. Probable spill size
2. Material compatibility

3. Weight
4. Cost
5. Portability
6. Availability
7. Reuse or disposal requirements
8. Environmental compatibility
9. Interfacing with spill removal systems

Polyethylene film is stocked in clear, black or reinforced versions, in 0.1 to 0.25 mm (4-10 mil) thicknesses, up to 12 m by 30 m (40 ft x 100 ft) size rolls, weighing 34-91 Kg per 372 m^2 roll (75-200 lb per 4000 ft roll), and in an economical cost range of 9 to 93¢/m^2 (1-10¢/ft^2). It can easily be heat sealed to form larger shapes, flotation chambers, or to repair leaks. Compatibility with most (solvent type) spill materials is generally limited. Polyethylene membranes may serve for a single response against many of the hazardous chemicals.

Carlisle Tire and Rubber routinely fabricates large elastomeric membranes for liquid containment or exclusion service in ponds or reservoirs as liners and/or covers. These materials are compatible with the floating, hazardous chemicals.

Depending upon chemical resistance requirements, a variety of synthetic rubbers (butyl, EPDM, neoprene, hypalon, etc.) can be supplied. Standard sheets are commonly 0.8 to 3.3 mm (.03-.13 in.) thick, up to 12 m by 30 m (40 ft x 100 ft) size rolls, weighing 227 to 1000 Kg/372 m^2 roll (500-2200 lb/4000 ft^2 roll), and costing $2.69 to $10.76 per m^2 ($.25-$1.00/ft^2). Sheets can be provided with reinforcing fabrics for added strength. Larger lengths are feasible, but larger sections are usually made up by appropriate joining methods (vulcanizing, gluing,

mechanically). When used for cover service, suitable flotation or mechanical support provisions must be obtained to keep these materials from sinking.

Deploying the thin covers over a hazardous chemical spilled on water presents a more difficult problem than covering sewage lagoons, reservoirs and other landlocked waters. Combining the operations of deploying the cover and a boom appear to be the best approach. The cover would be slid over the boom or unfurled as the boom was being set in place. This operation would be done from the upwind side of the spill to avoid the vapor hazard.

The difficult conditions encountered for deploying these membrane covers over spills of floating, hazardous chemicals may be assumed to double normal installation costs. The installed costs of chemically resistant covers would be in the range \$40-65/m^2 (\$3.72-6.04/ft^2). Total cost for equipment and materials necessary for this encapsulation technique would be approximately \$150,000 to \$250,000.

Close-Packed Particles as a Spill Response Technique

The distribution of light particulates over a liquid surface is another means for preparing a physical barrier to encapsulate the liquid and reduce evaporation losses. This technique is presently used for open storage tanks, ponds and reaction vessels, where evaporation losses create air pollution or increase process costs. Evaporation is reduced by the presence of the densely packed layer of particles and its ability to reduce convection currents and insulate the liquid surface.

Plastic Systems, Inc. of Santa Ana, California has developed an evaporation control system which incorporates the geometrical ordering of dodecahedrons to produce this

close-packed array. The producers say that one thousand particles will cover an area of 0.38 m^2 (4.12 ft^2).

Solid particulates are spread over the surface by gravity, surface tension and convection forces. The dodecahedron geometry permits a single layer to cover more than 99% of a surface, when in the close packed arrangement.

Polypropylene foam lacks the chemical resistance necessary for responding to spills of floating, hazardous chemicals. Some research and development would be required to improve compatibility or develop a similar process for forming this geometry with other materials. Polyurethane appears to be the most promising material at the present time.

This technique would require the dispersal of approximately 10^7 particles to cover a spill of 38 m (10,000 gal). The present price for these dodecahedron particles is $0.03/each; predicted prices may be as low as $0.01/each, as the process develops. Total material costs would be in the range of $100,000 to $300,000 for this technique. Auxiliary equipment for storage and dispersal would be similar to that used for sorbent materials, described within Task I. Dispersal equipment would have to be specially selected to avoid damage to the particle geometry.

Reaction as a Candidate Spill Response Technique

Using chemical reactions to ameliorate the vapor hazards resulting from chemical spills involves the transport of large gas volumes through a reactor, where controlled reactions produce inert or innocuous products. Factors which influence the utilization of this technique include:

1. Reaction kinetics
2. Blower capacities
3. Product toxicities
4. Reactor capacities

Large volumes of air containing low concentrations of the hazardous chemical vapors must be handled, which translates into large equipment having very large power requirements. Many commercial reactors are capable of handling 280 to 1400 m^3/min (10^4 to 5 x 10^4 ft^3/min) gas flowrates. Equipment capable of handling 1400 to 2800 m^3/min (5 x 10^4 to 10^5 ft^3/min) gas flows should be possible with slight modification and moderate cost increases.

Reactions used in this technique must be very rapid. This aids the equipment sizing and removes the possibility of side reactions producing less desirable products. Rapid organic reactions are limited to neutralizations and catalyzed reactions. Neutralizations are applicable to only a few of the compounds found in the list of floating, hazardous chemicals. Oxidation reactions are possible with all of these compounds and most can be catalyzed.

The relative toxicities of products determine the practicality of applying this technique for spill response, where the products will probably be retained in the aquatic environment. This combination of factors strongly favors the use of catalytic oxidation.

Catalytic oxidation systems are manufactured for treating stack gases and process effluents. Most of these installations are not designed for operating in a hazardous vapor environment but could easily be modified to do so. The most obvious modification necessary for safe operation would be a recuperative heat exchanger. These are presently used in some installations to minimize the energy requirements of pollution control equipment and would provide an excellent basis for designing for spill response applications.

A system capable of handling the quantities of gas occurring at a spill would cost between $100,000-$500,000. It would be necessary to fabricate the components from special alloys to minimize corrosion. This significantly increases construction costs but would minimize maintenance. The system would be a self-contained unit occupying approximately 12 m^3 (130 ft^2) and having a volume of approximately 30 m^2 (1060 ft^3).

Either noble metal or transition metal oxide catalysts could be used, but the "catalyst poisoning" properties of many of the floating hazardous chemicals would promote the use of the latter. Transition metal oxide catalysts are more durable under such strenuous conditions and are less expensive. Proper maintenance and operation of the system should permit response to several spills before catalyst renewal is necessary. This would involve approximately $10,000.

Evaluation of Candidate Techniques in Task II

Dilution - The dilution technique for responding to spills of floating, hazardous chemicals will be best applied when temperatures are low. It can be used to augment an existing wind and in sparsely populated areas. The technique will not reduce hazardous chemical vapor concentrations below their threshold limit values under feasible operating conditions. It may provide the vapor concentration reductions required to ameliorate flammability hazards, but its rating in the effectiveness index is conditionally acceptable.

Dilution equipment is available for use aboard ships and is generally compatible with the aquatic environment. It is not inexpensive, but may be used in response to almost any chemical spill. The rating in the efficiency index is acceptable.

The dilution of hazardous vapors creates large volumes of air containing minute quantities of these chemicals. In most cases, this concentration will not be below the threshold limit value (8 hour exposure limit concentration). In those cases where the concentration can be reduced sufficiently below the TLV, data are limited concerning long term exposure to concentrations less than the TLV.

The tremendous volumes of "clean" air which must be moved in this response technique limit the choice of equipment. Jet engine blowers will provide the volumes necessary, but also will release some combustion pollutants. These must also be considered a part of the environmental impact resulting from the use of this candidate response technique. The dilution response technique is rated as unacceptable for the compatibility index.

Cryogens - Cryogens could reduce the concentration of vapors and replace O_2 above a spill of floating hazardous chemical. It is impossible to prepare an accurate estimate of the heat load for a typical spill, and vapor concentration reductions would result from a combination of condensation, vapor pressure reduction of the spilled chemical as heat was absorbed and diluted as the cryogen sublimed or evaporated. The effectiveness index for the cryogenic cooling response technique is conditionally acceptable.

The quantities of cryogen and rates of dispersal required in response to these spills presuppose the use of the largest blowers and material handling facilities. Response to a spill would be seriously impeded by the necessity to carry large storage vessels. Incorporating cryogenic regeneration units into the response equipment significantly increases the equipment costs. The efficiency index for this technique is conditionally acceptable.

Selection of cryogenic materials for the condensation of floating hazardous chemical vapors is limited to solid or liquid carbon dioxide and liquid nitrogen. In addition to the deleterious environmental reactions noted previously for carbon dioxide, this response technique would also face the problem of generating uninhabitable gas mixtures near the surface of the spill where response personnel must function. The compatibility index of this technique is conditionally acceptable.

Absorption - The "Dynactor" possesses some operating characteristics which may be advantageous in responding to discharges of hazardous, floating chemicals. There are few parts or complicated structures which are prone to wear and corrosion. They have had some use for treating both air and water containing small quantities of contaminants. The basic unit may need some modifications, however, when used to treat larger amounts of chemicals which exist as separate layers. The effectiveness index of this technique is conditionally acceptable.

Previous experience and engineering practice reinforce the extrapolation of the present design for use in handling most air or water flows. Previous equipment has been designed for use on land, exclusively, but would be readily modified for marine applications. The efficiency of this response technique would be established by the number and sizes of units which could be used to ameliorate a spill and their method of deployment. The efficiency index of the sorption response technique is conditionally acceptable.

The "Dynactor" has been designed and developed for responding to chemical spills. A part of this development has been directed towards making the system conform to pollution regulations. The compatibility index of this technique is acceptable.

Encapsulation - Encapsulation is a direct means for localizing both the spill and vapor hazards arising from it. The equipment presently available has the ability to contain most hazardous chemicals for subsequent removal or recycle. Vapors are presently being contained at near 100% effectiveness over lagoons, where off gases are collected. The effectiveness index of the encapsulation technique is adequate.

There appears to be no problem for acquiring membrane covers which are capable of encapsulating floating, hazardous chemicals. Several areas are uncertain, however, in the deployment over large areas of water and in joining the separate sheets into one impermeable cover. The efficiency index of this technique is conditionally acceptable.

The materials and equipment required for encapsulating hazardous chemicals spills will not present an environmental burden, if specifically chosen for compatibility. Polyethylene, polyvinyl chloride and some of the other common plastics may be attacked and dissolved by some of the solvents included among the hazardous chemicals, creating more problems than they solve. The compatibility index of this technique is acceptable for most of the elastomers, such as neoprene.

Reaction - A technique involving catalytic reaction of the vapors to ameliorate a spill of floating hazardous chemical would be applicable under most conditions, against the hazardous chemical vapors. The technique could reduce vapor concentrations below the TLV under optimum circumstances, but prolonged operation with vapors producing "catalyst poisoning" products would reduce the efficiency of the system. The effectiveness index rating for this technique is conditionally acceptable.

Commercial equipment for catalytic oxidation is available and could easily be modified for shipboard use. Adequate control of the vapors emanating from a spill would require multiple systems and, preferably, unmanned operation. The efficiency index rating for this technique is also conditionally acceptable.

Catalytic oxidation will reduce the concentration and hazardous properties of the chemical vapors. In most applications it will provide continuous treatment for the period of time necessary to remove the spilled material. In those cases where "catalyst poisons" are present during operation the catalyst will degrade slowly through these "poisoning reactions" and the efficiency will be reduced. The concentration of toxic constituents in the effluent gas stream must be monitored to maintain a constant safety check, provide adequate protection for response personnel and determine the time for catalyst renewal. The compatibility index rating for this technique is also conditionally acceptable.

This combination of ameliorating characteristics should provide some reductions in the hazards associated with spills of floating hazardous materials. The approach must be considered as an area for research and development, however, as there are no reports of the equipment being used under these conditions.

Summary and Ranking for Task II

The investigation within this task concerned five candidate techniques to achieve vapor concentration reduction above spills of floating, hazardous chemicals. Only one of these appears to possess a practical combination of features necessary to fulfill the objectives of this task.

The encapsulation technique appears most promising of the candidate techniques. The others appear to have restricted practical application against such materials when the tremendous volumes of vapors and their toxicities are considered.

This technique exhibits some of the best characteristics for treating hazardous chemical spills to contain both the liquid and vapor phase. The total protection obtained is directly related to the efficiencies of deployment and sealing of the cover material, wherein lie the uncertainties of using the technique.

A variety of cover materials are available to enable a selection which would avoid problems of incompatibility. Nevertheless, the deployment of a combination boom and cover, under inclement conditions, on water, should be a formidable task.

Any of the recovery devices presented in Table 2 could be used in conjunction with this technique. Some difficulties could arise, however, if it became necessary to operate within the encapsulating device. Suction head and weir skimmers would be better for recovery of chemicals under these conditions.

TASK III - VAPOR FLAMMABILITY REDUCTION

The objective of this task was a critical evaluation of methods which could be used to ameliorate the fire hazards associated with floating, hazardous chemicals. Potential techniques for reducing flammability were assessed on the basis of published, measured and estimated data for the pertinent controlling factors.

The candidate techniques selected for evaluation within this portion of the program were selected on the basis of acceptable performance in one of the five flame reduction areas. Vapor flammability measurements can be made in terms of the following five parameters:

1. "Apparent flame strength"
2. Burning velocity or flame speed
3. Flammability limits
4. Extinction
5. Flame structure

"Apparent flame strength" is the term used to describe the phenomenon of flame breaking, observed with opposed jet, diffusion flames. Increasing the gas flowrates through the jets of this burner, a point is reached where an opening appears at the center of the flame. This is explained as the point where the mixing rate exceeds the reaction rate of the flame. Additions of flame suppressants decrease the flow velocity at which this "break" occurs. Common practice is to compare the efficiencies of flame suppressants in terms of the amounts required to attain an arbitrary "break point."

Burning rates have been extensively studied by Blinov and Khudiakov (1957) and Burgess et al. (1961). The

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Blinov, V.I. and Khudiakov, G.N., "Certain Laws Governing Diffusive Burning of Liquids", Dokl. Akad. Nauk. U.S.S.R. 113, 1097 (1957).

Burgess, D.S., Grummer, J. and Wolfhard, H.F., "Burning Rates in Liquid Fuels in Large and Small Open Trays", International Symp. on the Use of Models in Fire Research, NAS Publ. 786 (1961).

results of their work may be summarized by the equation:

$$\frac{V_\infty(\Delta H_{vap}) + \int_{T_f}^{T_s} C_f dt}{\Delta H_{comb}} = 0.0076 \text{ cm/min}$$

in which V_∞ is the burning rate of a large surface, H_{vap} is the heat of vaporization, ΔH_{comb} is the heat of combustion, T_f is the average flame temperature, T_s is the surface temperature and C_f is an average heat capacity for the flame gases.

An empirical correlation exists between the burning velocity reductions achieved by flame suppressants and their ability to suppress and eventually extinguish flames. These correlations and extrapolations should be limited to systems where a minimum of experience or experimental data is available.

Flammability limits are measured for premixed gaseous mixtures. They are measured in terms of the maximum and minimum fuel concentrations, in fuel/air mixtures, which will develop a self-propagating flame. The limits close as flame inhibitors are added until, at some maximum concentration, flame propagation is impossible for any fuel/air ratio.

Extinction or extinguishment of an existing flame can be measured in several ways. It is usually specified in terms of the mass of extinguishing material used per unit area of fire. Factors such as the application rate, physical state, size of particles, and surface area also influence extinction and complicate the extrapolation of experimental measurements to large scale operations.

Flame structure is a more detailed and complicated description of the combustion reaction. The structure, com-

position, temperature and aerodynamic history of a gas volume experiencing a flame reaction can be used to determine the suppression efficiency of various materials.

Vapor flammability reductions can be achieved by either physical or chemical means, in a homogeneous or non-homogeneous system. Physical means include smothering or cooling. Chemical means include a wide variety of reactions and reaction mechanisms which have been the subjects of considerable investigation. General reviews by Berl (1961 and 1964), Fristrom (1967) and McHale (1968) outline the major important results of these investigations and their applications in practical fire prevention programs.

Specifications to ameliorate vapor flammability hazards are the least demanding of those used in this program. Lower flammability limits (LFL) of organic vapors are in the range of 1% concentration. This increase of two or three orders of magnitude in concentration over the TLV provides a commensurate decrease in the severity of equipment specifications for vapor flammability reduction.

Berl, W.G., "Current Fire Research Problems", Fire Research Absts & Revs. 6, 1 (1964).

Berl, W.G., "Survey of Current Fire Research Activities", Proc. Symp. on Fire Control Res., Fire Research Absts. & Rev. 3, 113 (1961).

Fristrom, R. M., Combustion Suppression - A Literature Survey with Commentary, Fire Research Absts. & Rev. 8, 192 (1967).

McHale, E. T., Survey of Vapor Phase Chemical Agents for Combustion Suppression, N68-37380, Report No. CR 73263 (August, 1968).

Five candidates were evaluated in relation to the objectives of Task III. The candidate techniques include:

1. Inhibitors
2. Dilution
3. Cryogens
4. Foams
5. Aerosols

Inhibitors have included both vapor phase and liquid phase additives which operate on the principle of chemical intervention in the deflagration reaction. Inhibitors reduce vapor flammability by removing the reactive intermediates involved in the self-propagating reaction mechanisms. Dilution operates on the simple expediency of adding inert materials to a concentration where their presence interferes or defeats the self-propagation reaction. Cryogens absorb heat energy and decrease the probability of excess energy being available for initiating these reactions. Foams operate through a combination of all these mechanisms and also offer the possibility of increasing their effectiveness through modifications in their formulation or means of generation. Aerosols may be evaluated as simple diluents or reactive materials chosen to combine energy absorption with active suppression or inhibition of the flame reactions.

Dilution of the vapors released from spills of floating, hazardous chemicals has been previously treated in Task II. The tremendous differences between lower flammability limit concentrations and threshold limit value concentrations provide a more feasible specification for this spill response technique.

Vapor flammability is controlled by four factors:

1. Fuel concentration
2. Oxidizer concentration

3. Activation or initiation energy
4. Reaction energy

Fuel concentrations are determined by the vapor pressure of the spilled chemical and environmental conditions at the scene of the spill. The concentration is limited to the partial pressure at equilibrium of the individual chemicals, but for many hazardous chemicals this exceeds the lower flammability limit.

Oxygen concentrations of the gas mixtures generated by chemical spills are set by the ambient atmosphere. Both the fuel and oxidizer concentrations may be reduced by the addition of inert gases, but this has limited applicability for some hazardous chemicals (e.g., tert-butyl hydroperoxide) which do not require additional oxidizer.

Activation or initiation energies demonstrate the broad range of properties exhibited by the floating, hazardous chemicals. The amount of energy required to initiate a combustion reaction may be increased by the addition of energy-absorbing or reactive-intermediate-absorbing materials. Any response technique which operates on these properties should create an inert gas mixture to rank well in the evaluation of safety.

The reaction energies available from combustion of floating, hazardous chemicals are frequently sufficient to make these reactions self-propagating. The amount of energy, or strength of the reaction, will depend upon the components and their relative concentrations in the reacting mixture. The energy released from combustion reactions may be controlled by dilution with inert materials or various reaction mechanism inhibitors. The methods available to ameliorate combustion reactions all require the expenditure of a considerable amount of energy to prepare homogeneous gas mixtures. Flames propagating through heterogeneous

mixtures, even containing suppressants, have greater strength than those of equivalent, homogeneous mixtures.

Flame Inhibitor Technology

Flammability hazards of chemical vapors can be reduced by the addition of inert materials or flame reaction suppressants, also called inhibitors. This technique involves the dispersal of gases, liquids or solids over the spill to interact with the spilled chemical. This technique is applicable to all flammable compounds and may be applied either as additions to the fuel or to the air supply (oxidizer). Creitz (1972) has reported significantly greater efficiencies when the inhibitor is added to the air supply.

The most common chemical suppressants have been cited in reviews by Creitz (1970),Berl (1964), Fristrom (1967) and McHale (1968). As with dilution, a major part of using any flame suppressing chemical is maintaining its proximity to the reactive vapor species and their source. Huggett (1973)

Creitz, E.C., "Extinction of Fires by Halogenated Compounds-A Suggested Mechanism", Fire Technology 8 (2), 131 (1972).

Creitz, E.C., A Literature Survey of the Chemistry of Flame Inhibition, NBS, Vol. 74A, 4(July-August 1970), pp 521-530.

Berl, W.G., "Current Fire Research Problems-Review", Fire Research Abstracts and Reviews 6, 1 (1964).

Fristrom, R.M., "Combustion Suppression-Review", Fire Research Abstracts and Reviews 8, 125 (1966).

McHale, E.T., Survey of Vapor-phase Chemical Agents for Combustion Suppression, CR 73263, Atlantic Research NASH N68-37380.

Huggett, C., "Habitable Atmospheres Which Do Not Support Combustion", Combustion and Flame, 20, 140 (1973).

proposed the use of fully fluorinated carbon compounds as flame suppressants. He also suggests that these materials would not present the hazards to response personnel that many other flame suppressants are known to have. His correlation of the heat capacity of gaseous mixtures per mole of oxygen provides a convenient measure for predicting inert atmospheres.

Other candidates which could be used in the gaseous state include nitrogen, carbon dioxide, stack gas, water vapor and low molecular weight organic halides. Those which could be used in the liquid state include water, organic halides, organic amines and organic acids. Solid inhibitors would include such candidates as limestone, carbon dioxide, ice, inert dusts and alkali metal halides or carbonates.

Lewis and von Elbe (1961) have reported the influence of carbon dioxide on combustion reactions of hydrocarbon/oxygen mixtures and compared the results with similar tests using nitrogen. The results of their investigation are reproduced in Table 10.

Some deleterious conditions could also result from the use of large quantities of carbon dioxide, especially as the solid. The active inhibition and suppression of flammability hazards would be accompanied by changes in the pH of the water and depletion of the dissolved oxygen at the surface.

Organic halides, such as 2-chloropropane and 2-methyl, 1-chloropropane, have lower solubilities and vapor pressures while retaining a significant amount of their inhibitor characteristics. Although no threshold limit values have been published, their similarities to other halogenated compounds having significant toxicities indicate a cautious evaluation is necessary before recommending their use.

Lewis B. and von Elbe, G., Combustion, Flames and Explosions of Gases, Academic Press Inc. (1961).

TABLE 10- LIMITING OXYGEN CONTENTS (Vol %)
FOR DILUTION WITH N_2 or CO_2*

Hydrocarbon	Maximum Safe Oxygen Concentration N_2 as Diluent	CO_2 as Diluent
Methane	12.1	14.6
Ethane	11.0	13.4
Propane	11.4	14.3
Butane	12.1	14.5
Pentane	12.1	14.4
Hexane	11.9	14.5
Gasoline	11.6	14.4

*Lewis, B. and von Elbe, G., Combustion, Flames and Explosions of Gases, Academic Press, Inc. (1961).

The dispersion equation developed as a part of this investigation reveals that flammable concentrations of vapors would exist only close to the spilled chemical, except for the two cryogens (butadiene and vinyl chloride) included among the floating, hazardous chemicals. It is estimated that the flammable concentration occurs within 0.5 m (1.6 ft) of the spill surface for most of the chemicals investigated.

Flame Inhibitors as a Candidate Spill Response Technique

2-Chloropropane (isopropyl chloride) appears to be the most effective inhibitor for responding to spills of these hazardous chemicals. Creitz (1972) reported that inhibitor additions to the fuel are less effective than those mixed with the air. A combination of vapor and liquid concentrations, sufficient to inhibit combustion, would be obtained by the use of a volume of inhibitor equivalent to 5 to 8% of the spill volume. This would correspond to a maximum delivery of approximately 3000 l (800 gal) in response to the largest typical spill.

The inhibitor would be dispersed through a nozzle, similar to those used for generating aerosols and foams. One of the turret nozzles, manufactured by Rockwood Systems Corporation, and described in Appendix C, could be used as a typical example of this equipment. The response system would include a storage tank, pump, piping, valves and other controls, in addition to the dispersing nozzle. This system would weigh about 910 Kg (2000 lb), occupy about 3.6 m^2 (39 ft^2) of deck space, and cost approximately $12,000. The total cost of equipment and materials required for the flame inhibitor type response technique would be approximately $100,000.

Creitz, E.C., "Extinction of Fires by Halogenated Compounds. Suggested Mechanism", Fire Technology 8(2), 131 (1972).

Dilution as a Candidate Spill Response Technique

Dilution techniques have been evaluated within the objectives of both Task II and Task III, concerning their application for vapor concentration reductions and vapor flammability reductions. Reference is made to Task II, for the detailed description of specifications for this technique. The requirements for vapor flammability reduction are several orders of magnitude less than those for vapor concentration reduction, and the technique has been evaluated and compared for both specifications.

Although the amounts of "inert or pure" gases required for diluting the hazardous chemical vapors are significantly reduced by specifying that dilution only be carried out to the lower flammability concentration, only the largest blower equipment would be capable of delivering them. As mentioned previously, the "Hurricane" model jet-engined blower, manufactured by Railway Maintenance Corporation, is an example of the equipment required. The total cost for equipment necessary in this response technique would vary according to the modifications required for marine service, but would be in the range of $75,000.

The dilution technique has been evaluated as conditionally acceptable in terms of its effectiveness index. The efficiency index has been rated as acceptable, and the compatibility index has been evaluated as unacceptable.

Cryogens as a Candidate Spill Response Technique

The use of cryogens in response to spills of floating, hazardous chemicals has implications in all three tasks of this program. This technique can, therefore, be evaluated with respect to the objectives of each individual task. Using cryogens to ameliorate vapor flammability hazards combines the capabilities of these materials for vaporization rate reduction, vapor concentration reduction and vapor flammability reduction.

Any inert cryogen is capable of meeting the general requirements for reducing evaporation or for condensing vapors. Most cryogens will not inhibit combustion reactions, however, and must be considered to act as diluents. Halogenated refrigerants and carbon dioxide are the only materials which combine active flame suppression and good coolant properties.

The effectiveness of cryogens to ameliorate flammability hazards depends upon the chemical characteristics of the spilled chemical. Generally, the amount of inhibitor required to extinguish combustion reactions is in the range of 3-5% by volume for halogenated materials and 5-8% by volume for carbon dioxide. Calculating the amounts required for a typical spill on the basis of these general specifications will lead to erroneous conclusions, however. The addition of cryogens to a spill of floating, hazardous chemical will affect the vapor concentration by reducing evaporation and instigating condensation as well as by inhibiting combustion reactions in the vapor phase. It is difficult to estimate the relative influences of each of these phenomenon on the overall amelioration requirements.

There are several aspects associated with the use of cryogens to ameliorate spills of floating hazardous chemicals which may be considered independently in assessing the response technique. Dilution, condensation and vapor flammability suppression occur simultaneously with the use of cryogens.

Each volume of cryogenic flame suppressant would expand approximately 700 times as it attained ambient temperature. The combination of vaporization rate (source) reduction and change-of-state expansion (dilution) would reduce the concentration of hazardous chemical vapors in the vapor cloud.

Various methods and equipment may be used to spread the cryogen over the spill, but each will require some contact

between the cryogen and the vapors above the spill. Condensation of the hazardous chemical vapors will occur as a result of this contact. The amount of material condensed will depend upon the contact time, the dispersion of the cryogen and the dew point of the vapor.

The primary attribute of this response technique is due to the flame suppressing capabilities of these cryogens. Carbon dioxide provides the best combination of properties, but halogenated hydrocarbons (refrigerants) could also be used.

The results of this technique can be estimated on the basis of specifications developed within the objectives of Task I. Vaporization rate reductions would require the dispersal of about 1.1×10^4 Kg (12 ton) of solid carbon dioxide over the largest spill. This rate may be converted to a coverage of approximately 1.3 Kg/m^2 (0.3 lb/ft^2) over the surface of the spill.

The rate of coverage would be equivalent to using 8×10^{-3} m^3/m^2 (0.03 ft^3/ft^2) of solid carbon dioxide. This material would expand approximately 700 times as it was heated to ambient temperature, releasing 5.6 m^3/m^2 (21 ft^3/ft^2) of gaseous carbon dioxide. If this rate of coverage can be maintained on an hourly basis, then the 5.6 m^3/m^2hr (21 ft^3/ft^2hr) may be compared with evaporation losses of from 1 to 3.5 m^3/m^2hr (3.3 to 11.5 ft^3/ft^2hr), calculated from the dispersion equation.

The carbon dioxide added in this response technique would release approximately 1.6 times as much vapor as the spill, reducing its concentration by approximately 60% and reducing the possibility of ignition. The combination of evaporation reduction, concentration reduction and nearly equal concentrations of fuel and suppressant should be sufficient to significantly reduce the possibility of igniting the mixture.

Carbon dioxide would be dispersed with the equipment described under Task I. Flammability suppression requirements would mirror those of vaporization rate reduction, making this technique applicable as previously described. A total cost of approximately $80,000 has been estimated for equipment and material for this response technique.

Liquid nitrogen could also be considered for this response technique, although it is not an active flame suppressant. Dispersing liquid nitrogen over the spill would combine its cooling properties with the process of dilution and decrease the total volume to be handled. The liquid volume would be increased approximately 700 times as it was heated to ambient temperature.

A conservative estimate of the quantity of liquid nitrogen to be used in response to a spill of hazardous chemical can be made on the basis of the dilution requirements reported in Task II. It was estimated that a maximum of 1.3×10^6 m^3/hr (4.7×10^7 ft^3/hr) of "pure" air would be required to be mixed with the chemical vapors arising from a spill of 38 m^3 (10,000 gal) to maintain their concentration below the lower flammability limit.

This specification corresponds to a volume of 1.9×10^3 m^3/hr (6.7×10^4 ft^3/hr) of liquid nitrogen to be delivered over the surface during the time necessary to ameliorate the spill. Delivering 1.9×10^3 m^3/hr or approximately 2.5×10^4 kg/min (5.5×10^4 lb/min), would be within the capabilities of commercial equipment. The total cost of materials would be prohibitive, since the cost of liquid nitrogen is $0.073/kg ($0.033/lb).

Low Expansion Foam as a Spill Response Technique

Foams may be used to ameliorate spills of floating hazardous chemicals in two separate hazardous areas. They may be applied, as in Task I, to reduce evaporation, or they

may be used to reduce vapor flammability, the objective of Task III.

This technique involves the generation of a volume of foam sufficient to cover the spill area with a continuous layer. This layer need not be the full 15 cm (6 in.) thickness required for vaporization rate reduction, but must be continuous (allow for wind and wave action).

Experimental tests of foams generated at various expansion ratios showed that, while all foams will reduce flame propagation rates, only those generated at expansion ratios less than 10 to 1 would not support combustion after equilibrium contact with representative chemicals. These tests also indicated that low expansion foams would act as a flame arrestor to stop any vapor flame reaction from flashing back into the liquid pool.

A 10 cm (4 in.) layer of low expansion foam would be sufficient to inhibit combustion and arrest flames before they could flash back into the pool of floating, hazardous chemical. The foam layer would require the use of 3800 to 11,400 l (1000 to 3000 gal) of foam solution to cover a 38 m^3 (10,000 gal) spill. MSA "Type L" foam would be made from a 30% solution, while National Foam Systems, Inc. "Universal Foam" would be made from a 10% solution; both should be generated at an expansion ratio of approximately 10/1.

Some typical foam equipment required for this response technique is described in Appendix C. The turret nozzles, manufactured by Rockwood Systems Corporation, may be used in preparing a typical system. This system would consist of one or more storage tanks, a pumping system, connecting lines, valves and other controls, in addition to one or more foam nozzles.

A low expansion foam generating system would weigh approximately 910 kg (2000 lb), occupy about 3.7 m^2 (40 ft^2) of deck space, and cost approximately $15,000 for an electric powered system. This cost would double if the power was supplied by a gasoline motor, to make the system completely self-sufficient. The foam response technique requires one man to operate the equipment and direct the foam over the spill. The service life of foam generating systems would be expected to be in the range of 10 to 20 years, with proper operation and maintenance.

The cost of a low expansion foam system to ameliorate hazardous chemical spills would include $100,000 to $150,000 for the foam concentrate. Total cost for this response system would be in the range of $115,000 to $183,000, installed.

Aerosol Technology

There are two different applications for aerosols in the response to spills of floating hazardous chemicals. Fast-setting aerosols can be used as an alternative procedure for the preparations of surfactant films. Slow-settling aerosols can be used as flame inhibitors or arrestors.

These two applications include two sets of criteria for selection and evaluation. The preparation of surfactant films was a part of Task I, where the objective was to reduce evaporative losses. Flame inhibitors and arrestors are a part of Task III, where the objective is to reduce vapor flammability.

The composition and size of the aerosol particles are the primary variables for selecting and preparing an aerosol, whether it be for covering a surface (paints and insecticides) or producing a long-lasting, homogeneous aerosol (natural fog).

Particles formed by aerosol generators at ambient conditions vary widely in size and distribution. Some

methods for giving a measure of this droplet-size characterization are defined as follows:

SMD - Sauter Mean Diameter is a means of expressing the fineness of a spray in terms of the surface area produced by the spray. It is obtained by taking a summation of the surface areas of every drop produced by a given spray, together with a summation of the total volume of all these drops. Then the diameter of a drop having the same volume-to-surface ratio gives the SMD of this spray.

MND - Mean Numerical Diameter is a means of expressing particle size in terms of the number of particles in the spray. This means that 50% of the particles present by count or number are smaller, and 50% are larger than the given (MND) particle size.

MVD - Median Volume Diameter is a means of expressing particle size in terms of the volume of liquid sprayed. The MVD size of a spray is that value where 50% of the total volume (or mass) of the liquid sprayed is made up of droplets having diameters larger or smaller than this median value.

The term aerosol is commonly applied to a solid or liquid particle in the 0.005 to 50 μ size range. In addition, other terms such as fog, mist, rain, dust, fumes and smoke are used to further clarify the type of particle (solid vs. liquid) and to impose further restrictions on the particle size range. In normal outdoor air, for example, fog, mist and rain refer to condensed water vapor in the size ranges of 1-40, 40-400 and 400-5000 microns, respectively. Normal outdoor fog is typical of the aerosol of interest in Task III of this program. Fine mists of $\leq$100 μ diameter were considered in Task I. A tabular comparison of aerosols is presented in Table 11.

TABLE 11 - AEROSOL COMPARATIVE SIZE DATA

Particle Size Range Microns*	Comparative Subject in Particle Size Range	Time for Particle to fall 10 ft. Seconds	Drift in 3 MPH wind 10 ft. fall Feet	No. of Particles per Sq. In. if applied at rate of 1 Gal./Acre	Nozzle Types and Sizes Generally Falling in Given Particle Size Range Under Stated Condition
Below .001	Molecular dimensions	-	-	-	----------
.001 to 0.1	Smoke	**	-	-	----------
0.1 to 1.0	Fumes	**	-	-	----------
2 to 5	Dry Fog	25,400 4,070	112000 18000	144,060,000 9,220,000	Small Pneumatic Atomizing Siphon Nozzle Set-ups operating at the higher air pressures.
10 to 40	Wet Fog	1,020 64	4500 280	1,152,500 18,000	Pneumatic Atomizing Nozzles, small capacity Atomizing and Spray Dry Type Nozzles operating at high pressures (500 psi and up)
50 to 100	Misty Rain	40 11	175 48	9,200 1,152	Large capacity Pneumatic Atomizing Nozzles; the larger capacity Atomizing and Teejet Nozzles operating at pressures around 100 psi.
200 to 400	Light Rain	4.2 1.9	19 8	144 18	The smaller capacity Whirljets, Fulljets, and Veejet Nozzles operating at pressures around 40 psi.
500 to 1000	Moderate Rain	1.6 1.1	7 5	9 1	Intermediate sizes of Whirljet, Fulljet and Veejet Nozzles, approximately in the range of 5 to 15 GPM spraying at pressures around 40 psi.
2000 to 5000	Heavy Rain	0.9 0.85	4 3.5	21 per sq. ft. 1 1/3 per Sq. Ft.	The large size Hydraulic Nozzles operating at pressures around 10 and 20 psi and intermediate sizes operating at very low pressures.

* Note: One micron equals 1/25400 of an inch. There are 25.4 microns to .001 (one thousandth) of an inch.

**Note: Below 0.1 micron, particles are suspended in air due to molecular shock (Brownian Motion).

[1] Spraying Systems Company brochure

Other terms are used to describe and identify aerosols which, in some cases, may appear to be contradictory. For example, Lapple (1968) of SRI states that "mists" range from 0.01 to 10 μ and that "sprays" range from 10 μ to ~1000 μ. Conversely, a spray nozzle manufacturer defines a liquid aerosol in the 2-5 μ size as a "dry fog" and in the 10-40 μ size as a "wet fog". Fuchs (1964) defined condensation and dispersion aerosols with liquid particles as "mists", regardless of their size. Dispersion aerosols with solid particles are called dusts, irrespective of their size while condensation aerosols are formed when supersaturated vapors condense and form a nonvolatile product, such as soot. The condensation aerosol is usually smaller in size than the dispersion formed aerosol. The important point is that descriptive terminology must be defined in terms of particle size and character. In this program, we have referred to liquid aerosols in the $\lesssim$100 μ range as fogs.

Aerosol technology also involves an understanding of mechanisms of formation of particulates and the physical forces at work on these particulates. Friedlander, et al (1952) described mists and fogs as resulting from the disintegration of a liquid or from condensation of vapor on suitable nuclei. If water droplets in air coalesce, they are apt to precipitate as rain. Mists and fogs remain stable if the vapor pressure is low or is saturated. Most aerosols are heterogeneous and polydisperse, while sea fog, which is ~38 μ, is almost monodisperse. Dry fogs may be generated from pneumatically operated nozzles at very high

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Lapple, C.E., "Particle Size Analysis and Analyzers", Chem. Eng., (May, 1968).

Fuchs, N.A., The Mechanics of Aerosols, MacMillan Co., (1964).

Friedlander, S.K. et al., Handbook on Air Cleaning Particulate Removal, U.S.A.E.C. (1952).

air pressure. Other means of producing liquid aerosols include direct condensation from saturated vapor, spinning disc generators and the oscillating reed. Some particulate sizes and their relative concentrations in aerosols generated by hydraulic nozzles are presented in Figure 5.

Once the aerosols are formed, they are subject to various physical forces. Inertial effects, the tendency for a particle to remain in uniform motion, have a decided influence on relative particle motion of aerosols in the 1-10 μ range. Particles about 1 μ diameter tend to follow the streamline, particles in 0.1 to 0.2 μ size range are subject to diffusion and Brownian Motion. Particles 0.01 μ are in the size range where electrostatic effects are most significant. Other forces which affect liquid droplet behavior include particle concentration, surface structure and physicochemical characteristics such as dipole interactions. Coalescence is reported to occur readily when particles larger than 20 μ diameter collide.

Dust and smokes were studied by Knutson (1965) and his associates for reagglomeration. They found a significant tendency for particles to agglomerate and determined the coefficient agglomeration of powders in the 2-7 μ size range to be 7.5×10^{-7} cc/sec. Important parameters studied were size, charge and turbulence.

Existing technology and presently available hardware for generating small particulate aerosols were reviewed for methods which were applicable to generating the quantities required for typical spill response conditions. The thorough literature survey by Lappel et al. (1967) was used

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Knutson, E., Aerosol Studies, Vol. I, Rept. No. AD 477 575 (1965).

Lapple, C.E. et al., Atomization - A Survey and Critique of the Literature, Report No. AD 821 344 (1967).

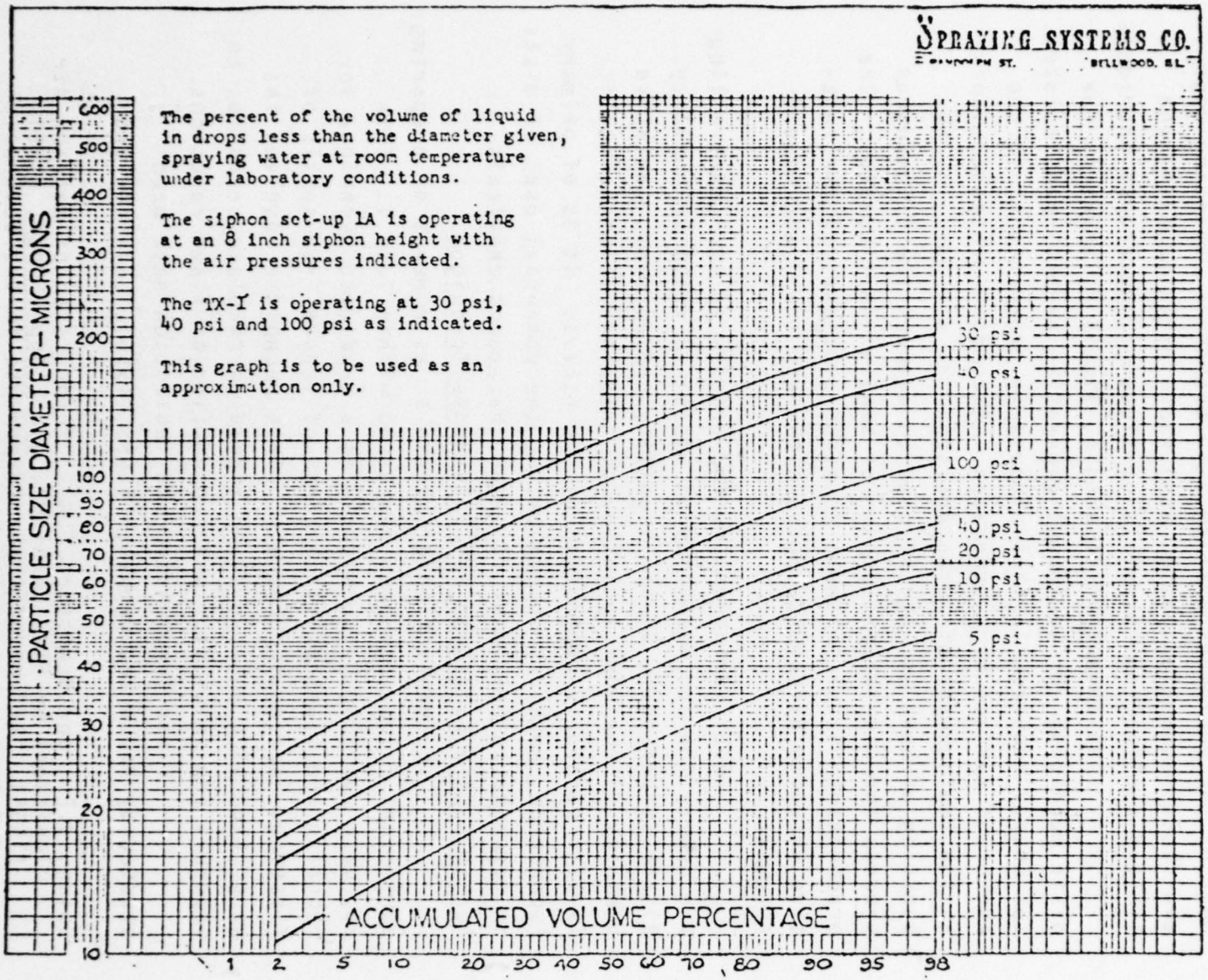


FIGURE 5 - TYPICAL AEROSOL PARTICULATE DIAMETERS GENERATED BY HYDRAULIC NOZZLES

as the primary source for the selection of applicable devices. Most of the equipment available (ultrasonics, spinning discs, two-fluid pnuematic nozzle, etc) had limited capacity and limited application to spills of floating, hazardous chemicals.

The formation of a thin, liquid filament is the basic mechanism for equipment generating aerosol particulates. The energy required in this process is proportional to the amount of surface area generated. Secondary processes, such as the impingement of turbulent steam or air jets, or the bursting of bubbles, may be used to augment the filamentous process and aid the production of smaller particulates. The predominant factor in these combined processes is the relative velocity difference between the air (gas) and liquid filament.

Four variables are the primary factors controlling the generation and stability of mists: 1) relative humidity, 2) air temperature, 3) air stability and 4) wind. Relative humidity is the most inclusive of these variables, since it is also partially controlled by the others. It is of primary importance, however, in evaluating the potential uses of mists in response to spills of floating, hazardous chemicals.

Aerosols as a Candidate Spill Response Technique

The generation of aerosols, as a means of preparing surfactant films, has been discussed within Task I. This approach can also be considered as a candidate technique for reducing the flammability hazards of vapors from spills of floating, hazardous chemicals. This technique involves the generation of either solid or liquid particulate aerosols, to suppress the initiation and propagation of flame reactions.

Flame suppression and inhibition have been studied by Dolan and Dempster (1955, 1956), Laffitte and

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Dolan, J.E., and Dempster, P.B., "Suppression of Methane Air Ignitions by Fine Powders", Jour. Appl. Chem. 5, 510 (1955), "Effect of Inert Components in the Detonation of Gelatinous Explosives", Discussions of Faraday Soc. 22, 196 (1956).

Bouchet (1959), Friedman and Levy (1963) and Rosser, Inami and Wise (1966). The inhibitive effects of aerosols show rather complicated influences from chemical composition, total aerosol mass and particulate size and surface area. The dispersed particulates used in response to spills of hazardous chemicals must be inert towards response personnel, while actively suppressing flames.

Aerosols may be prepared from water, or other liquid suppressants, and from powdered solids, usually common salts or minerals. The effectiveness of this technique can be modified by proper selections of the inhibitor material, particle size, surface area and particulate loading. Inhibitor materials can be chosen which have no toxicity, but flame inhibition requires particulate loadings in the range of 2×10^4 to 3×10^4 mg/m^3 (1.2×10^{-3} to 1.8×10^{-3} lb/ft^3), which are well into the range of nuisance dusts. The accepted TLV for most nuisance dusts is approximately 10 mg/m^3 (6×10^{-7} lb/ft^3) which indicates the necessity for having response personnel wear particulate filter masks.

Small particles of inorganic salts may be used as aerosols or mixed in the spill to suppress flammability. The amount required to secure a spill would depend upon the surface area of the particles (size), the rate of settling, density of the particles and chemical interaction between the spilled chemical and particulates.

Lafitte, P. and Bouchet, R., "Suppression of Explosion Waves in Gaseous Mixtures by Means of Fine Powders", 7th Int'l Symp. of Combustion, p. 504 (1959).

Friedman, R., and Levy, J.B., "Inhibition of Opposed Jet Methane-Air Diffusion Flames. The Effects of Alkali Metal and Organic Halides", Combust. and Flame 8, 51 (1963).

Rosser, W.A., Inami, S.H., and Wise, H., "The Quenching of Premixed Flames by Volatile Inhibitors", Combust. and Flame 10, 287 (1966).

Many of the candidate inhibitor materials must be dismissed on the basis of their toxicity towards humans. Recent experimental evidence has been compiled by the Manufacturing Chemists Association (1975) concerning the possible environmental damage resulting from the release of organic fluorides. The results of similar tests, indicating some deleterious environmental reactions, have been reported by Hester and Stephens (1975) and the Interdepartmental Committee for Atmospheric Sciences (1975).

The flammable gas volume has been estimated, using the modification of the natural dispersion equation developed for this program. A conservative estimate has been made that a layer approximately 0.5 m (1.6 ft) above the spill would contain flammable concentrations. This estimate has been used to prepare equipment specifications for this response technique.

The rate at which the aerosols must be generated depends upon the size of the particles and wind speed. Two approximations have been used to estimate an average settling speed. Data developed by Spraying Systems, Inc. are shown in Table 11. These data have been tabulated as a means of describing their fog nozzles. A mathematical formula reported by Raabe (1976):

$$V_s = \frac{g\rho C(D)(D^2)}{18\eta}$$

where V_s is the settling speed; g is the gravity constant; ρ is the particle density; C(D) is an aerodynamic correction factor, D is the particle diameter and η is the viscosity of air, has also been used to calculate the settling speed.

Manufacturing Chemists Association, Effect of Fluorocarbons on the Atmosphere, Summary Report, MCA Review 1, Dec. 1975.

Hester, E.R., and Stevens, O.C.I., "Fluorocarbon Air Pollutants", Atmos. Environ. 9(6-7), 603 (1975).

Interdepartmental Committee for Atmosphere Sciences, "Effect of Fluorocarbons on the Atmosphere", Statement of MCA Report cited above.

Raabe, O.B., "Aerosol Aerodynamic Size Conventions for Inertial Sampler Calibration, J.A.P.C.A. 26 (9), 856 (1976).

Using these assumptions, the aerosols will settle at rates between 33 cm/sec and 50 cm/sec (1.1 to 1.6 ft/sec). Aerosol requirements, calculated from the typical spill dimensions used in this program, would be as much as 5700 kg/min (12,500 lb/min).

Several manufacturers supply equipment capable of preparing aerosols to the specifications required for responding to spills of floating, hazardous chemicals. The maximum particulate generation is estimated at 5700 kg/min or 12,500 lb/min, which corresponds to approximately 3.4×10^5 kg/hr or 375 tons/hr. The problems of storing and delivering these quantities of solids could be overcome, but may be used to emphasize the greater practicality of water aerosols. These aerosol specifications may be translated to liquid flowrates of approximately 5700 ℓ/min or 1500 gal/min.

Pneumatic systems can be used to generate and distribute aerosols. Commercial equipment, such as that used for orchard spraying or fertilizer spreading, is adaptable for aquatic spill response. Snow blowers and mulch spreaders appear to be particularly well suited for the required specifications. Typical examples are manufactured by Finn Equipment Company, Kool Brothers and American Snowblast Corporation. Power requirements for these units are between 50 and 100 hp and they are fabricated as separate units, occupying 3.7 to 9.3 m^2 (40 to 100 ft^2).

The capacity of most commercial pneumatic systems is limited to between 1/4 and 1/3 of the calculated maximum application rates. Multiples of three or four units could easily be used without interference and possibly obtain a more uniform aerosol distribution. Each blower unit would be mated with supply pumps and controls to make a response system cost approximately $15,000.

The expected life of these systems, in use against spills of hazardous chemicals, would be in the range of 5 to 20 years. Proper maintenance and storage are assumed in estimating this operating lifetime. Exposure to salt water during operation and the rigors of deck exposure would make frequent maintenance checks necessary, but these would require minimal time and effort. Operation would require 1-2 men for start up; only a minimum amount of control or adjustment would be necessary during long term spill response applications.

Hydraulic equipment could also be used to generate liquid particulate aerosols. This equipment is manufactured for fire fighting and for spraying insecticides or fertilizers. Rockwood Systems Corporation, Vandermolen, Inc., Fire Control Engineering Company and FMC Corporation are representative of the companies manufacturing hydraulic systems which could be adapted for spill response.

A typical example of this approach is the Rockwood Systems Corporation's "Fog FOAM Turret Nozzle", which is capable of handling water flows to 1900 ℓ/min (500 gal/min). The fog nozzle could be permanently mounted or a similar portable model used in conjunction with a pumping unit sized to meet the capacity. Such a unit would occupy approximately 5 m^2 (54 ft^2) and require a 75 hp motor and pump assembly for 500 gpm at 150 psi. Electric, gasoline or diesel power could be used, with the cost of the system varying between $10,000 and $15,000

Normal capacities of commercial hydraulic systems are 1900 ℓ/min (500 gal/min) maximum. This would mean that three or four units would be necessary to secure the largest spill area.

The expected life of hydraulic systems would be approximately 5-20 years, in their occasional use against spills of floating, hazardous chemicals. Normal operations would require 1-2 men; this would not change significantly for long term action against the largest spills.

Evaluation of Candidate Techniques for Task III

Inhibitors - Using flame inhibitors in response to spills of floating, hazardous chemicals would be best applied for isolated spills or under extenuating circumstances, where ignition appears imminent. The technique will not reduce toxicity, and may increase this hazard, but could provide adequate control of flammability hazards. Its rating in relation to the effectiveness index is conditionally acceptable.

Commercial equipment could be used in this technique and could be easily modified for shipboard use. The amounts required for securing a chemical spill would necessitate large storage areas or large pumps to provide the necessary quantities of inhibitors. The efficiency index rating is conditionally acceptable.

Most compounds which would suppress the flammability of the vapors would increase the toxicity hazard. In those cases where the toxicity of the inhibitor is minimal, there would be no reduction of the toxicity hazard related to the spilled chemical. This technique can only be rated as unacceptable in terms of its compatibility index.

Cryogens - Cryogenic techniques have implications in all three areas of spill amelioration. The technique has been evaluated according to the objectives of each, individually, and ranked on the basis of overall performance characteristics.

Cryogenic cooling of hazardous chemical spills is a direct route for ameliorating the vapor hazards. It is applicable for all spills, except other cryogens, where evaporation rate reductions and vapor concentration reductions

will not reinforce the flammability reductions obtained by the presence of the flame inhibitor. This technique has been evaluated as conditionally acceptable for its effectiveness index.

Cryogens may be handled by commercial equipment without significant modifications. The technique requires that large volumes be stored for treating a spill, however, which impedes any rapid response. The efficiency index of this technique is conditionally acceptable.

The solubility of carbon dioxide could pose an environmental problem for this response technique. Other coolants which have flame suppressing characteristics would not be compatible with the aquatic environment. The compatibility index for this technique is also conditionally acceptable.

Foams - Low expansion foams may be used on floating, hazardous chemicals for vapor flammability reduction. Although they are not as effective as high expansion foams for maintaining vapor concentrations below their threshold limit values, they will reduce vapor flammability. The effectiveness index for low expansion foams used to reduce the flammability of vapors is rated as acceptable.

The total volume of low expansion foam required to reduce vapor flammability is approximately 67% of that required to reduce evaporation. The foam layer must be approximately 15 cm (6 in.) to reduce evaporation, whereas a layer of 10 cm (4 in.) will reduce flammability.

"Universal" and "Type L" foam concentrates were the only ones found to have sufficient compatibility with floating, hazardous chemicals. Both may be used with most foam generation equipment. A variety of commercial foam generators may be used and selections should be possible for all sizes and typical response situations. This technique is rated as acceptable for the efficiency index.

Both foam candidates appear to be completely compatible with the environment and have no human toxicity. It is difficult to assess the interfacing and interactions which may occur as the chemical spill is being removed, however. Present equipment has been designed for use against petroleum and petroleum product spills, where only a minimal amount of frothing or foaming occurs. It is also difficult to estimate the amount of breakage, which must occur during spill removal,which is necessary before the securing characteristics of the foam layer could be defeated. The foam technique is rated as conditionally acceptable in its compatibility index.

Aerosols - The aerosol technique for responding to spills of floating, hazardous chemicals would be applicable in all cases where flammability reductions are desired. This technique would have little or no effect upon the vaporization of the chemical and less than 1% of the hazardous chemicals would dissolve in the aerosol particles. Flame suppression or extinguishment does require that an adequate concentration of particulates be maintained in the vapor phase. This technique is rated as adequate for the effectiveness index.

Equipment is available to handle the types and quantities of materials required for this response technique. Water is assumed as a part of the liquid particulate aerosols, since it would be easily obtained in large quantities and have the desired suppression and toxicity characteristics. This technique is rated as adequate for the effectiveness index.

The amount of aerosol required to suppress combustion ($>2 \times 10^4$ mg/m^3 or $>1.2 \times 10^{-3}$ lb/ft^3) will present a problem to response personnel. Nuisance dusts have been given a TLV of approximately 10 mg/m^3 (6×10^{-7} lb/ft^3).

The minimum safety requirements for response personnel would be the use of particulate filter masks. This technique is rated as conditionally acceptable for the compatibility index, only for the use of water as the aerosol particulates.

Summary and Ranking for Task III

Task III was an evaluation of five candidate techniques which could be used for reducing the flammability of vapors released from floating, hazardous chemicals. Foam and aerosol techniques were ranked approximately equal in their capabilities to achieve this objective.

Foams having an expansion ratio of 10/1 or less were found to be more effective for reducing flammability than those with higher expansion ratios. A continuous foam layer approximately 10 cm (4 in.) thick was enough to prevent ignition of flammable liquids in experimental tests. Flames could be initiated in the vapor phase after approximately 45 minutes to 1 hour static exposure. These flames were arrested by the foam before they ignited the liquid phase. Winds and convection currents found under normal conditions would reduce the possibility of generating a flammable vapor mixture, since low expansion foams also reduce the vaporization rate.

As with other foam techniques, the selection of the foaming agent must be made on the basis of chemical compatibilities. The foaming agent must not react with the hazardous chemical or be miscible in it. Foams will collapse rapidly when placed over hazardous chemicals having a dielectric constant greater than 3.

The aerosol technique has been considered practical only when water is used as the dispersed phase. The amount of water required to reduce the vapor flammability

of hazardous chemicals will vary with the reactivity of the chemical but this technique can be used against all hazardous chemicals. The necessity for using large amounts of non-polluting material eliminates all other alternatives.

Aerosols have negligible effects on the vapor concentrations of hazardous chemicals (except cryogens) and will not ameliorate the hazards associated with the toxicity of vapors. Very few of the floating, hazardous chemicals are soluble in water and few would be physically adsorbed to the particles. It is also doubtful that the water particles would significantly promote condensation.

Any of the removal devices listed in Table 2 could be used in conjunction with the aerosol response technique. Several problem areas may be envisioned during the removal of the hazardous chemical in the presence of aerosols. Some experimental verification tests could be done to determine which recovery devices and procedures could be used without disrupting the layer of floating chemical, visibility and safety of response personnel.

SUMMARY AND CONCLUSIONS

Fifteen response techniques were evaluated within the three separate tasks of this program, to determine their feasibility for use against discharges of floating, hazardous chemicals. Six of these were considered to have some feasibility in their present state of development, to achieve the objective of the tasks, as outlined by the U. S. Coast Guard.

Surfactant films, foams and sorbents appear feasible for reducing vaporization rates, which was the objective of Task I. Encapsulating the spill with an impregnated fabric or otner impermeable material appears to be the only technique presently available for reducing vapor concentrations, the objective of Task II. Both aerosol and foam techniques may be used to reduce the flammability of vapors, which was the objective of Task III.

The use of surfactant films involves the dispersion of a fluorochemical chemical-water mixture over the surface of the spill. This is usually accomplished by using either fog or foam nozzles to disperse the solution and allow it to spread over the surface as a very thin film.

Vaporization rates have been significantly reduced in experimental tests, but these solutions may not be used over spilled materials having a surface tension less than 20 dyne/cm (1.4×10^{-3} lb/ft). Environmental pollution by the fluorochemicals and efficiencies which may be obtained under field conditions are the two major areas of uncertainty for this technique.

The thin films generated by the use of this response technique should be removed with the hazardous chemical by most of the removal devices listed in Table 2. The various weir and skimmer configurations appear best for ultimate removal of the discharge. Some experimental tests should be done, however, with the removal techniques, to determine the best procedure for removal while retaining the protective film.

The foams considered in Task I are those having expansion ratios between 10 and approximately 200 to 1. These would be generated by commercial equipment, which could be used aboard ships. Foams would be used in conjunction with booms or other equipment which would help maintain a continuous layer over the surface of the spill.

Foams generated at expansion ratios of 100/1 or greater have been found to be more impermeable to benzene vapors, in screening tests. They may become flammable after extended periods of exposure to hazardous chemicals (>1 hr in lab tests). Foams generated at expansion ratios of 10/1 or less require more material to be used to reduce vaporization, but they are not flammable and will act as an arrestor against possible ignitions of the liquid phase.

Present deficiencies of foams lie in their sensitivities towards chemicals having a dielectric constant greater than 3 and some incompatibilities with solvents which will dissolve the components of the foaming agent. There are several formulations of foams available and a proper selection will require a knowledge of the chemical to avoid incompatibilities and foam collapse.

Foam layers, used to reduce vaporization from hazardous chemicals, should be more durable than the surfactant films during removal operations. This would provide more protection and greater safety for the people

responding to the spill. Skimmers appear to be the best removal devices from those listed in Table 2. Some weir configurations and the belts or moving sorbent layers used for removing the hazardous chemical could break the foam layer and eliminate the protection.

Sorbents include a great variety of materials which may be selected, for the objectives of Task I, on the basis of capacity, durability and price among many other features (properties). Many of the commercial sorbents have been developed for treating spills of petroleum or petrochemicals, but they may be used for treating other hazardous chemicals also.

The attributes of the sorbent response technique are a general applicability towards hazardous chemicals and the ease with which the hazardous materials may be accumulated for removal. A judicious selection of the sorbent must be made to realize the full potential of this technique, but it is generally applicable for removal.

The deficiencies of this technique are primarily the uncertainties of the extent of protection. These uncertainties arise from the lack of experience and verification concerning capacities and buoyancy. When the sorbent is saturated by any combination of hazardous chemical and water the vaporization rate may be increased by the large surface area of the sorbent.

Sorbents also present some special problems of vaporization rates when entering the removal and disposal steps of spill response. Removal devices are presently incorporated in systems designed for the recovery of petroleum products. The greater hazards presented by the chemicals considered in this investigation exceed the capabilities of present equipment.

All the candidates considered in Task II of this investigation have some areas which are uncertain or are incapable of meeting the objectives in their present status. Encapsulation appears to be the most promising candidate for further development.

Several materials have been used to form covers over lagoons and other waste ponds. These appear to be feasible for use against spills of hazardous materials, also, but a rapid, safe method for deployment has not been advanced. Experience, to the present time, has been limited to land applications, which do not present the same conditions as maritime use. A similar situation is found for packed particles, which have been recommended for further research and development.

Both foams and water aerosols are considered feasible for obtaining the objectives of Task III. The use of foams was discussed previously among the candidates for Task I. This technique would have similar attributes and deficiencies when used to obtain vapor flammability reduction. Since the conditions for vapor flammability reduction are not as severe as those for vaporization rate reduction, the feasibility of foams becomes somewhat better.

The aerosol technique involves the dispersion of fine water particles ($\sim$100μ), which would remain in suspension throughout the time necessary for collecting and removing the hazardous chemicals. The attributes of this technique stem from the proximity of large sources of water and its general applicability.

The use of aerosols would create a visibility problem and other interferences in the removal of hazardous chemicals that float. The large quantities of water required could also pose a discomfort for response personnel.

Foams, in the forms of aqueous film-forming and long-life formulations appear to be the most promising methods for reducing vaporization and vapor flammabilities of hazardous chemicals that float on water. The toxicities and flammabilities of the vapors from these chemicals appear to be too great to be handled by techniques involving sorption, gelling, dilution, cryogenic cooling or inhibitors.

Vapor concentration reductions, the objective of Task II, appears to be beyond the capabilities of most techniques available. Encapsulation was determined to be the most feasible approach, but would require significant testing and development.

PROPOSED DEVELOPMENT PROGRAMS

The evaluation of available mechanisms to control the vapor hazard from spilled chemicals that float on water has delineated several which have significant potential. Each, however, show areas needing further development and appraisals. The evaluation process has served to delineate the uncertainties, deficiencies and data inconsistencies. This provides a base to evolve recommendations for development work. The degree and direction of further effort varies for each technique. In the subsequent sections each mechanism is reviewed, suggestions made as to further work required, the expected magnitude of the program defined, and to the degree possible a rating of each proposal in terms of degree of success and impact on vapor hazard control.

The techniques to be considered are surfactant films, foam, both low and high expansion, sorbents, gels and cryogens. With each of these, adequate technology exists to show that they have merit in alleviating at least one form of vapor hazard. Covers and packed particles will also be considered but in these basic technology still needs to be defined and it is not yet certain that their potential can be realized. Dilution through water sprays is the only technique considered to have application for which no further work will be recommended. Although much might be done in terms of application rate, droplet size, etc., it is doubtful the data could be used in a meaningful manner in the field.

Foams

Of the available techniques, foams have probably seen the greatest utilization in attempting to control the vapor hazard from spilled chemicals. Although an extensive body of data exists for certain chemicals, LNG, gasoline, SO_3 and others, the capabilities of foam with the broad range of chemicals found in the hazardous lists is not adequately defined.

The potential of foam has led EPA to fund a program, now in progress, to fully evaluate foam capabilities. The program has three objectives to be accomplished in a progressive manner: fully define currently documented capabilities of foam systems now available to those agencies concerned with spill control and cleanup; through experimentation, provide the necessary data for a capability manual on the available systems; and through development of new or improved systems advance the capabilities of foam in vapor hazard control. This program is being conducted over a 30-month period at a level of effort of 1-1/2 man years per year.

It is expected that the program will fully address the current and future requirements of foam systems, both low and high expansion. Thus, additional effort by the Coast Guard does not appear warranted at this time. The program is addressing a broader range of chemicals than just those that float on water and it is possible that as the program develops it will be shown that certain categories of chemicals will require special attention. Based upon current data, however, the smaller the water solubility limit of the chemical the better the capability of foam

will be with respect to vapor control. Thus, those chemicals that float should be adequately covered by the present program and no recommendations are made for Coast Guard sponsored work at this time for foam.

It will be necessary for the Coast Guard to monitor the EPA program to insure that it is providing the data needed for floating chemicals. There are three areas that may not receive attention in a program primarily designed for land based spills which may require special investigations. These concern the influence of flowing or otherwise moving water on foam persistence, the possibility of interaction between foam and the floating chemical to produce a soluble hazardous substance, and the inerting of foams, particularly high expansion, by controlling the composition of blowing air.

Waves and Other Water Action

It is expected that the collapse rate of foams will be one factor in the selection of an acceptable system. To provide adequate vapor control, it will be necessary to maintain a minimum foam thickness. This becomes an economic consideration in the long run, so that persistent foams become the desirable situation. Because wave action or other water motion may exaggerate foam collapse, Coast Guard requirements may be more severe in this regard than land base spills. Thus, consideration may be warranted to develop foams of sufficient persistence to economically as well as technically be useful with spills on water.

Foam Inerting

Current technology shows that all foams ultimately absorb measurable quantities of the liquids they are covering.

Thus, air-gas mixtures can develop which fall within the flammable and explosive ranges. With low expansion foams, the flammability hazard is negligible due to the fact that the foam acts as an inhibitor. With higher expansion foams, explosions cannot be propagated but they do burn back at high rates.

Work sponsored by the Maritime Administration on tanker inerting has shown that high expansion foams can be blown using stack gases or gases produced by an inert gas generator. Foams so blown cannot be ignited even after assimilation of significant quantities of flammable gases due to the lack of oxygen. Ships available to the Coast Guard may have the capability of utilizing such gases to blow foam, a capability which may not be readily available in land spills.

The ability to deliver a non-flammable high expansion foam may alter the recommendations for foam in spill situations. If economic or other conditions can be shown to favor the use of high expansion foam, and the flammability which can develop is the only drawback, it may be advantageous to work out procedures to blow foam with the stack or other inert gases.

Foam Effects and Solubility

The final consideration is the possibility of interaction, such as saponification, between foam and chemicals and the spilled material which would result in conversion of the floating material to one which is soluble or a sinker. The latter occurrence is probably remote but solubility is possible. Foam-chemical interaction would be confined to the interface area, but foam drainage passing through the spill into the water substrate would carry such reaction products into the water.

In land spills penetration into the substrate is to be expected and some exaggeration due to the influence of foam will probably be of little significance. With spills on water, soluble products will end up in the water. These reactions may be minor and the amount carried into the water negligible given dilution and diffusion rates. Data in this regard is not defined at present. If, as expected, foam is found to be a principal spill control mechanism, investigation of this effect will become necessary.

Surfactant Films

For suppression of the vaporization rates, surfactant films, most specifically fluorocarbon surfactant films, theoretically are the most efficient. This is based upon 100% coverage of the spill surface. Small discontinuations in the film coverage result in large losses in efficiency, however. In practice, maintenance of a continuous film may be difficult, particularly so where the spill is floating on water where waves, flow and other undulations are common conditions. Thus, it appears that mechanisms are necessary to maintain the integrity of the film, under practical conditions. Films are usually delivered as a foam which collapses to form the film. Developing persistence in the foam would give a barrier to wind effects while providing a slow drainage system to continuously make up the film.

The fluorocarbon surfactants pose one other difficulty. The available data shows that these materials can be toxic to aquatic life at reasonably low concentrations. At minimum coverage levels the concentration bleeding onto the water substrate may not be significant

but the excess that seems to be necessary to maintain the film may raise the concentration into the toxic range. This possibility needs to be investigated, measuring short range toxic levels, assessing passthrough of the fluorocarbon into the water, and determining the rate of dispersion in the water column.

Whether fluorocarbons are deemed acceptable or not, consideration should be given to similar materials which are ecologically safer to use. Patents exist on silicone base surfactants which reportedly possess the necessary characteristics. In addition, there are tallow ester derivatives which also appear promising, although their surface tension is not as low as the fluorocarbons.

It is recommended that programs be undertaken to consider four subjects concerned with surfactant films. The first should investigate the maintenance of surfactant films on floating chemicals given the practical conditions of a field spill. If these data show negative results, a program to investigate techniques to overcome the practical difficulties should be initiated.

Concurrently with these two tasks, a third investigation is necessary to fully define the toxic hazard of the fluorocarbon surfactants entering the aquatic environment. The maximum tolerable levels should be compared against those which could occur during the use of surfactant films on spills. The data from the first two tasks should be able to define the quantities to be employed to maintain adequate coverage as a function of time.

In parallel with the further definition of fluorocarbons, a development program appears warranted to investigate alternate materials. The silicone base surfactants and

tallow ester derivatives offer a starting point but other materials may also possess the necessary qualities.

Definition of the practical capability or difficulties of surfactant films should be definable in six calendar months at a 2 man-year level of effort, with an additional 9 months at the same level of effort to assess methods such as foam stabilization to minimize the difficulties.

Determination of toxic levels and the concentrations which can build up in the water column may require up to 1 year at 1.5 man-year level of effort. This program could overlap the two tasks above in calendar time.

The development of alternate materials is difficult to assess. It would appear that the possibility of developing alternate materials from the silicones or tallow esters could be established in less than 9 months along with the potential such materials can offer. In this preliminary effort, 1 to 1.5 man years should be adequate. The larger time effort for newer materials on full development of the silicones and tallow esters and the justification of such effort will only become clear as the preliminary program progresses.

Sorbents

The evaluation of sorbents has shown that effective materials exist but are quite costly. Reticulated resins are available and work is already in process in developing buoyancy in other effective sorbents such as activated carbon. The cost and logistics of this type of material may legislate against their use. Their applicability may depend in some part on the availability of equipment capable of efficient application with small losses outside of the spill area.

Other sorbents, particularly urethane foams, offer a less efficient medium but also a less costly medium. Urethane chips have been used as a sorbent and technology exists to produce these over a wide range of pore sizes. These materials also would benefit from efficient dispensing equipment. One difficulty exists, however. As has been described as part of the evaluation, as the urethane absorbs the spilled chemical and possibly water, it submerges into the spill and can exaggerate the vaporization rate by essentially increasing the surface area available for evaporative losses.

Proposals have been made to circumvent the difficulty. They would generate the urethane on site, forming a continuous urethane blanket rather than a mat of chopped pieces. These have failed to take into consideration that the urethane must be rigidized before it contacts liquid. Before being fully reacted it can degrade releasing isocyanates which are toxic chemicals of themselves and soluble and reactive in water. To build a blanket there must be a suitable substrate.

The potential of continuous urethane foam blankets warrants some consideration of mechanisms to effect them. One approach is to develop an initial mat of urethane chips with the subsequent overlay of a continuous blanket generated in place. The technology for generating urethane foam continuously in the field is well developed and urethane chips are available. Thus, this program would be minimal. Other approaches may be possible, and a program is recommended that would evaluate mechanisms for developing urethane foam blanket over spill surfaces. Conducted independently of equipment requirements for application to real time spills, the program should not take more than 9 months nor exceed $50,000 in cost.

Application of any of these sorbents is dependent on the availability of suitable dispensing equipment. Those which are now available have been derived from other systems. They tend to be inefficient and there are large losses of materials outside of the spill area. Equipment is needed which can dispense the sorbent directly into the spill surface from close proximity to it with a narrow range of discharge.

It appears that booms or bridge units will be the type of units to be evolved, systems which can stretch out over the spill or completely span it to discharge a granular or powdered material from multiple ports directly down onto the spill surface. They will need propulsion to move them parallel to the spill flow direction. The propulsion and the sizes involved will pose the basic problem in development. Technology for the pneumatic, mechanical, or hydraulic transport of bulk materials is available.

Based upon costs and development times for similar equipment for land spills and other equipment for water use the evolution of prototype equipment including field tests could take up to three years and cost in excess of $500,000. This plus the cost of sorbents provides a costly spill control technique. A decision in this area needs to weigh the cost of clean-up against the potential damage to the environment.

The type of dispensing equipment needed for the sorbents would also be needed with gels, solid CO_2 and packed particles. If those procedures are found to have practical application to spill control, the cost of developing dispensing equipment will be further justified.

Gels

The applicability of gels to aid in the control of vapor hazards from spilled chemicals has not been given a high ranking. Although they show some retardation of vaporization, it is small. This coupled with the cost, the difficulty of efficiently applying them, and the fact that those now available are not specific for organics and absorb water as well make them unattractive.

It should be noted that gels may have significant benefits in immobilizing the spill and otherwise assisting in the clean up operation. These factors have not been included in the evaluation criteria employed in this program. The prime benefit of gels may be as an adjunct to foam. If the spill can be immobilized, the surface area can be minimized and foam more readily applied. Further, since gels do decrease vapor release they will provide an add-on to the foam block extending the time required for vapor permeation through the foam and/or reduce the minimum foam thickness required for control.

The major purpose gels may play, although other materials may also be effective, is as a base for foam support. It has been shown that foam is degraded by a number of chemicals in the hazardous list. In many cases this degradation occurs only upon contact of the foam with the liquid. If the foam can bridge the liquid so that it contacts vapor only, the degradation is minimized if not eliminated. Gelation, at least of the spill surface, may be a means of avoiding foam-liquid contact. This is one area expected to receive attention in the third phase of the current EPA program.

Since the EPA program addresses a broader range of chemicals than just floaters, consideration may be principally

directed to the so-called universal gelling agents. There are gels available, some only experimentally, which tend to be specific for organics to the exclusion of water. These are more complicated in their gelling mechanism, but foam-gel interactions or the manner of application may allow practical utilization. If foam continues to be attractive and the results of the EPA program warrant, it may be worthwhile for Coast Guard investigation of gel-foam combinations which have advantages where spills are on water.

A program in this area given to preliminary evaluation and subscale testing could be conducted in a 6 to 9 month period at a cost not more than $40,000. If the results were encouraging scale up and field test work would be needed. An additional six months at an equivalent dollar cost should be adequate for that work. This assumes the availability of required equipment at no cost to the program, at least for field tests.

Cryogens

On the basis of the data available for the evaluation of cryogens in this program, the conclusions to be reached were that cryogens were not a practical technique in controlling any facet of the vapor hazard from spilled chemicals. CO_2 in the form of snow or liquid exhibited the greatest possibility. Considered as a coolant only or inert diluent only it received a poor rating. With the realization that both effects are achieved simultaneously and being heavier than air it tends to blanket the spill even as a gas, its potential increases.

CO_2 has other difficulties: logistics of a subliming solid, procedures of application, and the possibility of adversely affecting the aquatic balance in terms of pH. It is felt that the necessary data was unavailable to fully and

accurately assess the difficulties particularly the acidulation of the water substrate. In light of the technical potential of cryogenic CO_2, it is recommended that a program be conducted to investigate in detail the following: the pH changes which could occur as a function of the amount of CO_2 used on a spill; the quantities which would be needed to produce a measurable effect in a spill situation as a function of spill size; the storage, transportation, and application to the spill of cryogenic CO_2. From these data a new assessment can be made as to the practicality of CO_2 as a mechanism of vapor control.

This effort should be possible to complete in less than a year at a cost not to exceed $70,000. This should be primarily a study program supported by laboratory size tests. Some final verification in larger size outdoors would be necessary.

Covers and Packed Particles

The evaluation of techniques to reduce vapor concentrations failed to show those available to have merit, short of actually providing essentially impermeable covers over the spill. Physical covers have been used in fixed installations on land to contain vapor hazards. Packed particles, the development of a layer of closely spaced spheres on top of the spill,has shown some promise but it suffers from the inefficiency of packing. Recently, interesting tests have been run using dodecahedrons of urethane foam. These pack more efficiently and reported vapor containment has been good.

Although there is interesting data for both covers and dodecahedrons, it is not believed that either has been established as sufficiently promising for application to spills floating on water. Covers are difficult to deploy

even with fixed installations; attempting this on water where there are no firm anchors appears to be an impossible task. The dodecahedrons would not appear to offer problems in application but there is an unanswered question as to the ability to manufacture the dodecahedrons in quantity without even worrying about cost.

At this time, the recommendation is that the companies proposing these techniques substantiate that they can be brought to a point of utility for spills floating on water. This data would then be used to reach decisions on supported programs to further the concepts. Such substantiation was not made available during this program.

The proposed development programs are summarized in Table 12.

TABLE 12

SUMMATION OF PROPOSED DEVELOPMENT PROGRAMS

PROGRAM	OBJECTIVE	COST	DURATION	RATING(1)	SUCCESS(2)
Foam Development					
1. Foam Collapse	Determine effects of wave and other water motion on foam collapse and improve if necessary	$90-100,000	1 year	B	Excellent
2. Solubilization Task I-Evaluate Potential Task II-Define rate of introduction & dispersion in the column	Evaluate the potential of foam-chemical interaction to produce soluble toxic chemicals	Task I - $30,000 Task II - $60-70,000	4 mos. 10 mos.	A	Excellent
3. Inert Foams	Develop procedures to allow the generation of foams with stack or other inert gases.	$50,000	8 mos.	B	Excellent
NOTE: It is recommended that foam programs be deferred until the current EPA program has completed its first phase.					
Surfactant Films					
1. Stable Foams	Incorporate persistence and slow drainage into fluorocarbon foams	$70-80,000	9 mos.	A	Good
2. Film Maintenance	Investigate the ability to maintain surfactant films on spills under practical conditions.	$40-50,000	6 mos.	A	Excellent

PROGRAM	OBJECTIVE	COST	DURATION	RATING(1)	SUCCESS(2)
3. Toxicity of Fluorocarbons	Determine toxicity levels for fluorocarbon surfactants, the rate they would enter the water and their dispersion in the water.	$70-80,000	1 year	A	Excellent
4. Develop New Film forming Surfactants Task I-Appraise existing materials	Evolve less toxic, more persistent or more effective film formers	Task I - $80,000	9 mos.	B	Good
Task II-Develop new materials		Task II - $100-150,000	Up to 2 yrs	C	Fair
Sorbents					
1. Urethane Foam Blankets	Develop techniques using existing technology and equipment to allow formation of continuous urethane foam blankets over spill surfaces.	$50,000	9 mos.	B	Good
2. Dispensing Equipment	Develop equipment for the efficient application of sorbents or other solids to spill surfaces.	$500,000	3 years	A	Fair

PROGRAM	OBJECTIVE	COST	DURATION	RATING(1)	SUCCESS(2)
Gels					
1. Gel-Foam Systems	Investigate combination gel-foam systems to achieve combination of properties, with subsequent field evaluation.	Task I - $40,000 Task II - $40,000	9 mos. 6 mos.	B B	Good Good
Cryogens					
1. Solid CO_2	Provide further evaluation of solid CO_2 as a coolant, vapor diluent and inert blanket for spilled chemical.	$70,000	1 year	A	Excellent

(1) Rating: A - Programs necessary to allow utilization of techniques or to verify applicability
B - Programs to improve techniques deemed useful.
C - Longer range developments

(2) Success: An assessment of the potential of realizing the stated objectives.

APPENDIX A

EXPERIMENTAL MEASUREMENTS OF VAPOR SUPPRESSION WITH FOAMS

Experimental Test Results From This Investigation

The evaluation of candidate spill response techniques for ameliorating vapor hazards required some experimental tests to measure their capabilities and verify field experience. The general approach and outline of experimental tests were evaluated and incorporated into the program at a meeting with the Project Officer, Mr. John Sinclair, in the Mine Safety Appliances Research Laboratory on 20 November 1975.

The experimental work was prepared to fulfill a two-fold objective: measuring the permeation of hazardous chemical vapors and determining the optimum technique for evaporation suppression. Estimates of chemical compatibilities and the working lives of these systems were to be made concurrently with performance measurements in these experimental tests.

The variables investigated in these tests included:

1. Hazardous chemical species
2. Thickness of hazardous chemical layer
3. Amount of ameliorating agent
4. Compatibilities
5. Expansion ratios (foams)
6. Permeabilities

Although foams have been used for extinguishing fires, their use for covering hazardous chemicals is only now in development. Therefore, an initial screening of foams was done, to determine those which would be compatible with typical, hazardous chemicals, and thus offer some capability to ameliorate vapor hazards. Results of these screening tests are presented in Table A-1.

TABLE A-1- FOAM CAPABILITIES
(Relative foam stabilities* when placed over a pool of hazardous, floating chemicals)

Hazardous Chemical	Foam Candidates				
	National Foam Systems		Mine Safety Appliances Co.		Fire Chemical
	Universal	Aer-O-Foam	Salt Water	Type-L	Chemical Foam
Hydrocarbons					
Cyclohexane	fair	poor	fair	good	fair
Isooctane	good	fair	fair	excellent	fair
Kerosene	fair	poor	poor	good	poor
Tetrahydronaphthalene	poor	poor	poor	good	poor
Aromatic					
Benzene	fair	fair	poor	fair	poor
Aniline	fair	poor	poor	fair	poor
Esters					
Ethyl Acetate	fair	poor	poor	fair	poor
Amyl Acetate	poor	poor	poor	poor	poor
Alcohols					
Amyl Alcohol	poor	poor	poor	poor	poor
n-Octanol	fair	poor	poor	good	poor
n-Decanol	fair	poor	poor	good	poor

*Collapse Rates

poor <1/2 hr fair ~1 hr good >1 hr excellent >2 hr

Apparatus

The test apparatus, shown in Figure A-1, provided a means for obtaining a rapid assessment of relative vapor suppressing capabilities. The apparatus consisted of a glass dessicator, having a volume of 14.5 liters (0.51 cu ft), which was fitted with a dip tube, for charging liquids, and a discharge outlet, from which gas samples were obtained.

Experimental test measurements included: liquid temperatures, amounts of hazardous chemicals, vapor concentrations, chemical and ameliorating agent layer thicknesses, gelling times, sorbent settling rates and foam collapse rates. Those techniques which would ameliorate vapor hazards were retested using more sensitive test procedures.

A typical test involved the use of a pool of water at 25-27°C (77-80°F) in the bottom of the dessicator; placing the ameliorating agent over the surface; and finally, adding the hazardous chemical, through the dip tube, beneath the surface of the water.

Gas samples were taken in the free air volume at the top of the dessicator prior to adding the hazardous chemical, just after the addition; and then every ten minutes thereafter, until the vapor concentration increased to approximately 5%. These vapor samples were analyzed with a Hewlett-Packard Model 5750 gas chromatograph using flame ionization detection.

Test Results

Data from these experimental tests have confirmed the few reported in the open literature and expanded the general background of vaporization rate reduction by foams. These data may be used for comparison of vaporization rate reductions, but the nature and scope of the investigation do not permit exceptional accuracy or theoretical interpretation. They have have been found to be sufficient for the generation of a linear

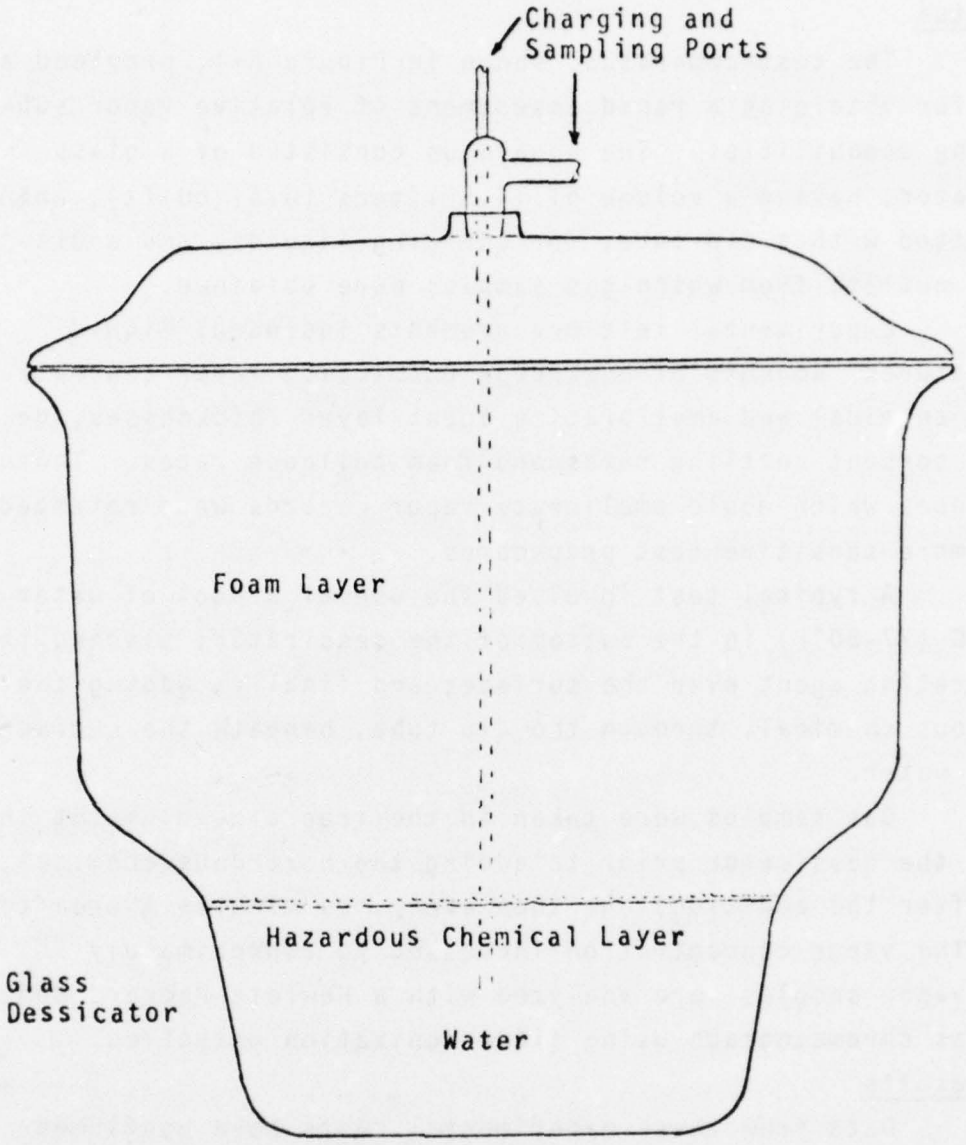


FIGURE A-1 - PRELIMINARY TEST APPARATUS

expression representing the transfer of vapor into the gas phase.

The original design of the experimental tests was directed towards the investigation of aqueous foam systems. After screening tests verified the general concept, the test series was expanded to include gels, sorbents and cryogens.

The penetration of benzene vapor through various ameliorating agents has been fitted to a linear equation, by least-mean-squares-fit, for an approximately two-hour time interval. These results are presented in Table A-2 as milliliters of benzene vapor passing into the free air volume per minute.

The results presented in Table A-2 have been developed from several series of tests with foams and other ameliorating agents. Comparisons of individual tests are presented graphically in Figures A-2 to A-4.

Plotting the benzene vapor concentrations above these agents as a function of time, shows a short penetration time and then a reduced diffusion rate through the foam cover. Similar results were obtained even when the foam layers varied by an order of magnitude (one-inch layer of foam expanded approximately 5 to 1 and ten-inch layer of foam expanded approximately 200 to 1).

Some indication of the protection provided by various response techniques against a benzene spill is portrayed in the preceding figures. It required approximately 25 minutes to develop a flammable mixture above a simulated benzene spill with no ameliorating agent. If a gelling agent was used, it required approximately 18 minutes. When urethane foam covered the benzene layer, it required 38 minutes. A ten-inch layer of National Foam Systems, Inc. "Universal Foam" (150/1 expansion) increased the time to achieve a flammable mixture to 50 minutes.

TABLE A-2 - RELATIVE PERMEABILITY OF BENZENE VAPOR THROUGH SPILL RESPONSE TECHNIQUES

Conditions	Time Interval (min)	Benzene Vapor Permeation (ml/min)
Through Open System	10-35	18.16
Through one-inch layer of low expansion[1] "Universal Foam"	30-90	8.57
Through two-inch layer of low expansion "Universal Foam"	30-150	3.72
Through five-inch layer of high expansion[2] "Universal Foam"	20-70	6.19
Through ten-inch layer of high expansion "Universal Foam"	30-60	0.69
Through three-quarter-inch layer of low expansion "Type-L Foam"	70-140	1.92
Through ten-inch layer of high expansion "Type-L Foam"	30-100	0.51
Through one-half-inch layer of flexible Urethane Foam	30-100	8.14
Through 2 to 1 volume ratio of HYCAR-1422 Gelling Agent	5-90	11.09
Through 2 to 1 volume ratio of Amberlite IRC-50 ion-exchange resin	50-80*	1.01
Through 0.8 to 1 volume ratio of Amoco Floating Carbon	5-70	12.25
Through open system at 32°F (0°C)	10-80	4.83

* Protection retained only until the resin was completely wetted

[1] Approximately 5 to 1 expansion

[2] Approximately 200 to 1 expansion

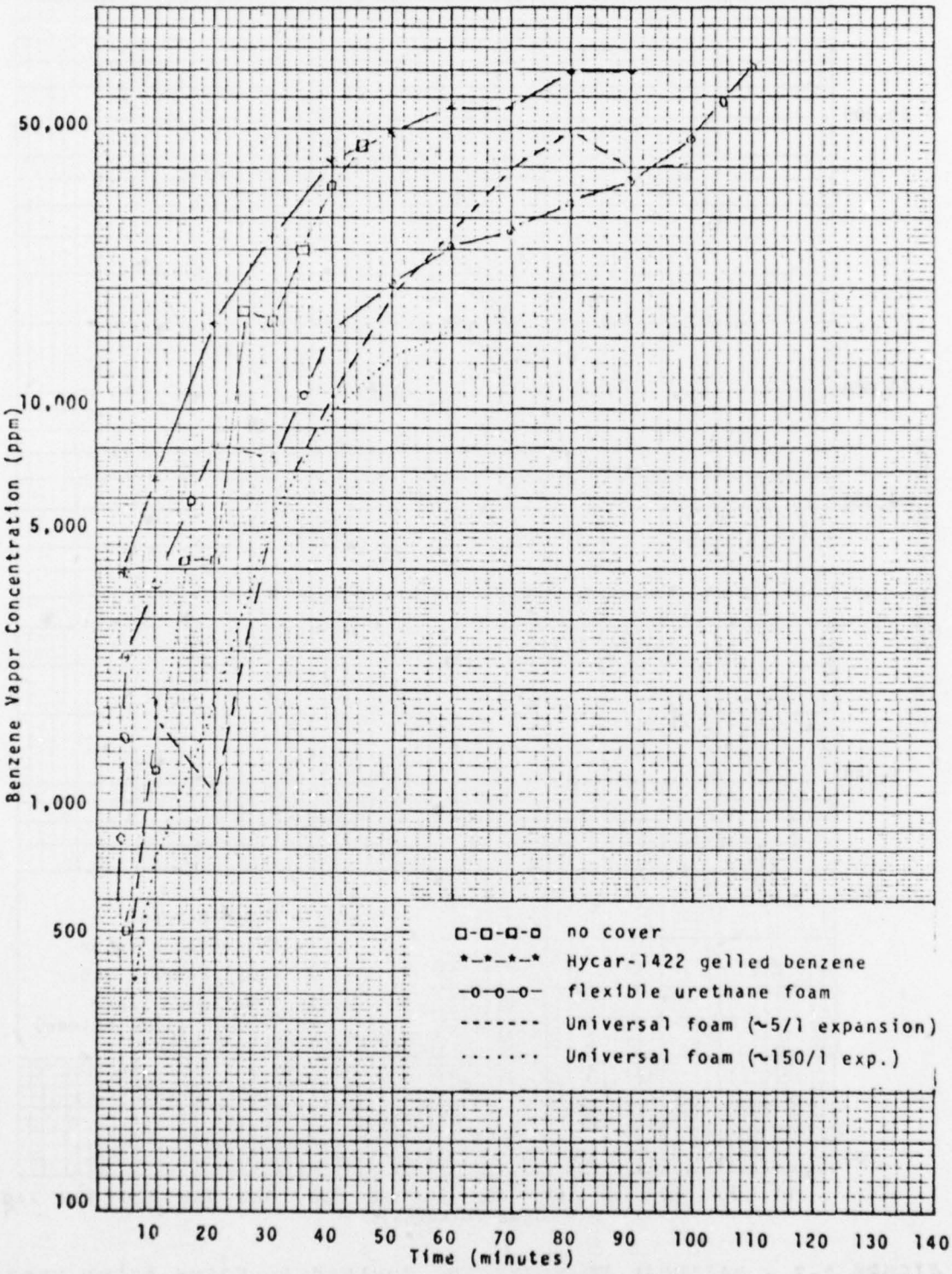


FIGURE A-2 - CANDIDATE RESPONSE SYSTEMS USED OVER BENZENE FILM

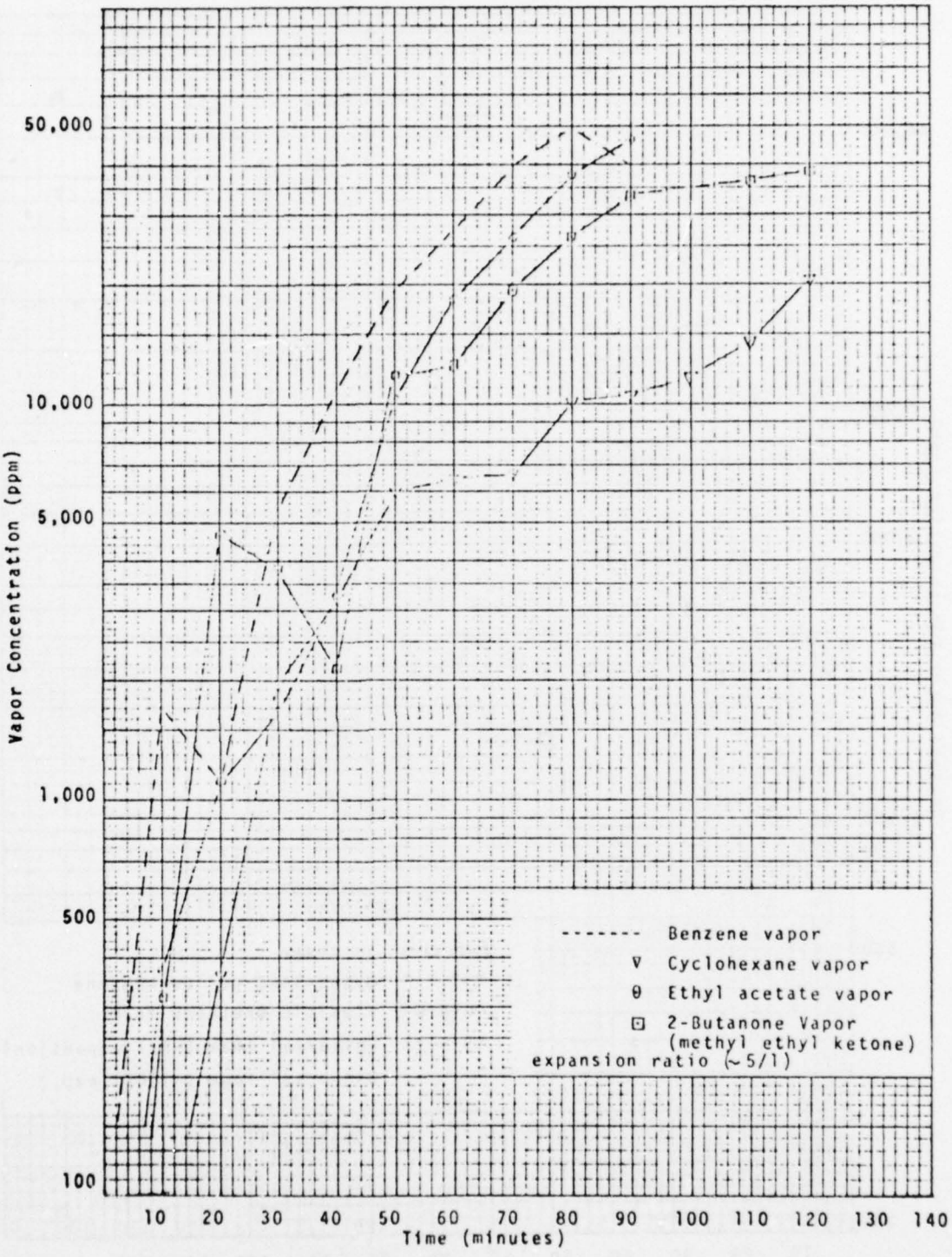


FIGURE A-3 - NATIONAL FOAM SYSTEMS "UNIVERSAL FOAM" AGENT USED IN 10% SOLUTION OVER VARIOUS HAZARDOUS CHEMICALS

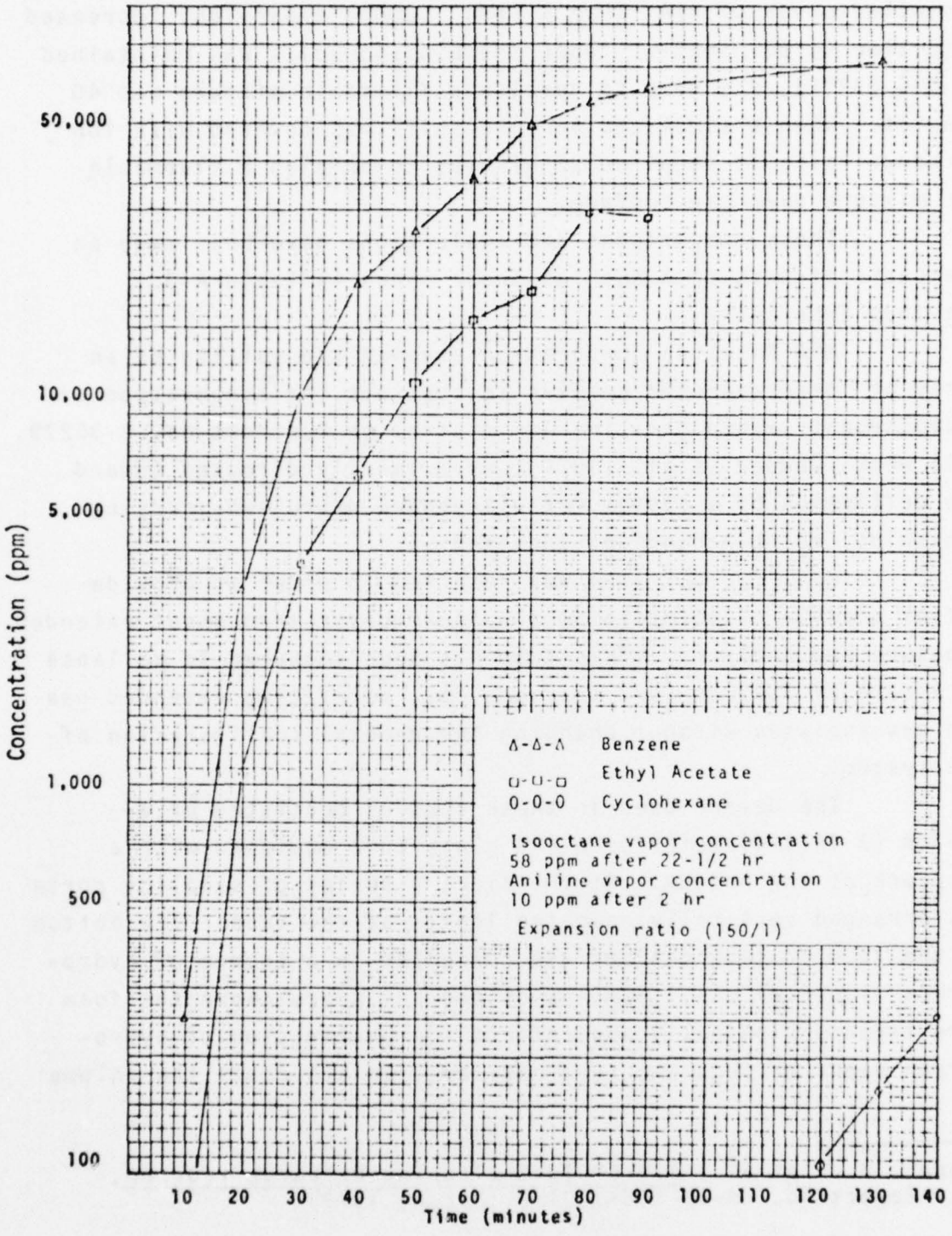


FIGURE A-4 - MSA TYPE L FOAM AGENT USED IN 30% SOLUTION OVER VARIOUS HAZARDOUS CHEMICALS

A similar cover of MSA "Type L Foam" (200/1 expansion) increased this time to 60 minutes. When the benzene spill was maintained at 0°C (32°F), the time to develop a flammable mixture was 40 minutes. When a simulated benzene spill was covered with ion exchange resin it required 92 minutes to develop a flammable gas mixture over the surface.

These comparisons and evaluations have been made on the basis of test data such as those shown in Table A-3.

Previous Experience

MSA Research Corporation studied the ability of an array of interconnected bubbles to suppress the evaporation of hydrocarbons within Maritime Administration Contract No. 2-36279. This work, Cooper et al. (1974),was primarily directed toward the definition of a system for use aboard petroleum-carrying tankships, for cleaning and inerting.

MSA "Type L" foam was selected in order to provide a foam capable of maintaining a uniform cover throughout extended exposure and analyses. This foam has been measured to collapse at a rate of 1.27 cm (1/2 in.) per day, permitting extended use and gas analyses without changing the general configuration of the system.

The device used in these studies consisted of a 7.6 cm (3 in.) diameter open end glass tube equipped with a stopcock at the bottom. At the side, a series of sampling ports was arranged vertically down the length of the tube. The bottom of the tube or test chamber was connected to a source of hydrocarbon liquid or gas. Samples of the air space above the foam were taken periodically and reflect the penetration of hydrocarbon vapor through the foam barrier. In all cases the volume

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Cooper, W.J. et al., Tanker Tank Cleaning Research Program, Report No. MA-RD-900-74017 (March, 1974).

Table A-3 - Diffusion of Benzene Vapors Through Experimental Apparatus

A. Free Diffusion

Concentration	Time
160 (ppm)	2 (min)
500	5
1250	10
4100	15
4150	20
17100	25
16600	30
25000	35
36600	40
45700	45

B. Through 25 cm (10 in.) of Hi-Expansion "Universal Foam"

Concentration	Time
758 (ppm)	10 (min)
1838	20
5460	30
9928	40
13370	50
15750	60

C. Through 5 cm (2 in.) of Low-Expansion "Universal Foam"

Concentration	Time
300 (ppm)	10 (min)
600	20
1400	30
2750	40
6900	50
9000	60
14300	70
21000	80
24200	90
10500	100
34100	110
31900	120
37800	130
36400	140
38900	150

D. Through 25 cm (10 in.) of Hi-Expansion "Type-L Foam"

Concentration	Time
30 (ppm)	10 (min)
352	20
1370	30
3512	40
5292	50
10580	60
11950	70
15800	80
18000	90
21200	100

expansion of the foam was about 150/1. Analyses were performed using the gas chromatograph.

Figure A-5 shows a plot of the buildup of isooctane vapor in the air space above a 21 cm (8-8.5 in) layer of foam above a liquid reservoir of isooctane. For comparison the vapor concentration at the same height but without foam is also shown. It is evident that foam can form a very effective vapor barrier for at least 18 hours.

The maximum concentration found within any bubble was 9000 ppm isooctane, found in the layer of bubbles almost directly in contact with the liquid hydrocarbon. Removing air samples from within a bubble was achieved by first wetting a hypodermic needle with the clean foam agent solution. This procedure facilitated entering and removing the needle through the bubble wall without causing bubble rupture. It was noted, however, that if a portion of the liquid phase of the bubble (wall area) was accidentally removed the hydrocarbon content was exceptionally high. This indicated that the bulk of the hydrocarbon escaping from the liquid reservoir below the foam resides in liquid phase of the foam.

It was also noted during the course of these tests that the foam layer in immediate contact with the liquid hydrocarbon deteriorated with time. At some time after the fifth hour the complete array of bubbles initially in contact with the isooctane had collapsed. The remaining bubbles of foam, instead of collapsing onto the liquid hydrocarbon, formed a bridge over the liquid by arching from the surrounding walls. The net result was that for the last 15 hours the foam barrier was separated from direct contact with the liquid isooctane.

The penetration of butane gas through 8.9 cm (3.5 in) and 15.2 cm (6 in) layers of foam is shown in Figure A-6. The percent composition refers to the buildup of butane gas which

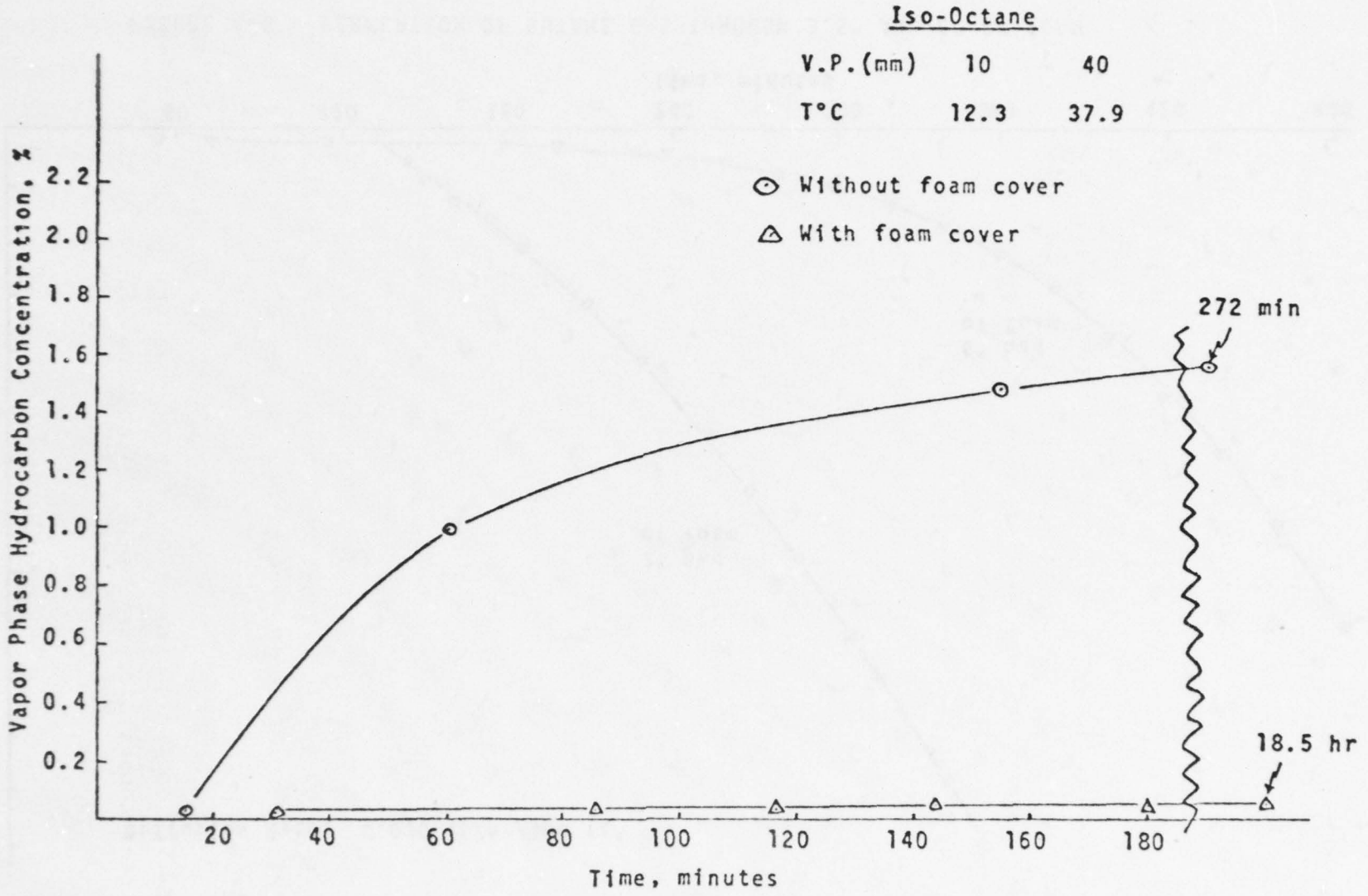


FIGURE A-5 - VAPOR SUPPRESSION OF ISO-OCTANE WITH FOAM

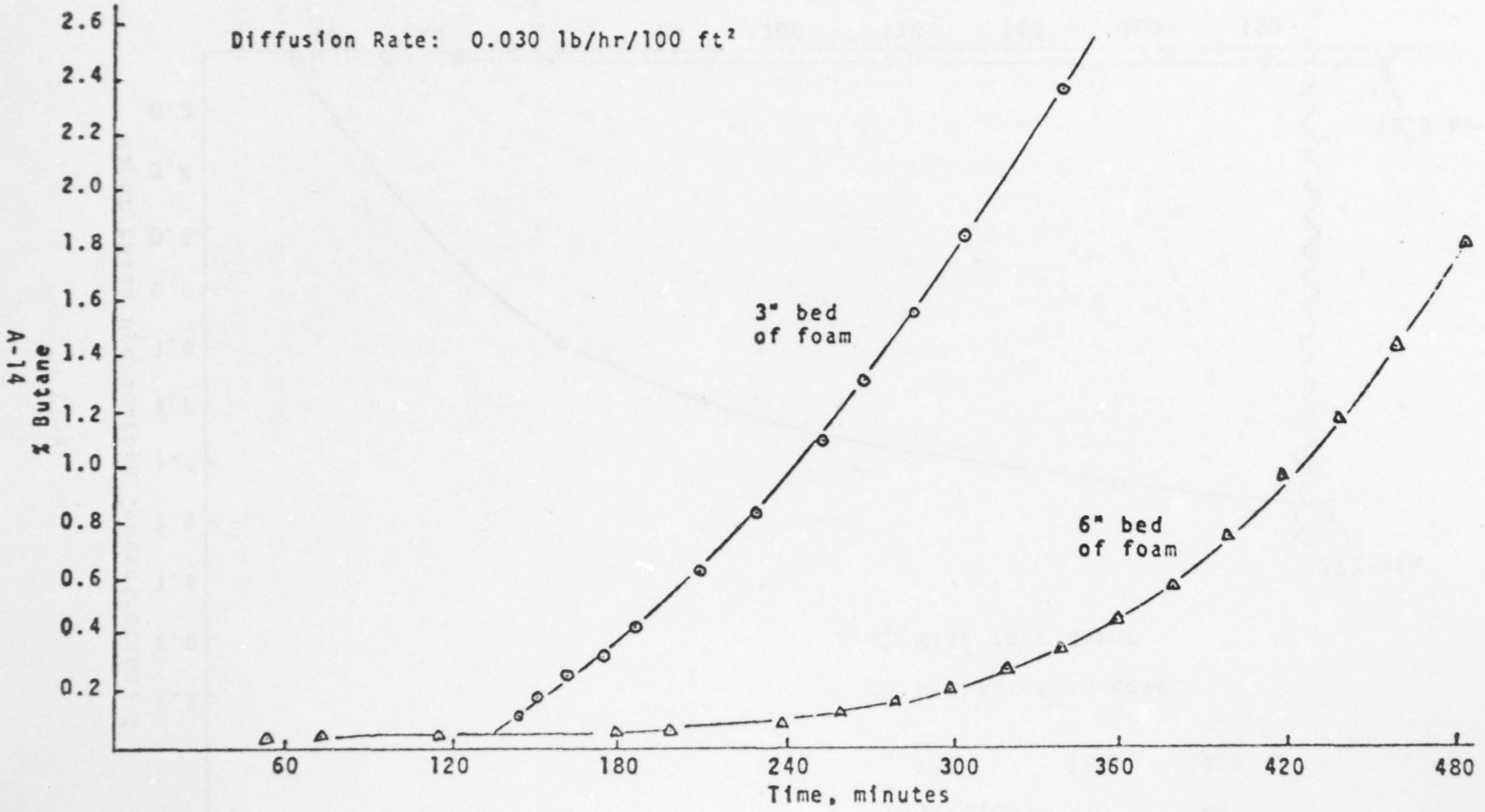


FIGURE A-6 - PERMEATION OF BUTANE GAS THROUGH 3.5" AND 6" OF FOAM

penetrated through the foam barrier and accumulated in a 400 cc (24.4 in^3) void area above the foam. In these runs pure butane gas was bled continuously under the bed of foam. Vapor samples were collected above the foam mass as before.

With about a 7.6 cm (3 in) bed of foam as a barrier, the time to reach an explosive mixture in the enclosed area directly above the foam was about 5 hours. Similarly, the 15.2 cm (6 in.) bed of foam maintained the butane vapor below the explosive range for slightly more than 8 hours.

A rough approximation of both curves show the same general rate of buildup of hazardous vapor. This is most evident at the vapor concentration of about 1% which presumably reflects an apparent equilibrium condition throughout the foam mass. The rate of butane diffusing or entering into the air space above the foam is approximately 1.45 g/m^2hr/(0.03 lb/hr/100 ft^2). As is evident in Figure A-6, once equilibrium is established within the foam mass the amount of escaping butane is independent of the foam height.

The minimum height of foam required to maintain the butane concentration in the void area above the foam at less than 0.2% for periods of time up to 24 hours is predicted by extrapolation of the test data in Figure A-7. For example, a 15.2 cm (6 in.) layer of foam would be effective in limiting the butane vapor above the foam to less than 0.2% for 5 hours.

A particularly vulnerable part of the foam mass is the array of bubbles directly in contact with the liquid. Significant foam breakdown occurred between 1-2 hours after the tank had been completely filled.

Sampling of the interior of specialized foam bubbles by the use of a wetted hypodermic syringe showed maximum vapor control to exist in the array of bubbles directly in contact with a liquid hydrocarbon. After 18 hours of contact with liquid and vapor of isooctane maximum vapor composition at

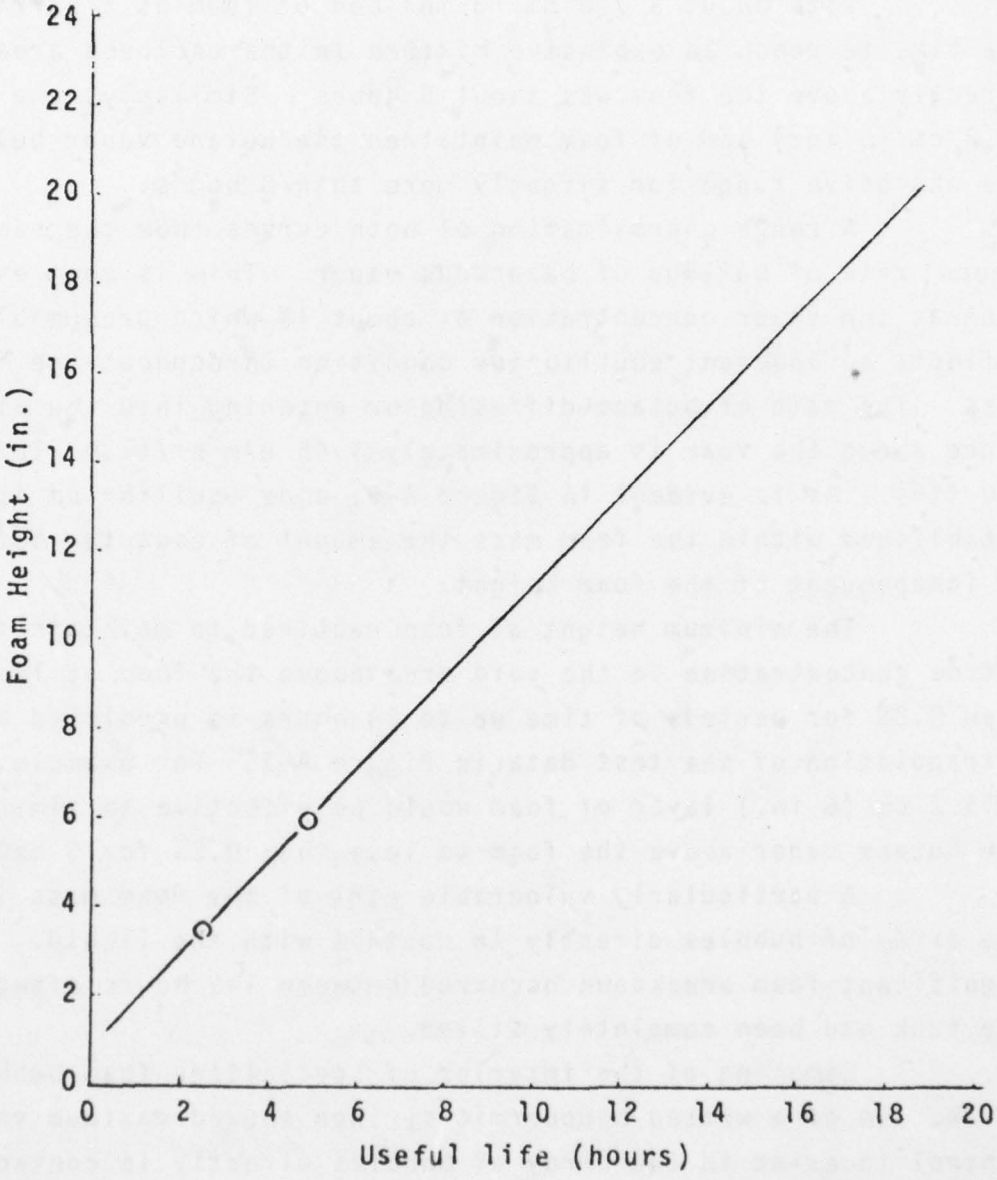


FIGURE A-7 - CRITICAL FOAM HEIGHTS TO LIMIT BUTANE VAPOR TO LESS THAN 0.2%

the interface showed bubble concentration of 0.9 percent vapor versus 0.25 percent for the bulk of the foam mass. Prolonged contact with the liquid isooctane caused foam breakdown at the interface hence not all of the foam was in direct contact with the liquid isooctane during this time interval.

A brief summary of findings show:

1. Most foam formulations could successfully cover aliphatic hydrocarbons, using from 100 to 120% of the calculated foam volume.
2. CO_2-blown foams required approximately 3 times more foam than calculated foam volume requirements. A foam filled with 12% CO_2 and 88% N_2 (simulated flue gas) showed no loss in volume expansion factor.
3. All foams demonstrated erosion or decay at the hexane-foam interface. In non-CO_2 blown foams a permanent arch formed above the hexane which retained a 0.76 m (2.5 ft.) *head of foam.*
4. With CO_2 blown foams there was an obvious tendency of gas pockets to form which mechanically pushed up through the foam cover.

The increased volume of CO_2 filled foam can be attributed to the loss of CO_2 gas through the bubble walls. In these small scale studies large foam surface/volume ratios existed and undoubtedly favored higher losses of CO_2.

The results obtained using 12% CO_2 and 88% N_2 intended to simulate flue gas filled foam showed no anomalous behavior.

APPENDIX B

COMPUTER PROGRAM FOR MATHEMATICAL MODEL OF VAPOR DISPERSION

```
LIST


CDIFF   BASIC-03


1 REM 11/21/75
2 DATA 80, 96, 78.108, 0.0181, 100
4 DIM Q8(20)
5 READ T, V2,M2,U,P3
8 RESTORE
10 PRINT "TEMP",T,"DEG F"
15 LET V1=29.9\LET M1=29
20 PRINT "MOLAR VOLS",V1,V2
25 PRINT "MOLECULAR WEIGHT",M1,M2
30 LET T1=(T+460)/1.8
35 LET D=0.0166*T1*SQR(T1*(1/M1+1/M2))/(V1↑0.333333+V2↑0.333333)↑2
40 PRINT "DIFFUSIVITY", D,"SQ FT/HR"
45 LET R=M1*492/(359*(T+460))
50 PRINT "DENSITY",R,"#/CU FT"
55 PRINT "VISCOSITY",U,"CENTIPOISE"
60 LET U=2.42*U\REM #/HR FT
65 PRINT "VAPOR PRESS",P3,"MM"\LET P0=P3/760
70 LET S1=U/(R*D)\LET S2=S1↑0.166667\REM SCMIDT NUMBER
75 PRINT "AIR VEL MPH"\INPUT V
80 LET V=5280*V\REM FT/HR
85 PRINT "SOURCE LENGTH, WIDTH- FT"\INPUT L, W
90 PRINT "CONC LIM"\INPUT C9
95 LET W=W/2\REM SET UP FOR SUB 1501
100 PRINT "CY, CZ, N TURBULENCE CONS"\INPUT C2,C3,N0
102 PRINT "TIME HRS"\INPUT T1
105 LET C1=C2\LET C2=C2/SQR(2)\REM SET UP FOR SUB 1501
110 LET L8=5E5*U/(V*R)\REM TURBULENCE LIMIT
111 REM CALC Q AT 10 POINTS
112 FOR I=1 TO 10
113 LET X9=L*I/10
114 LET X8=X9-L/10
115 LET Q=0
116 IF L8<X9 THEN 118
117 GO SUB 1600\GO TO 123
118 IF L8>X8 THEN 120
119 GO SUB 1650\GO TO 123
120 LET X9=L8\GO SUB 1600
121 LET X8=L8\LET X9=L*I/10
122 GO SUB 1650
123 LET Q(I)=Q*P0\LET I2=I2+Q(I)
124 NEXT I\PRINT "EVAP RATE",I2*W*2,"CU FT/HR"
125 REM CALC X LIMIT DOWNWIND
126 LET L9=L/10\LET X=L\LET Y=0\LET Z8=0\GO SUB 1500
127 IF C>C9 THEN 128\PRINT "ERROR",C\STOP
128 LET Y7=X\LET C7=C
130 LET X=2*X\LET Y8=X
132 GO SUB 1500
135 IF C>C9 THEN 128
140 LET C8=C
145 FOR I2=1 TO 5
155 GO SUB 1400
160 LET X=Y9\GO SUB 1500
165 IF C=>C9 THEN 175
```

```
170 LET Y8=X\ LET C8=C\GO TO 180
175 LET Y7=X\LET C7=C
180 NEXT I2
185 LET X7=X\PRINT\PRINT "XLIM",X7\PRINT "CONC",C
186 IF X7>L*1.1 THEN 190\PRINT "WARNING: POOL SIZE TOO LARGE"
190 PRINT "X","YMAX","ZMAX","AREA","VOLUME"
192 LET Y6=W\LET Z7=L/10\LET D=(X7-L)/10
195 FOR X=L+0.5*D TO X7 STEP D
200 LET Z8=0\LET Y=0\GO SUB 1500
205 LET C0=C
206 IF C0<C9 THEN 370\REM END
208 REM FIND YMAX
210 LET Y7=Y\LET C7=C
215 LET Y=2*Y+Y6\GO SUB 1500
220 IF C>C9 THEN 210
225 LET Y8=Y\LET C8=C
230 FOR I2=1 TO 5
235 GO SUB 1400
240 LET Y=Y9\GO SUB 1500
245 IF C>C9 THEN 255
250 LET Y8=Y\LET C8=C\GO TO 260
255 LET Y7=Y\LET C7=C
260 NEXT I2
265 GO SUB 1400\LET Y6=Y9\REM MAX Y
270 REM FIN MAX Z\LET Y=0
295 GO SUB 1700\LET Z7=Z8
305 PRINT X,Y6,Z7,
307 WRITE X,Y6,Z7,\LET I9=I9+3
308 LET S2=0
310 REM V1=RUNNING VOL,S1=RUNNING AREA OF BASE, S2=VERT AREA
320 FOR Y=0.05*Y6 TO Y6 STEP 0.1*Y6
322 LET Z8=0\GO SUB 1500\LET C0=C\IF C<C9 THEN 345
325 GO SUB 1700\LET Z7=Z8*1.01
340 LET S2=S2+Z8
345 NEXT Y\LET S2=S2*Y6/5
350 IF X<>L+0.5*D THEN 360
355 LET S1=(W+Y6)*L\LET V1=(1+0.5*W/Y6)*S2*L/3
360 LET S1=S1+2*Y6*D\LET V1=V1+S2*D
365 PRINT S1,V1,
368 WRITE S1,V1\LET I9=I9+2
370 NEXT X
380 PRINT\PRINT "VOLUME",V1
385 PRINT "AREA",S1
388 IF KEY(0)<>0 THEN 388
390 GO SUB 1800\GO TO 380
1300 REM CALC INTEGRAL OVER Y FOR PARTICULAR X,Z8,T
1301 REM C2=CY/SQR(2),N0=1-N/2,W=W/2,C3=CZ
1302 REM A,C1,C2,C3,N0,Q,Q8,V,T,T0,W,X,X0,X2,Y,Z1,Z8,Z9
1303 REM SUB 2000
1305 LET T0=(V*T)↑(N0/2)
1310 LET Q=0
1325 LET X2=C2*T0
1330 LET Z1=(Y-W)/X2\GO SUB 2000
1335 LET Z9=A\LET T0=T0↑2
1340 LET Z1=(Y+W)/X2\GO SUB 2000
1341 LET X2=((Z8/C3)↑2+((X-X0-V*T)/C1)↑2)/T0
1342 IF X2=>100 THEN 1345
1343 LET Q=Q(I)*EXP(-X2)
1345 LET Q8(J)=(A-Z9)*Q/T0
```

```
1355 RETURN
1400 REM CALC TRIAL Y9 FOR CONC C9 WITH LIMITS Y7,Y8
1405 REM C7,C8 CONC FOR Y7,Y8; R2=R↑2
1408 IF C8<>0 THEN 1410
1409 LET Y9=(Y7+Y8)/2\RETURN
1410 LET R2=(Y8↑2-Y7↑2)/LOG(C7/C8)
1415 LET Y9=Y8↑2-R2*LOG(C9/C8)
1420 IF Y9=>Y7↑2 THEN 1428
1425 LET Y9=Y7↑2\GO TO 1430
1428 IF Y9<=Y8↑2 THEN 1430
1429 LET Y9=Y8↑2
1430 LET Y9=0.75*SQR(Y9)+0.125*(Y7+Y8)
1435 RETURN
1450 REM INTEGRATE Q8 FROM I1 TO 20
1451 REM C,I1,J,Q8,T8
1455 FOR J=I1 TO 20
1460 LET C=C+Q8(J)*T8\NEXT J
1465 LET T8=T8/2
1470 LET C=C-(Q8(20)+Q8(I1))*T8
1475 RETURN
1500 REM CONC AT X,Y,Z8 FOR SOURCE FROM TIME 0 TO T1
1501 REM SUB 1300, 1450
1502 REM C,C1,C2,C3,I,I1,J,J1,L9,Q8,Q9,T,T1,T8,X0
1504 LET C=0
1505 FOR I=1 TO 10
1510 LET X0=(I-0.5)*L9
1511 LET T8=T1/20\FOR J=1 TO 20\LET T=J*T8
1512 GO SUB 1300\NEXT J
1513 FOR J1=1 TO 10
1514 LET I1=0\LET Q9=0\FOR J=1 TO 20\IF Q8(J)<=Q9 THEN 1516
1515 LET Q9=Q8(J)\LET I1=J
1516 NEXT J
1518 IF I1=>16 THEN 1532
1520 LET I1=10\GO SUB 1450
1522 FOR J=10 TO 1 STEP -1
1524 LET Q8(2*J)=Q8(J)\NEXT J
1526 FOR J=1 TO 19 STEP 2
1528 LET T=J*T8\GO SUB 1300\NEXT J
1530 NEXT J1
1532 LET I1=0\LET Q8=0\GO SUB 1450
1550 NEXT I
1555 LET C=0.63662*C/(C1*C3)
1558 GO SUB 1800
1560 RETURN
1600 REM Q LAMINAR
1601 REM R=DENS,D=DIFFUSIVITY, S1=SCMIDT NO
1602 REM S2=S1↑(1/6),VAR H,Q,X8,X9,Z9
1603 REM V=U WIND VEL,U=VISC
1605 LET Z9=X9*V*R/U
1610 LET H=0.331*SQR(Z9)*S2↑2
1615 LET Q=Q+2*H*D*(1-SQR(X8/X9))
1620 RETURN
```

```
1650 REM Q TURBULENT
1651 REM H,J,L9,Q,R,S1,S2,U,V,X0,X8,X9,Z9
1655 LET L9=(X9-X8)/10
1660 FOR J=0.5 TO 9.5
1665 LET X0=X8+J*L9
1670 LET Z9=X0*V*R/U
1675 LET H=1.305*Z9↑-0.1*(S1-1)/S2
1680 LET Q=Q+L9*0.0296*V*Z9↑-0.2/(1+H)
1685 NEXT J
1690 RETURN
1700 REM FIND Z HEIGHT
1701 LET C=C0\LET Z8=0
1702 LET Y7=Z8\LET C7=C
1703 LET Z8=2*Z8+Z7\GO SUB 1500
1704 IF C>C9 THEN 1702
1705 LET C8=C\LET Y8=Z8
1708 FOR I2=1 TO 5
1710 GO SUB 1400
1715 LET Z8=Y9\GO SUB 1500
1720 IF C>C9 THEN 1730
1725 LET Y8=Z8\LET C8=C\GO TO 1735
1730 LET Y7=Z8\LET C7=C
1735 NEXT I2
1740 GO SUB 1430
1742 LET Z8=Y9\REM MAX Z
1745 RETURN
1800 IF KEY(0)<>0 THEN 1830
1805 PRINT "***"
1810 RESTORE
1815 FOR I8=1 TO I9
1820 READ A\PRINT A,\NEXT I8
1830 RETURN
2000 REM A=INT FROM - INF TO Z1
2001 REM A,Z,Z1,Z2
2005 LET Z=ABS(Z1)\LET Z2=Z↑2
2010 IF Z>2 THEN 2025
2015 LET A=((9.37006E-4-4.61712E-5*Z2)*Z2-9.52218E-3)*Z2+6.60974E-2
2020 LET A=0.499981+(A*Z2-0.39879)*Z
2022 GO TO 2030
2025 LET A=((2.35498-3.52874/Z2)/Z2-1)/Z2+1
2026 IF Z2<=100 THEN 2028
2027 LET Z2=100
2028 LET A=A*EXP(-Z2/2)/(Z*2.506628275)
2030 LET A=0.5-SGN(Z1)*(A-0.5)
2040 RETURN
2045 END
```

APPENDIX C

HAZARDOUS CHEMICAL SPILL RESPONSE ENGINEERING TECHNOLOGY

Pneumatic Conveying

One means for broadcasting solid and liquid particles over the surface of a chemical spill is pneumatic transport. The basic application involves the acceleration of a volume of gas to entrain particulates. This basic principle has been extended into the design of many pneumatic conveying systems, used for transporting solids and liquids in industry, which is equally useful for transporting spill ameliorants.

Most systems are used for gathering or transporting particulates in a closed system. These range from the common vacuum cleaner to sophisticated systems for loading, unloading, and distributing such products as grain, chips, sand and cement. A few systems are designed for product dispersal involving various broadcasting purposes. These include crop dusting/spraying, forage/snow blowing, mulch-seed-fertilizer spreading, coal mine rock-dusting, abrasive blast cleaning, and other special purposes. The principles involved are readily adaptable for broadcasting assorted particulate spill ameliorants over the range of spill areas.

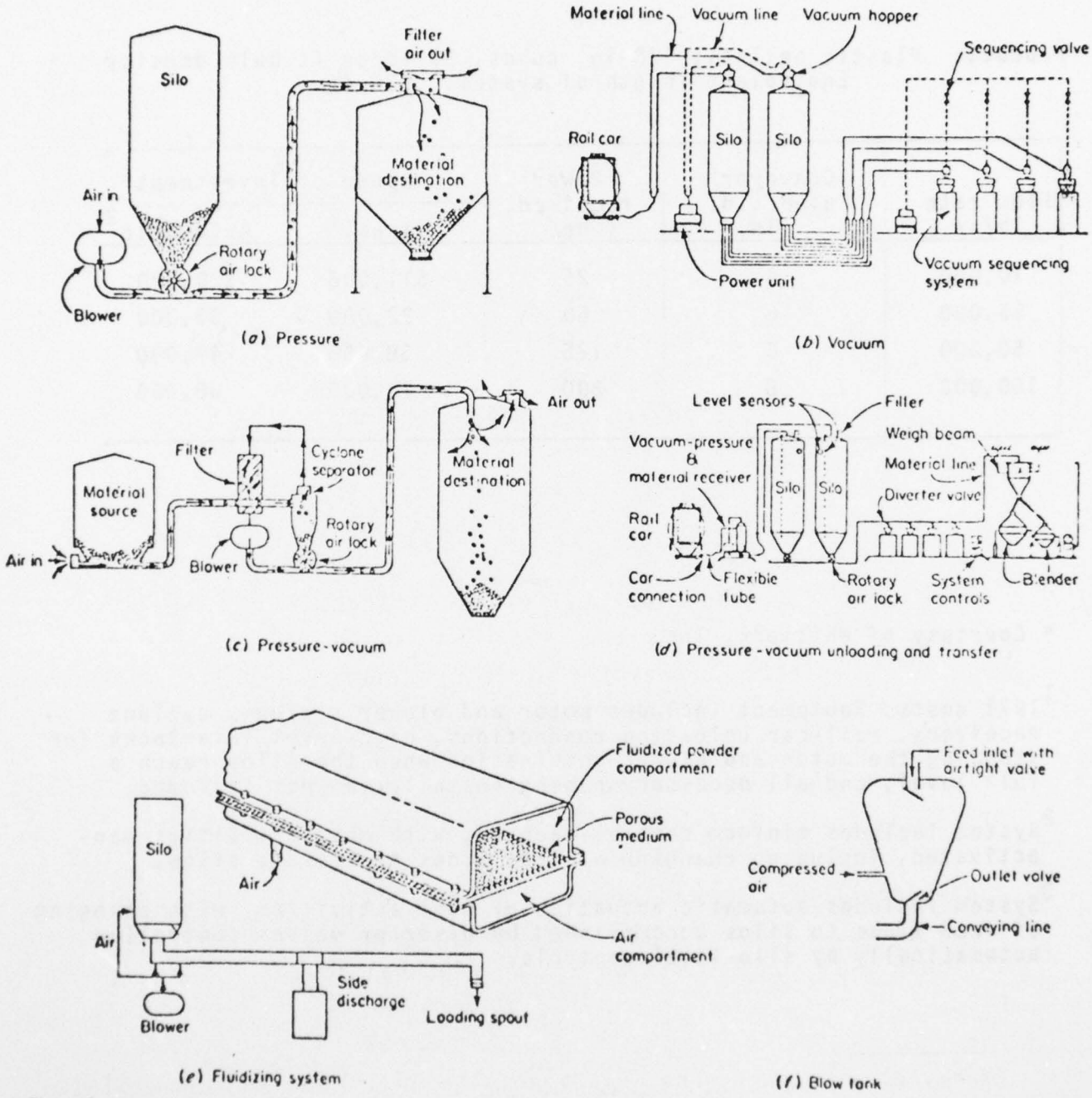
The design of pneumatic systems frequently involves more art than science. Rapid current advances in pneumatic conveying of solids have generated considerable theory and performance data. However, this is generally limited to a few selected materials, with given particle size and related properties, for transport purposes within a certain system. Empirical design formulas for universal application are not available. Special systems, as considered for spill applications, must therefore be individually tailored to the combination of material properties and the objectives of transporting.

Selection of equipment for handling spill ameliorants varies with such factors as:

1. Physical properties and characteristics of the materials
2. Necessity for preserving those properties
3. Quantities to be handled for storage and transport
4. Broadcasting requirements for rate, range and uniform coverage
5. Flexibility for handling assorted material properties
6. Accessory equipment for storage, distribution and control
7. Safety provisions for operation in flammable vapor areas
8. Modifications for shipboard operation
9. Operating requirements for power, utilities, personnel
10. Costs for development, modification, installation, storage, maintenance and operation.

Pneumatic conveyor equipment is commercially available as standard "off-the-shelf" components, or preferably as integrated systems, from several suppliers. Various types of pneumatic systems, indicating some of the components used, are illustrated in Figure C-1. Typical system costs (1971) are illustrated in Table C-1. Preliminary design data and recommendations are readily available (Perry [1973] and Kraus [1968]). This is illustrated for required air velocities in Table C-2, and for sizing a low pressure blower in Figure C-2.

Perry, et al., Chem. Eng. Handbook, 4th Ed., 1963, 5th Ed. 1973.
Kraus, N.B., Pneumatic Conveying of Bulk Materials, 1968.



Types of air-conveying systems. (*a*) Pressure. (*b*) Vacuum. (*c*) Pressure-vacuum. (*d*) Pressure-vacuum unloading and transfer. hitlock, Inc.) (*e*) Fluidizing system. (*Fuller Co.*) (*f*) Blow tank.

FIGURE C-1 - TYPICAL PNEUMATIC CONVEYOR SYSTEMS

TABLE C-1 - APPROXIMATE PNEUMATIC CONVEYER COSTS*

Product: Plastic pellets, 1/8-in. cubes, 30 lb/cu ft bulk density
Equivalent length of system: 600 ft

Flow rate lb/hr	Conveyor pipe i.d. in.	Power required hp.	Range of Investment[1]	
			Manual[2]	Automatic[3]
10,000	4	25	$11,000	$20,000
25,000	6	60	22,000	33,000
50,000	6	125	38,000	49,000
100,000	8	200	77,000	88,000

* Courtesy of Whitlock, Inc.

[1] 1971 costs. Equipment includes motor and blower package, cyclone receivers, rail-car unloading connections, high-level interlocks for stopping the motor and blower combination when the silos reach a full level, and all necessary piping installation not included.

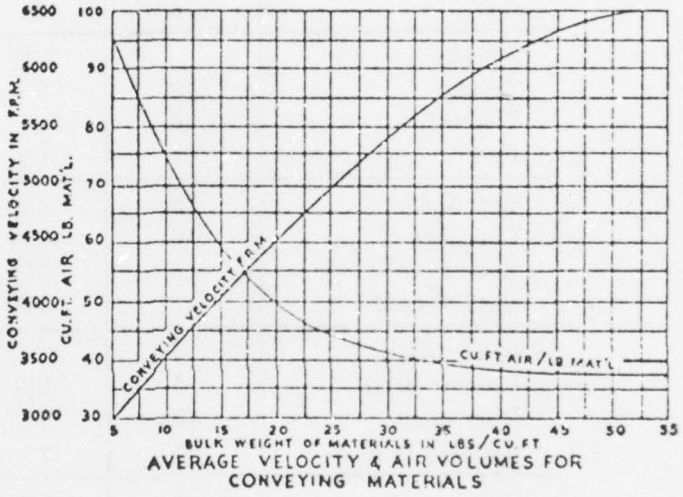
[2] System includes minimum control package, with most activities man-activated, including changing of feed lines to storage silos.

[3] System includes automatic actuation of most activities, with changing of feed lines to silos accomplished by diverter valves controlled automatically by silo-level controls.

TABLE C-2 - SUCTION REQUIRED FOR PICK UP*

MATERIAL	Approx. Weight per Cu. Ft. Lbs.	Suction to Pick up, Inches of Water
Ashes, coal	30	3
Barley	38	3½
Beans	28	4
Bran	16	2
Buffing		2½
Cement	100	5
Cinders	46	4
Cork	14	1½
Corn Cobs	25	2½
Corn, ear	56	4½
Corn meal	40	3½
Corn, shelled	45	3½
Cotton (Dry)	5	2
Feathers (Dry)	5	1½
Fruit, dried	30	3
Grinding Dust	30	2
Hair	5	1½
Lime, hydrated	30	3
Malt	35	3
Mineral wool	12	2
Paper cuttings	20	3
Rags, dry	30	2½
Sand	105	5
Sawdust (Dry)	12	2½
Shavings, light	9	2½
Shavings, heavy	24	3
Tan bark	20	2½
Wheat	46	4
Wool (Dry)	5	2

*Courtesy of Cincinnati Fan & Ventilator Company



AVERAGE VELOCITY & AIR VOLUMES FOR CONVEYING MATERIALS

FIGURE C-2 - CONVEYING VELOCITIES *

*Courtesy of Cincinnati Fan & Ventilator Company

Feasibility evaluations in this survey are based largely on analagous use of existing systems, components and available data for similar service. This preliminary approach is taken to indicate likely problem solutions, without attempting to yield a firm design criteria for any particular system. Final systems selected should be detailed by knowledgeable personnel, experienced in this field. Actual experimentation is normally involved to verify physical properties and system characteristics, followed by pilot-plant tests and finally, judicious scale-up including accessory features for the actual application.

Low Pressure Blowers

Low pressure type blowers, operating at less than 1 psi, are the main component of most simple pneumatic conveying systems. These blowers generally utilize self-cleaning radial blade fans for conveying particulates.

Preliminary blower sizing for a particular system is illustrated in Figure C-2. Typical small blowers, available from stock, are described in Table C-3. They are relatively inexpensive ($100-$1000 complete w/motor) in moderate capacities (500-5000 cfm) and at low static pressures (5-15 inches Water Column). Larger blowers are available on special order, or from stock, when commonly used in special applications.

Snow Blowers

Snow blowers represent one common application which could be modified for handling spill ameliorants. They are available in a variety of commercial stock types.

The small home style thrower has a range of 4-40 ft. with snow conditions ranging from slush to very dry. They normally use a 6-8 HP gasoline engine, in a 30 ft^3 x 260 lb assembly, selling for $500-$600.

Higher capacity machines for highway use are described in Table C-4. They have been used for handling sawdust. How-

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FEASIBILITY STUDY OF RESPONSE TECHNIQUES FOR DISCHARGES OF HAZA--ETC(U)
OCT 76 J S GREER DOT-CG-51870-A
UNCLASSIFIED MSAR-76-125 USCG-D-56-77 NL

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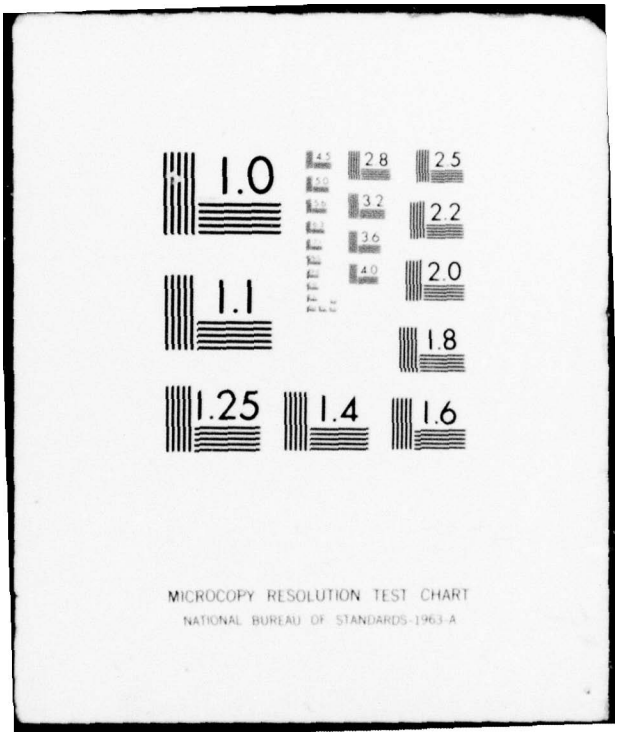

1.0
1.1
1.25
1.4
1.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE C-3 - BLOWERS, SMALL RADIAL BLADE
FOR CONVEYING GRAIN, SAWDUST, PARTICLES
(W.W. Grainger, 1976 Stock)

Rating	CFM	510	937	1480	3050	5600
	System pressure inches water	5	5	10	10	10
Power Reqd., HP		1	2	5	10	20
Fan	Speed, RPM	3450	3450	2811	2445	2250
	Diam, inches	10.6	12.5	15.6	19.1	22.6
Size: Height, Width, Depth inches		18 x 21 x 16	19 x 21 x 18	31 x 36 x 24	36 x 38 x 29	39 x 40 x 34
Weight, lbs.	Blower only	26	36	200	245	385
	Blower w/ motor (& drive)	52	70	(326)	(408)	(656)
Cost, $	Blower only	66	94	430	509	597
	w/Motor & Drive (230V, 3ϕ)	117	187	591	749	961

TABLE C-4 - SNOW THROWERS*, LARGE FOR UTILITY VEHICLE, TRACTOR, LOADER MOUNTING

Model	R-300-76	RHS-300-76	RHS-500-76
Capacity, Tons/hr Snow @ 5-40#/CF	300	300	500
Range, feet to max deposition	40	10-60	40-60
Engine, Horsepower Gasoline, 4-Cyl	30	37	60
Snow Cut, Size & Rate w/2-Stage System	60" Wide x 32" Deep to 15 MPH, using 26" ϕ Helical Cutter and 26" ϕ Blower Fan, through 9" ϕ x 7'H Chute w/270° rotation		
Size, OA approx, feet	5 Wide x 4.5 long x 9.5 high w/chute		
Weight, lbs	1420	1620	2500
Cost, $	5,620	7,260	13,725

*Courtesy of American Snowblast Corp.

ever, the specialized helical feed cutter and road provisions at relatively high costs limit their application for applying spill ameliorants at sea.

Other specialized snow blowers include those used for cleaning railroad tracks by dispersing the snow with a high velocity air blast.

Forage Blowers

Forage blowers, as used for farm service, could also be utilized for handling spill ameliorants. Typical forage blowers, available from stock, are described in Table C-5. These are large radial fan blowers, specially fitted for filling farm silos.

Capacity, range and horsepower required are affected by several factors: type of crop, moisture content, particle size, PTO speed, condition of blower pipes used, or wind conditions for free discharge. Capacity is frequently limited by the external feed supply system used.

Special modifications have been tested by Kool Brothers. Free discharge was tried with apple cores and paper cups, indicating most ameliorants can be broadcast over a 15-30.5 m (50 ft-100 ft) range. Blowers have been fitted with 60-80 HP electric motors, indicating that integral power sources are also feasible.

Mulch Spreaders

Mulch spreaders provide an integrated system, designed for radial fan blower systems, commercially available for broadcasting a wide range of materials. (Data on broadcasting various adsorbents is currently being accumulated).

Commercial use of mulch spreaders includes seeding, mulching, fertilizing, misting and combinations of these operations, restoring vegetation and minimizing erosion of landscapes.

TABLE C-5 - FORAGE BLOWERS

MODEL*						
	International Harvester	IH-48	---	IH-56	---	---
	Kool Bros.	(KB-30)	KB-54	---	KB-60	KB-1000
CAPACITY Tons/hr	Haylage	50	70	70	100	100
	Corn Silage	70	100	100	150	150
RANGE Feet	Vert Ducted	100	100	>100	>100	120
	Est Free	50	50	75	80	100
HORSEPOWER Req'd		35	50	50	70	90
FAN	Rotation, RPM	540	540	540	540	1000
	Tip Speed, MPH	77	86	90	96	142
	Diam., inches	48	54	56	60	48
	No. of Blades	4	6	6	6	6
SIZE OA Approx. Feet	Length	7	7	7	7.8	7.2
	Width	5.5	5.8	6	6.2	5.7
	Height	5	5.3	5.5	7.2	4.6
WEIGHT, lb		790	900	950	1320	970
COST, $		1050	1290	1325	1665	1345

*Standard Assemblies include:

Feed Hopper(10 CF) fitted w/auger for fan injection;
Liquid injection nozzle on fan housing;
Discharge Nozzle, 9" ϕ, 180° adjustable, quick inspection opening;
Towing provisions include hitch & 2-wheels (4.00-8);
Direct PTO drive line for external tractor power source.

Common mulching materials are hay or straw, but a variety of materials, ranging from leaves through wood chips, can be handled. These can be conveyed over 61 m (200 ft) at application rates of up to 15 tons/hr. A comprehensive description of typical mulch spreaders is presented in Table C-6.

The mulch spreader is similar to the forage blower (Table C-5) in using a high velocity radial fan blower. It has been further developed, through modifications for both solid and liquid feeding units, for using a controlled discharge nozzle and generating mists. These systems can also be made independent by incorporating a gasoline or diesel engine.

Mulch spreaders have been undergoing tests and modifications for marine operation for some time. A complete system requires a separate storage or material transfer unit to feed the blower. Experimental applications were done at the Santa Barbara oil spill and have been continued by interested parties such as Finn Equipment Company and ACME Products Company in cooperation with the Coast Guard.

Abrasive Blasters

Abrasive (sand) blasters represent completely integrated, high pressure pneumatic conveying systems. They are specially designed for delivering a high velocity (MACH 3) jet of air containing fine abrasive particles for cleaning a surface.

Venturi fed blasters have been checked by Michalovic et al.(1976) for broadcasting "Universal Gelling Agent". Satisfactory performance was found to include a rate of 1.6 Kg/min (3.5 lb/min) and a 6 m (20 ft) dispersion range. The blaster

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Michalovic, J., Akers, C.K., Baier, R.E., and Pilie, R.J., "Optimization of Universal Gelling Agent", p. 259 Proceedings of 1976 National Conference on Control of Hazardous Material Spills, New Orleans, La. (April, 1976).

TABLE C-6

MULCH SPREADERS

Model		(small) Bantam	(medium) Apache	(large) Eagle
Capacity*, Hay, Tons/hr		3	8	15
Range*, feet		40-55	65-75	85
Engine Horsepower	Gasoline	30	69	110
	Diesel	--	70	104
Blower Air Blast, MPH		150	175	175
Size, feet:	Length	11.5	13.7	14.5
	Width	5	6.9	7.5
	Heighth	7.5	9	10
Weight, lb		1650	4200	5200
Cost, $	w/Gas Engine	3890	7400	9295
	w/Diesel Engine	--	8050	10575

Standard features include:
- Discharge Spout, 8" diameter w/355° swivel & 70° vertical;
- Adhesive Spray System w/pump (8.5/24 GPM), HX, piping, nozzles;
- Feed Chute (manual/power) to beater & blower inlet;
- Operator access & control stations;
- Trailer mounting w/wheels, hitch, lights, accessories.

Optional Features Available:
- Adhesive trailer tank (600 gal) for towing behind mulch spreader;
- Higher (50 GPM) Adhesive Spray System;
- Misting Nozzles for tree misting applications;
- Discharge Extensions 8" ϕ x 50' long lay-flat sections, increasing range for Eagle as follows:

Extension	Discharge Range, feet	
	From Nozzle	Total from Spreader
None	85	85
1st 50'	60	110
2nd 50'	40	140
3rd 50'	15	165

*Capacity & Range vary with wind conditions (assumed 0) and with type of mulch being spread. For the Eagle, typical range w/various materials is:

Hay	Straw Sawdust	Feathers	Wood Chips	Mist
85'	75-90'	80'	250'	210'

**Courtesy of Finn Equipment Company
R Keyes & D Sharp Telecons w/MSA

tested by Calspan is no longer made by Clipper Mfg. Similar blasters, made by Empire, sell in the range of $100-$200. The air supply for such a system constitutes its largest cost. An Ingersoll-Rand G-85 (85 cfm at 100 psi) gasoline driven (41 or 48 HP) compressor sells for $5950, increasing system cost to just over $6000.

Pressurized tank type blasters are commonly used for larger production service. Typical systems of this type are described in Table C-7. Higher efficiency (~3 x sand/air delivery) is achieved, since there is no work loss requirement for vacuum injection of sand feed as for the Venturi-fed blasters. Higher (~10X) sand delivery rates for the same nozzle size are similarly achieved. Total abrasive delivery rate is further increased by use of multiple nozzles on the larger tanks. Automatic tank refill systems from storage have been similarly furnished at costs comparable to those for the basic sandblasters. Cost of the supporting air compressors again constitutes the largest cost of these complete systems.

Performance of spill ameliorants with sand blast equipment will depend upon such factors as:

Compatibility:	with compressed air, handling, humidity, oil, temperature, and other system factors
Particulate size:	≤1/2 nozzle size, to minimize plugging, and at lower delivery rates for larger sizes.
Bulk density:	Affects storage capacity by weight and broadcast range. Expelled at MACH-3 velocities, sand is expected to reach 50 ft distant, while lighter particulates will fall correspondingly closer, exclusive of existing wind effects.

TABLE C-7 - ABRASIVE BLASTERS***

PRESSURIZED TANK TYPE PRODUCTION SYSTEMS

Model* (Empire)		KX-59B	DX-61A	XL-300
Storage Capacity (125 psi Tanks)	Sand, lbs	650	1050	10000
	Vol, CF	6.5	10.5	100
Usage Rates**	Sand lbs/hr	1015	1440	2880
	Sand lbs/min	17	24	48
	Air @ 100 psi, CFM	137	196	392
	Nozzles, No. x Size	1x5/16"	1x3/8"	2x3/8"
Size, OA Approx. Feet	Length	2	2.5	11.6
	Width	3	3.5	7.4
	Height	4.5	5	8.5
Weight,	lbs	370	710	3575
Cost,	$	985	1735	6878

*Portable models are complete for operation when supplied with air and abrasive. Standard features include: ASME Tank mounted on wheels & complete with integral air piping, controls, moisture separator, exhaust silencer, abrasive control regulator, 50 ft of hose terminating with proper discharge nozzle, & operator safety equipment. The XL-300 is trailer mounted for highway transport and further equipped with dual nozzles and controls for 2-man operation. Optional features include skid mounting, larger tanks, additional blast nozzles & controls, automatic abrasive refill systems for tanks, & other special features.

**SAND & AIR CONSUMPTION/NOZZLE
@ 100 psig air supply & typical compressor costs

Nozzle, inches bore size		1/8	3/16	1/4	5/16	3/8	7/16	1/2
Sand Used	lb/hr	154	330	618	1015	1440	1980	2530
	lb/min	2.6	5.5	10.3	17	24	33	42
Air Reqd, CFM		20	45	81	137	196	254	338
Compressor Cost $ (Diesel Typical @ +25% Capacity)		3000		8000		16000		26000

*** Courtesy of Empire Abrasive Equipment Corporation
W. Deer Telecon w/MSA

Portable Power Sources

Portable power sources for driving blowers, pumps and related equipment for spill response work are limited primarily to internal combustion engines. These are used directly or through intermediate electrical, hydraulic or pneumatic transfer systems, as dictated by safety requirements.

Gasoline engines present the most versatile, compact and economical primary power source, where explosion resistance is not required. The small lightweight versions range from 2-16 HP, at a cost of $90-$400 (Briggs). Larger automotive types are also "off-the-shelf" items. They normally range from <50 to >300 HP, and cost from <$1000 to >$4000.

Diesel engines have the inherent advantage of increased explosion resistance, especially when equipped with water cooled exhaust systems. While overall performance is economical, higher initial costs and heavier weights are disadvantages, especially in the smaller (15-150 HP) sizes. Typical small to medium size diesel engine data is presented in Table C-8. Larger versions to 800 HP are available for portable service.

Tractors with power takeoffs (PTO) are normally used to drive forage blowers, since these are common farm implements. Common tractors stocked, ranged from 35-50-100 HP and cost $7,300-$11,000-$17,000 in diesel models. Comparable gasoline versions are slightly (5-10%) less. Unless ready availability or the added versatility of such tractors become factors in spill response systems, their added weight and cost would not be justified.

TABLE C-8 - DIESEL ENGINE DATA, TYPICAL

SUPPLIER		PETTER DIESEL			CUMMINSENGINE CO.	
Model		4:197PJ	PJ4W	PJ4M	V-504-M	V8-300M
Type		Air Cooled	Water Cooled	Marine	Marine	Marine
Rating	HP	45	45	45	210	300
	@RPM	2000	2000	2000	3300	3000
Cylinders	No.	4	4	4	8	8
	ci	198	198	198	504	785
Size, cu ft		36	36	37	38	47
Weight, lbs		1027	960	1525	1700	2512
Cost, $ (w/std Acc)		3730	4000	5000	8000	10000

Electric motors are the most versatile, compact and economical intermediate power source available, particularly when strict "explosion-proof" requirements exist. Typical electric motor costs are presented in Table C-9. Use of electric motors is most desirable when electrical power is readily available from existing supplies. Their desirability decreases when power generation becomes part of the spill response system.

Portable engine-generator units are available from stock in small sizes, while 2-6 months delivery time may be required for larger or special models. Sizes commonly range from 1-170 KW for gasoline models and 5-2500 KW with diesels. System weights average 22.7 kg/KW (50 lbs/KW) with costs nominally $150/KW. Diesel units are generally heavier, bulkier, and more costly, particularly in the smaller (5-25 KW) sizes.

Hydraulic or pneumatic motors similarly afford "explosion-resistant" features for a flammable liquid spill system. When remote engine-pump and hydraulic services are included, these systems are generally more limited, complex, and costly than comparable electric systems.

Rockdusters

Rockdusters represent completely integrated medium pressure pneumatic conveying systems, specially designed for coal mine service, to broadcast limestone dust (<74 μ, <200 mesh, 80#/CF), in order to minimize explosion hazards. The dust is fluidized at a high solids/air ratio, conveyed through lines which may exceed 1-kilometer (3280 ft) in length, and expelled from nozzles with an approximate free range of 1.5 to 6.1 m (5-20 ft). Typical rockduster units are described in Tables C-10 and C-11. These units normally require one or two operators when used in mines.

TABLE C-9 - ELECTRIC MOTOR COSTS, TYPICAL

SUPPLIER	W W GRAINGER, 1976 STOCK								L. ALLIS 1975
Horsepower 3 ϕ, 240 V	1	2	5	10	20	30	40	50	100
Drip Proof	72	87	102	180	302	419	526	637	1325
Enclosed Fan Cooled	84	102	132	215	364	520	694	883	2170
Explosion Proof	180	197	302	353	500	770	1030	1250	2530

TABLE C-10 - ROCKDUSTERS**

Mechanical Feed (Venture/Auger) Units*

MODEL				Trickle-Duster Wheel	Bantam-400 Skid	CSC Skid	SAS Wheel
	Mounting						
STORAGE CAPACITY (Atmos.)	Dust,		lb	1,000	160	3,500	34,000
	Volume,		CF	. 12	2	47.5	425
USAGE RATE	Dust,		lb/min	5-.5	100-20	230-50	300-50
	Hose	Length	ft	15-50	20-200	12.5-500	25-500
		Diam.	in	1.5	2	2.5	2.5
AIR SUPPLIED	Volume,		CFM	40	65	40 & 160	100 & 160
	Pressure,		psi	3	10	2 & 12	2 & 12
	Motor,		HP	1	5	15	30
DIMENSIONS	Length,		ft	7	6.4	12	26.9
	Width,		ft	3.5	1.5	3.1	7
	Height,		ft	3.7	2.3	2.5	5
WEIGHT			lb	775	700	5,000	12,000
COST			$	4,000	5,000	13,000	25,000

*Units described are complete for operation when supplied with dust and power (460V A-C). All system components, piping, wiring, and controls are furnished complete with up to 100' hose.

Optional features include special size & dimensions for feed storage hoppers, multiple dust nozzles, high volume transfer provisions, motor drive variations (electric hydraulic, pneumatic, engine), wheel or skid mounting, Accessory hose, fittings, etc.

**Courtesy of Mine Safety Appliances Company

TABLE C-11 - ROCKDUSTERS**

Pressurized-Tank Feed, Skid-Mounted Units*

SIZE, Tank Diam., (65 psig WP, ASME)			in	30	45	60
STORAGE CAPACITY	Dust,		lb	3,040	6,720	14,880
	Volume,		CF	38	84	186
USAGE RATE	Duct,		lb/min	350-50	470-80	600-120
	HOSE	Length	ft	250-2000	250-4000	250-4000
		Diam.	in	2	2.5	3
AIR SUPPLIED	Volume		CFM	100	134	220
	Pressure,		psi	34	32	39
	Motor,		HP	15	20	40
DIMENSIONS	Length,		ft	16	18	15.4
	Width,		ft	5	6	6
	Height,		ft	2.6	4.3	5.3
WEIGHT,			lb	3,800	5,000	7,700
COST,			$	13,000	15,000	20,000

*Units described are complete for operation when supplied with dust and power (460V AC). All system components, piping, wiring, and controls are furnished complete with 100' hose.

Optional features include special size & dimensions for tanks, multiple duct nozzles, motor drive variations (electric, hydraulic, pneumatic, engine), wheel mounting, accessory hose, fittings, etc.

**Courtesy of Mine Safety Appliances Company

MSA rockdusters have been tested and recommended for dispersing Universal Gelling Agent (UGA) by Calspan. The Bantam-400 (an auger-feed type Rockduster, Table C-10) was used with 30.5 m (100 ft) of hose to broadcast powdered (<.5mm) UGA. It was controlled to deliver 3.6 Kg/min (8 lbs/min), covering 6.1 m x 6.1 m (20 ft x 20 ft) target area, with less than 20% loss due to wind effect. Pressurized-tank-feed type rockdusters (Table C-11) were suggested as potential applicators involving higher capacity, rate and distance factors. They were assumed to handle larger particle sizes than CO_2 fire extinguishers (limited to 1 mm), however. Water condensate and other compressed air effects should receive prior test evaluation.

Conveying rates vary inversely with hose length and directly with hose area, at a given air supply. Rates for mechanically-fed Rockdusters (Table C-10) vary from 2.3 Kg/min (5 lb/min) for the smallest venturi-fed Trickle Duster to 136 Kg/min (300 lb/min) for the largest auger-fed SAS model. The latter can be used either without hose or as a bulk carrier to transfer dust at 545 Kg/min (1200 lb/min) through 4.8 m (15 ft) of 8.9 cm (3.5 in) hose. Highest transfer capacities are generally available from the pressurized-tank fed rockdusters (Table C-11). These vary normally from 159 to 272 kg/min (350 to >600 lb/min) depending upon the air supply; they can be prepressurized for almost instantaneous discharge. Larger systems can be furnished to handle continuously up to 9×10^4 Kg/hr (100 tons/hr) using 61 m (200 ft) of 12.7cm (5 in) hose, which is the maximum size that can be conveniently controlled manually at high pressures. Use of multiple nozzles can increase capacity.

Dust supply and replenishment become the limiting factors at all high usage rates. Large system tanks or hoppers can be provided within limits. These can be arranged for automatic refill from similar slave tanks or larger storage bins, commonly available up to 3.5×10^5 Kg (400 tons). Portable storage includes trailer trucks (2.7×10^4 Kg or 30 tons), railroad cars (4.5×10^4 Kg or 50 tons) and barges or ships (9×10^6 Kg or 10^4 tons).

Dispersion range from the hose nozzle is normally 1.6 to 6.1 m (5-20 ft) with dust. This would vary with other particulates dependent upon such factors as particle size, density, and aerodynamic properties. Sand would be expected to reach a dispersion range of 15 m (50 ft) using short hoses with increased pressure. Use of booms to position nozzles, together with existing or induced wind effects, can further aid in obtaining increased broadcasting range to cover most spill areas.

Particulate size ranges that can be handled by standard Rockdusters have not been comprehensively tested. Limestone dust (<74 μ, 200 mesh) size, which is the design basis, should present no problems for similarly size particulates. UGA powder (<.5 mm) was successfully tested by Calspan in the auger-fed Bantam-400. Some tests have been made by MSA using salt, ammonium nitrate and similar materials in the 3 to 6 mm (1.8-1/4 in.) size. Some particle degradation occurred, as a result of the high-speed auger-feed systems. Rotary air locks or interlocking gate-type feeders may be used for larger particles. Similar pneumatic systems will handle particles up to one-third the line size. Test evaluation of the pneumatic systems would be necessary to assure adequate design performance, prior to actual use.

Hydraulic Equipment

The basic unit for hydraulic systems is the pump, used to pressurize and transport the fluid, as well as supply a safe power source to power some of the foam generators. Hydraulic pumps are manufactured in many sizes and for many different applications. A few examples for use in spill response systems, and a general description of their operating characteristics, are presented in Table C-12.

Table C-12 - Hydraulic Pumps

Manufacturer	Model	Dimensions (in.)	Power	Flow Capacity (gal/min)	Weight (lb)	Price
Worthington Corporation	D1011	15x58x25	Elec.	500	1000	$1460
Marlow Pumps	4E1A	30x78x57	Gasoline	500	1250	$5820

A typical eductor unit is manufactured by Rockwood Systems Corporation. A type 2-1/2 FWB eductor, with pickup hose and metering equipment, which would be applicable for spill response systems, would cost approximately $250. A proportioning unit, which would increase the flexibility of the metering system, is also available from several suppliers. A typical unit, sized for this type of application, is available from Fire Control Engineering Co. for approximately $3500.

Aqueous Film Forming Foam Premix Units

Several companies manufacture standard sizes of tanks for premixing and holding aqueous film forming foam solutions. Several units, typical of the type required for hazardous chemical spill response systems, are presented in Table C-13.

Table C-13 - Aqueous Film Forming Foam Premix Units

Manufacturer	Model	Dimensions (in.)	Weight (lb)	Capacity (gal)	Price
Fire Control Engineering Co. or "Fire Boss"	LTW100N	36 x 48 x 63	2000	100	~$5000
	LTW250N	52 x 70 x 74	4800	250	~$7500

Foam Generators

There are some differences among foam generators which reflect the type of foam formulation used. Mechanical agitation is sufficient to form low expansion foams and those using the aqueous film forming surfactants. High expansion foams are generated by impacting a liquid spray against a screen or by using controlled orifices. Some examples of foam generating equipment are presented in Table C-14. A summary of high expansion foams and equipment costs are given in Table C-15.

Table C-14 - Typical Foam Generating Equipment

Manufacturer	Model	Operating Pressure (psig)	Dimensions (in.)	Weight (lb)	Foam Capacity (ft^3/min)	Price ($)
Low Expansion						
Rockwood Engineering, Inc.	DM-FFF	100		67	500	1,077
Rockwood Engineering, Inc.	LWP-500	150		75	500	1,100
High Expansion						
Mine Safety Appliances Co.	Mini-X	80-100	12 dia x 12	14	750	400
Rockwood Engineering, Inc.	S Jet-X	50-250	15 dia x 54	10	1,000	295
Mine Safety Appliances Co.	3000	150	19 dia x 35	15	2,800	1,300
Mine Safety Appliances Co.	6000	100	36 dia x 60	225	6,000	2,700
Rockwood Engineering, Inc.	Jet-X-2	30-120	22 dia x 25	48	2,000	650
Walter Kidde and Co, Inc.	WD-150	70	66 dia x 55	550	15,000	23,000
Walter Kidde and Co, Inc.	PI-135A	Electric Pump	58 dia x 102	1160	13,500	26,000

TABLE C-15

EQUIPMENT COSTS NOT INCLUDING THAT
TO PRODUCE OR CONTROL REQUIRED PRESSURE

HIGH EXPANSION FOAM GENERATORS

1. Electric Powered - Give 600 to 800:1 Expansion for 500 to 50,000 cfm

   Cost about $0.50 per cfm delivered

   Need 8 gpm for each 500 cfm at 40 psig

   Power required:

   1/4 HP for 500
   1 HP for 5,000
   3 HP for 10,000
   5 HP for 25,000
   8 HP for 50,000

2. Water Powered - Give 200 to 500:1 Expansion for 100 to 25,000 cfm

   Cost about $0.50 per cfm delivered

   Need 8 gpm for each 500 cfm at 60 to 80 psig

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