MODIFICATION OF SPILL FACTORS AFFECTING AIR POLLUTION,

Vol. I - An Evaluation of Cooling as a Vapor Mitigation Procedure for Spilled Volatile Chemicals

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report addresses the evaluation of cooling as a mechanism of reducing the release of toxic or flammable vapors from a spilled chemical. The results show the capabilities of a variety of coolants and demonstrate that dry ice is the best choice for most situations.

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ABSTRACT

Spilled chemicals that pose a hazard to the land and water ecosystem can also provide a significant vapor hazard. Although the vapors released by such chemicals may ultimately be dispersed in the environment with little long-term effects, they do pose a hazard to life and property downwind of the spill.

Among the vapor amelioration techniques that have been considered is the use of a coolant to lower the temperature of a spill and reduce its equilibrium vapor pressure. This program has been conducted as a feasibility study of that mechanism.

Four potential coolants were examined: water ice, dry ice, liquid carbon dioxide, and liquid nitrogen. Further evaluation based on laboratory studies and limited scaled-up tests established dry ice as the most versatile coolant choice.

Water ice does not cool sufficiently. Liquid nitrogen and carbon dioxide require large quantities of material, and produce a dense obscuring cloud that has some adverse implications.

Dry ice avoids the problems presented by the other coolants and is readily available at a reasonable cost, but a method is required for crushing and distributing the dry ice to the spill. A prototype unit was developed consisting of a crusher and a pneumatic conveyor to perform these functions.

A pool of diethyl ether with 2.23 m² (250 sq ft) of surface was cooled to -60°C (-76°F) using 408 kg (900 lb) of dry ice fed at a rate of 13.6 kg (30 lb) per minute. A measurable reduction in downwind vapor concentration was realized. Pool temperature was still below -10°C (14°F) two hours after dry ice discharge was terminated.

This program has established feasibility of the mechanism, but additional work is necessary to establish practicality, define materials to which cooling is applicable, and optimize the dispensing equipment.

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ABBREVIATIONS AND SYMBOLS

A	--	experimentally fitted constant (not dimensionless)
B.P.	--	boiling point
BTU	--	british thermal unit
^{o}C	--	degrees centigrade
c	--	concentration
cal	--	calories
cm	--	centimeter
D	--	diffusion coefficient
E	--	evaporation rate
F	--	film thickness
^{o}F	--	degrees Fahrenheit
ft	--	feet
g	--	gram
hr	--	hour
Hg	--	mercury
HP	--	horsepower
in.	--	inch
Kcal	--	kilocalories
Km	--	kilometer
K_m	--	mass transfer coefficient (equal to D/RT)
KW	--	kilowatts
kg	--	kilogram

kph	--	kilometers per hour
L, ℓ	--	liquid phase
LOX	--	liquid oxygen
lb	--	pounds
M	--	molecular weight of diffusing species
M.P.	--	melting point
m	--	meter
mm	--	millimeter (millimeters of mercury or torr when used to designate pressure)
mi	--	mile
min	--	minute
ml	--	milliliter
mph	--	miles per hour
oz	--	ounce
N	--	newtons (1 newton = 1 kg m/sec^2)
P	--	atmospheric pressure
P_{vap}	--	vapor pressure
p', p''	--	vapor pressures of diffusing species at liquid surface and far removed
ppm	--	parts per million
q	--	amount evaporated
reefer	--	refrigeration
R	--	gas constant
rpm	--	revolutions per minute
S, s	--	solid phase, S also used as area of spill
T	--	temperature
TLV	--	threshold limit value

t   -- time

torr   -- unit of pressure (1 torr = 1 mm Hg)

x   -- distance

Greek Letters

γ   -- radius of surface of simulated spill

ACKNOWLEDGMENT

SECTION 1

INTRODUCTION

Spilled chemicals that pose a hazard to the land and water ecosystem can also provide a significant vapor hazard. Although the vapors released by such chemicals may ultimately be dispersed in the environment and, because of degradation or dilution, have few long-term effects, they do pose an immediate hazard to life and property downwind of the spill. In addition, a hazard is posed to those responding to the spill who must remain in the area for the duration of the incident.

The vapor hazard from spilled chemicals takes two forms: (1) the release of toxic fumes that pose a life hazard even at low concentrations (parts per million), and (2) the release of flammable vapors where minimum dangerous concentrations are usually above one percent. Some chemicals may exhibit both hazards, but toxicity, with its lower allowable concentration, will be the controlling feature.

The great difference in minimum hazard levels creates two distinct problems. In the case of flammable vapors, small increments of reduction can be meaningful. For toxic materials, the ability to provide meaningful mitigation of the hazard may only lie with reduction of the equilibrium vapor pressure.

There are a number of possible vapor amelioration techniques which have received consideration. A review of techniques conducted under U.S. Coast Guard sponsorship (Greer, 1976) shows that a number of mechanisms are impractical or ineffective for field situations. The techniques of mechanical covers, induced air movement, vapor scrubbing and vapor phase reaction are in these categories. The techniques of foam cover and liquid phase modification are the only methods which in their present state of development have had any practical demonstration and can pass the criteria of cost, availability, deployment, and application. The degree of vapor control that can be experienced has been shown to be sufficient to be beneficial where flammable vapors are the hazard (Gross, 1980). Where vapor concentration from a spill can be expected to be much greater than the TLV, significant reduction of the toxic hazard does not appear possible within existing technology.

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A promising mechanism of vapor control is the use of a coolant to reduce the temperature of the spill. This method would reduce the equilibrium vapor pressure and the rate of vapor release per unit time.

This technique has been addressed in the prior referenced Coast Guard program (Greer, 1976) and also in a report to the USEPA (Brown, 1980). In neither study was any systematic investigation conducted. On the basis of these studies, EPA inaugurated a detailed program to evaluate the potential of cooling and if warranted to conduct a simulated spill scenario to define feasibility. This report presents a comprehensive documentation of the work that was accomplished, the conclusions reached, and recommendations for further validation of the procedure including additional equipment evaluation.

SECTION 2

SUMMARY AND CONCLUSIONS

This program has established the basic feasibility of the cooling concept. A literature review and data evaluation provided an extensive list of potential coolants. Practical considerations of cost, availability, safety and field handling reduced the candidate list to four materials: wet ice (solid water), dry ice (solid CO_2), liquid CO_2 and liquid nitrogen.

The application to spills of N_2 and CO_2 in their liquid form can produce significant reductions in the temperature of the spill but their use is accompanied by certain disadvantages. Both liquid CO_2 and liquid nitrogen produce a dense obscuring cloud above the spill surface. While this has the benefit of providing a nonflammable atmosphere above the spill, it has the disadvantage of being nonbreathable. Effective vapor phase control requires continued application of the coolant. The boiling of the liquid coolant can exaggerate the vapor release from the spilled material. There is a tendency of liquid CO_2 to sink into the spilled material, restricting the amount of cooling at the surface.

Liquid CO_2 can be converted to solid CO_2 by expansion of the liquid to atmospheric pressure. Conversion efficiency is only 15%, however, and the generation of the obscuring nonbreathable cloud still occurs.

Wet ice has certain advantages but its cooling ability is restricted. The minimum achievable temperature is only 0°C (32°F) unless the ice is super cooled prior to use. Ice may react with some materials and will increase the volume of the spill.

Laboratory tests showed dry ice to have the greatest potential for effective, persistent cooling with small material losses and minimal cloud formation. The best results were obtained where the dry ice was crushed and applied as an aggregate of particulates.

The standard commercial form of dry ice is a 25 cm (10 in.) square block. Large scale field application of dry ice requires a mechanism to crush the blocks and apply the particulates to the spill surface. After survey of commercial equipment and a

limited testing program a commercial shredder/crusher was se-
lected to convert the dry ice blocks to a suitable form. The
speed of rotation and the configuration of the tines were
altered to achieve a reasonable yield of particles within an
acceptable size range. The size distribution ranged from fine
particulates to coarse material of 0.635-1.27 cm (1/4 to 1/2 in.)
size. Because of sublimation losses which averaged 15 percent,
a true size range was never measured.

Several methods were evaluated for dispensing the crushed
dry ice onto the spill surface. A snow blower was originally
selected. Its operation reduced the effective dry ice discharge
to 65 percent of that fed to the crusher. The combination of
snow blower/crusher was not an satisfactory application device.
The dry ice discharge distance was insufficient to permit ope-
ration from a single location and the machine was difficult to
maneuver around a spill.

The crusher was then combined with a pneumatic conveyor
consisting of an auger, air blower, and a hose. The auger fed
the dry ice particles from the crusher into an air stream for
delivery to the spill via the hose. This apparatus was mounted
on a wheeled frame to provide mobility but the hose discharge
of the dry ice allowed an extended discharge pattern from a
single location. About 50 percent of the dry ice fed to the
crusher was effectively applied to a spill by the hose.

Field tests were conducted using diethyl ether as a haz-
ardous spill simulant. Seven hundred liters (200 gallons) were
spilled into a 7.6 by 6.1 meter (25 ft by 20 ft) impoundment.
Dry ice was charged at a rate of 13.6 kg/min (30 lb/min) for 30
minutes with an effective application rate to the spill of 6.8
kg/min (15 lb/min). The spill temperature was reduced to about
-60°C (-76°F) in about 20 minutes. The data showed that the
diethyl ether vapor concentration in the vicinity of the spill
was reduced to 25 percent of the pre-treatment value. Due to
wind effects an absolute measure of the vapor concentration re-
duction could not be obtained.

This program has shown that dry ice can significantly re-
duce the temperature of a spilled liquid with a concomitant re-
duction in the spill vaporization rate. Crushing commercially
available dry ice blocks to small particles and distributing
these particles over a spill surface can be achieved with com-
mercially available equipment. The equipment assembled and
modified for this program requires some further optimization in
terms of operation, configuration and materials of construction.
The tests conducted were not sufficiently extensive to clearly
show practical, efficient operation in a real-time spill scenario,
but they do support continued investigation and further evaluation
of the cooling concept.

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It is reasonably clear that the cooling concept is primarily for use on spills that pose a toxic vapor hazard rather than a flammable/explosive vapor hazard. It has been well substantiated that aqueous foams provide effective mitigation for those materials presenting a flammable hazard. The use of fire-fignting foams is a well developed technology in common use by emergency organizations. Foam cannot provide the degree of vapor control necessary where toxic levels are in the parts per million range, however. This provides a basic guideline for further evaluation.

SECTION 3

RECOMMENDATIONS

The continuing evolution of the cooling concept for vapor suppression of spilled volatile chemicals rests primarily on its practicality in real-time spill situations. Although additional testing with a broader range of chemical classes may be desirable along with a more accurate appraisal of the degree of benefit provided, the first question to be asked after acknowledging feasibility concerns logistic practicality and the first recommendation is to address that question. The first approach is to review actual spill scenarios to determine if the cooling concept could have been employed. This should be done with knowledge of equipment and material needs, the realities of deployment, and the limitations of maneuverability.

The availability of a piece of equipment, even though limited, allows actual response to a real spill situations. By assigning the current equipment to a spill response operation, a regional emergency response unit of EPA or a contractor response unit such as EERU, it would be available for deployment in a spill situation. As an alternate to that, the assigned unit could conduct mock up spill response based on real-time situations to determine practicality. Such evaluating procedures would be conducted concurrently with the theoretical analysis.

Should the analysis of the practical aspects of the cooling concept be positive, the next recommendation is for equipment modification. The unit developed in this program has a practical limit of 13.6 kg (30 lb) per minute dry ice feed. This limit is imposed basically by the size of the auger and the configuration of the hopper. More rapid feed through the crusher causes material buildup in the hopper which results in bridging over the auger. This blocks further material feed into the auger.

Some mechanical improvement appears possible by changes in the size of the hopper, the slope of the hopper walls and the capacity of the auger. There would appear to be limitations on the size increase the equipment can experience without affecting ease of deployment and maneuverability. Thus consideration needs to be given also to devices which prevent bridging such as vibrators, moveable vanes or similar devices mounted within the hopper.

A second area for mechanical improvement is in the configuration of the crusher. The current unit uses a hammermill design. It produces a large number of fines which tend to fully sublime in the discharge hose. A reduction in fines would increase the effective discharge percentage, while an increase in the number of coarse particles would assist in the uniformity of the discharge pattern and the projection distance. The potential benefits would appear to justify an examination of different arrangements or spacing of tines or the substitution of spikes in place of the tines.

Certain material changes have been indicated. It is certain that a review should be made of hose materials which remain fairly flexible at the temperatures experienced in the discharge line. Low friction materials may be a benefit on the sides of the hopper.

The final recommendation concerns the applicability of the concept to chemical classes. There is the temptation to recommend more extensive testing to establish in quantitative terms the degree of vapor control that could be achieved. There is a question as to how successful such efforts would be.

The rate of vapor release from a spill is dependent on its equilibrium vapor pressure. The amount of vapor released is influenced by time, the size of the spill surface, the wind velocity and to a lesser extent by the depth of the spill and the topography of the area. Since each spill scenario is different, the most meaningful data is the degree of temperature reduction that can be achieved. This will be influenced by the ambient temperature and probably by the depth of the spill and the wind.

Thus it would seem that additional evaluation should first look to the possibility that the application of the dry ice results in a reasonably constant temperature reduction. If this is the case it also allows the determination of which materials can be converted to solids.

Regardless of whether constant temperature reduction is likely, it seems questionable whether effort should be expended to attempt to interrelate spill size, ambient temperature and wind with the degree of reduction which can be effected in the downwind vapor concentration by applying dry ice to the spill. At this point in time such a recommendation does not appear justified.

Consideration should be given to classes of materials which respond differently to temperature than the simulant material. Three classes warrant consideration: 1) those which would solidify, 2) those whose boiling point is below ambient, and 3) those which fume in moist air.

Based upon thermodynamic theory it would be expected that the temperature of materials solidified by the application of a coolant would not be significantly reduced below their freezing point. The combination of the heat of fusion and the poor heat transfer expected between the subliming dry ice and the solidified spill would appear to preclude measurable temperature reductions below the freezing point. This assumption needs to be validated, however.

With liquefied gases the question is how significant will the heat of vaporization be in affecting the degree of cooling that can be achieved. Materials such as chlorine and vinyl chloride monomer would be likely candidates for study. An investigation of such materials is recommended.

Materials which react with water and are not amenable to control by dilution with either water or foam may also be candidates for vapor control by cooling. Typical materials are sulfur trioxide and anhydrous hydrogen fluoride. This type of material reacts strongly with water and direct application sorely aggravates the vapor release. Foam is a better mechanism for dilution but does not provide any short term benefits in vapor control.

Cooling with dry ice might have a benefit beyond simple cooling. Because of its density it tends to displace the air above the spill. The moisture is also displaced. Reduced vaporization could be helpful if only in controlling visibility.

The opposite situation may occur, however. In the field tests with diethyl ether, ice crystals appeared in the liquid. It is probable that some of this resulted from fractional crystallization of the water impurity in the ether. It is also possible that some of it developed due to condensation of the moisture in the air. If such condensation is significant, the precipitation of water ice into reactive materials would work against cooling due to the heat of reaction or solution. It is recommended that some analysis be made of these possible competing effects.

These recommendations were derived from the work to date. With more knowledge, other recommendations may become obvious.

SECTION 4

PROGRAM PLAN

The program had as its objectives the development of mechanisms to modify the vapor hazard of spilled volatile chemicals through reduction of the surface temperature of the spill. The plan to implement that program had three phases -- the evaluation and selection of coolants, the development of equipment to dispense the coolant, and a field demonstration of the fully developed system.

PHASE I - COOLANT EVALUATION AND SELECTION

The first phase covered six months of effort and was subdivided into three main tasks. To some extent the tasks overlapped each other rather than running consecutively.

The first task defined the available coolants. All potential candidates were identified, their physical and chemical properties compiled and refrigeration capabilities identified. These values allow definition of theoretical capabilities of each candidate. Other factors which influence the practical capabilities including on-site generation, long-term storage considerations, system costs, materials losses during application, potential environmental effects and heat transfer efficiencies under field conditions were identified and assessed. This task encompassed an eight week period.

The second task evaluated each candidate using the data acquired in the first task. The evaluation was conducted with consideration of two additional factors, spill size and the type of vapor hazard: flammable or toxic. Based upon existing knowledge best coolant candidates differed markedly as a function of these two factors. This task covered six weeks, beginning in the sixth week of the phase. It was expected that at the end of task two there would be certain factors which could benefit from further clarification. Environmental effects and heat transfer efficiencies were anticipated to be in that category.

The third task entailed the conduct of limited laboratory tests using representative volatile chemicals to provide the desired clarification. These tests were conducted over a ten-week period beginning in the tenth week of the phase using a test procedure previously successfully employed in assessing

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other forms of vapor hazard mitigation.

Upon completion of the third task, specific selections were made of coolants deemed most promising. A report defining this coolant and reasons for its selection was submitted to the contracting officer. This report set forth the requirements for effective application of the coolant. This included equipment specifications and a specific and detailed program to develop this equipment. This served as a detailed plan for Phase II and supplemented this program plan.

PHASE II - EQUIPMENT DEVELOPMENT

The selection of the coolants and delineation of the requirements of the equipment for application allowed the second phase to be initiated. In this phase, conducted in five tasks over a 9-month period, equipment to dispense the coolant and apply it to the spill surface was developed.

The first task provided a review of commercially available equipment to determine if the requirements could be met with existing units. This review surveyed a broad range of equipment designed for similar applications. This task encompassed a period of 8 weeks starting in the 30th week of the program.

In the second task a specific equipment design was evolved and the necessary equipment components acquired. Where possible, commercially available components were employed. Modifications or fabrication of nonstandard items were accomplished as required to build the equipment to meet the preset requirements including safe operation under real-time spill conditions. This task was conducted over a period of 10 weeks starting in the 34th week of the program.

As purchased or fabricated parts were received, equipment fabrication was initiated. Assembly began in the 42nd week of the program and continued for 18 weeks.

Upon completion of task three, the fabricated equipment was operated under simulated conditions. Modifications and changes were made as indicated during the shakedown operation. This work comprised task four and was conducted over an 8-week period starting in the 60th week of the program.

With the determination that the developed equipment met design specification, the final task was initiated. In this task manuals were prepared for the operation, maintenance and trouble shooting of the equipment. Suppliers and parts lists were provided for each individual component in the assembly. This task covered 4 weeks beginning with the 68th week of the program.

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PHASE III - FIELD DEMONSTRATION

Upon completion of the equipment development phase a full scale field demonstration was conducted using a simulated volatile hazardous material. This phase conducted over 8 weeks comprised three tasks.

The first step was a detailed plan and procedures for conducting the field demonstration. With approval of the plan, the field test was set up and conducted. This test verified the operation of the equipment, the efficiency of the coolant material and recommended mechanisms of spill removal. Full documentation was made of the data gathered along with photographic documentation of the test operations. These tasks took 6 weeks starting in the 70th week of the program.

The final task conducted over the final four weeks of the program was the preparation and submission of a comprehensive technical report covering the total effort on the control. A film documentation of the field demonstration in the form of slides and a narrated 16 mm film was included with the final report.

This submission concluded the program with the exception of those changes which might be required in the format or contents of the final report.

SECTION 5

COOLANT IDENTIFICATION, EVALUATION AND SELECTION

The objective of this first phase of the program was the selection of coolants that possessed the correct combination of properties to cool and reduce the vaporization rate of hazardous material spills.

IDENTIFICATION AND SELECTION OF COOLANTS

If cooling the spilled material is considered as a general *refrigeration process, then any substance capable of going* through the Joule-Thompson cooling cycle could be considered as a candidate to be used in the proposed system. A listing of materials meeting this criterion resulted in 60 candidate coolants. The fact that the coolant system is being designed for use as a response to spills of hazardous materials sets safety as an initial consideration. Applying the criterion that the coolant should not contribute a health or safety hazard at any time during the spill response, the removal or ultimate dis-posal of spilled substances reduced this to 50 materials. Six-teen others were rejected for logistic reasons, which included available in quantity, transportable, and ability to handle with a minimum of training.

Physical and Chemical Properties

For the 34 substances identified in the prior task, a list of properties were collected as given below:

Boiling point	Critical properties
Freezing point	Threshold limit values
Heat of fusion	Liquid density
Heat of vaporization	Vapor density
Flammability limits	Cost

The sources used in collecting these data included the Handbook of Chemistry and Physics (1978), Bureau of Mines Bulle-tin No. 503, National Fire Protection Association Fire Codes, Vol. 13, No. 325M, the 1978 Edition of Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom En-vironment, technical information circulars supplied by manu-facturers and technical papers in which properties for individual materials were reported. Costs were calculated on the basis of

prices quoted for ton quantities of the cooling material. These
data were compiled into the format shown in Table 1 to facili-
tate correlation and evaluation.

Preliminary Evaluation

A screening process was initiated to select the most pro-
mising coolants from among the 34 candidates. Using the cri-
teria of cooling capability, availability, safety in handling
during both application and cleanup, and the environmental
acceptability, the candidates were given a merit rating.

Three other factors were acknowledged as important. These
were application efficiency, the ratio of coolant used versus
the amount which reaches the spill surface; logistics, the de-
ployment of equipment and materials to the spill site and sub-
strate heat loads, heat inputs from the ground or containment
structure. Because they were difficult to measure, they could
only be assessed in general during this preliminary evaluation.

Materials costs were calculated and have been shown in Table
1. They were not a consideration in the initial screening, how-
ever.

Cooling Capabilities --

Cooling capacity can be calculated as the combination of
the available sensible heat of the coolant and the latent heat
resulting from any change of state that may occur. These values
are provided as part of the coolant properties given in Table 1.

The available cooling capacity basically determines the
volume of coolant required in any spill situation. The true
effectiveness of a coolant is the ultimate temperature which can
be obtained by its use. These two factors, cooling capacity and
minimum achievable temperature, determine the basic capability
of any material to be an effective coolant.

To the above factors must be added application efficiencies.
During handling and delivery of coolants to the spill surface
certain losses will occur. The greater these losses are, the
poorer will be the total cooling capacity. The efficiencies
cannot be accurately assessed without some experimental data.

Availability and Storage Characteristics --

Availability is defined in terms of ready supply in large
quantities through the U.S. on fairly short notice. It was
clear that many of the materials in the list of candidates could
not meet this requirement.

As an alternate to availabiity, the potential of storing

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TABLE 1. CANDIDATE COOLING MATERIALS AND THEIR PROPERTIES TO BE USED FOR EVALUATION

Coolant	Chemical Formula	Freezing Point (°K)	Boiling Point (°K)	LEL (%)	TLV (ppm)	Liquid Density (g/ml)	Vapor Density (g/l)	Critical Temp. (°K)	Critical Pressure (atm)	Cooling Capacity (J/g)	Cost $(\$/J \times 10^6)$
Air (l)	n.a.		78.8	n.a.	n.a.	0.92	1.29	122.6	37.2	210	1.7
Nitrogen (l)	N_2		77.4	n.a.	Asph	0.81	1.25	126.1	33.5	200	1.7
Hydrogen (l)	H_2		20.4	4	Asph	0.07	0.09	33.3	12.8	450	
Helium (l)	He		4.6	n.a.	Asph	0.12	0.18	5.4	2.3	24	
Argon (l)	A		87	n.a.	Asph	1.41	1.78	150.8	48.0	157	5.0
Neon (l)	Ne		27.3	n.a.	Asph	1.2	0.90	44.5	26.9	16	
Methane (l)	CH_4		111.8	5	Asph	0.42	0.72	190.3	45.8	575	1.5
Ethane (l)	C_2H_6		184	3.0	Asph	0.55	1.36	306	48.2	520	1.8
Ethylene (l)	C_2H_4		169.3	2.7	Asph	0.41	1.26	282.7	50.0	480	2.3
Propane (l)	C_3H_8		231	2.2	1000	0.56	2.00	176	42.0	425	0.6
Propylene (l)	C_3H_6		226.2	2.0	4000	0.61	1.94	365	45.6	435	0.5
Butane (l)	C_4H_{10}		273.7	1.9	500	0.60	2.52	426	36	385	1.0
i-Butane (l)	$(CH_3)_3CH$		263	1.8		0.59	2.67	407	30.2	365	3.1
Butylene (l)	C_4H_8	143.2	266.2	1.6		0.59	2.45	419.6	39.8	391	
Freon-12 (l)	CCl_2F_2		243	n.a.	1000	1.31	6.3	384	40.6	165	5.7
Freon-22 (l)	$CHClF_2$		232.4	n.a.	1000	1.19	4.7	304	49.1	234	5.7
Ammonia (l)	NH_3		239.8	16	25	0.68	0.77	405.5	111.3	1369	0.7
Methyl Chloride (l)	CH_3Cl		249.1	10.7	100	1.00	2.31	416	65.9	428	0.8
Carbon Dioxide (l)	CO_2	195(subl)	274 (20 atm)	n.a.	5000	0.99	1.98	304	72.9	272	0.7
Methyl Ether (l)	$(CH_3)_2O$	131.7	249.5	3.4				400	53.0	465	
Meth-Eth Ether (l)	$CH_3OC_2H_5$		261.1	2.0	1000	0.73	2.7	437			
Sulfur 6-Fluoride (l)	SF_6	209.4(subl.)		n.a.		1.91				145	59
Sulfur Dioxide (l)	SO_2	197.7	263.2	n.a.	2	1.43	2.93	430.4	77.7	368	0.6
Carbon Dioxide (S)	CO_2	195(subl)		n.a.	5000	0.99	1.98	304	72.9	297	0.7
Water (S)	H_2O	273.2	373	n.a.	n.a.	1.00		647.4	218.3	334	0.1
Ethyl Ether (S)	$(C_2H_5)_2O$	-156	308	1.9	1000	0.7	0.42	467	35.6	380	1.4
Ethanol (S)	C_2H_5OH	158.8	351.8	4.3		0.79	2.0	516	63.0	104	10(denatured)
Propyl Ether (S)	$(C_3H_7)_2O$	151.2	363.0	1.4				500			
Eth-Prop Ether (S)	$C_2H_5OC_3H_7$	194	335.0	1.9	300	0.73	3.74		32.1		
Cyclohexane (S)	C_6H_{12}	279.8	354.6	1.3		0.8		554.2	40.4	51.3	5.6
n-Octane (S)	C_8H_{18}	216.4	398.6	1.0	400	0.7	5.03	568.6	24.6	205	1.2
n-Decane (S)	$C_{10}H_{22}$	242	447	0.8		0.7	6.32	617.6	20.8	205	
1-Propanol (S)	$(CH_3)_2CHOH$	184.7	355.7	2.0	400	0.78	2.7	235	47		6.0
d-Dodecane (S)	$C_{12}H_{26}$	263.5	487.7	0.6		0.8	7.6	659.2	17.9	87.9	

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materials at strategic sites or including such storage within
the resources of spill response units was considered. In this
case long term storage in low loss, low maintenance facilities
was a necessary requirement.

Safety and Environmental Effects --

   One of the major requirements set forth early in the pro-
gram was that the coolant should not contribute to the inherent
hazard of the spill. This requirement referred to the coolant
as any possible interaction of the coolant with the spilled ma-
terial or the environment, and to the ultimate disposal of the
spill contaminated debris or residues.

   A number of chemicals, as listed in Table 2, were rejected
as coolants because of their inherently hazardous nature. Other
potential coolants, with safety or environmental deficiencies,
were not initially deleted since they were considered to be less
hazardous than the potential spill materials and might provide
benefits that would offset their disadvantages. A final de-
cision on these coolants required an in-depth review and com-
parison with other candidates.

Selection

   Although the collection and compilation of data concerning
cooling materials was done on an individual basis, in the early
portion of the selection process it was clear that some screen-
ing could be made on the basis of chemical classification. These
broad classifications included: rare gases, oxygen-containing
cryogens, general organic materials, freons, commercial re-
frigerants and hydrocarbons.

Rare Gases --

   The limited availability and cost of the rare gases are the
major problems associated with their use. Although logistical
problems may be encountered to varying degrees with all cooling
materials, the rare gases have the greatest problem and are not
considered convenient materials to be used for spill response.

Oxygen-containing Cryogens --

   Liquid air and other cryogenic materials that contain
oxygen were rejected as coolants because of their potential re-
activity with many substances considered to be in the low-boiling,
hazardous materials category.

General Organic Materials --

   Materials, such as alcohols and ethers, which can be con-
sidered within a general classification of organic materials,

TABLE 2. HAZARDOUS MATERIALS WITH
ACCEPTABLE THERMAL PROPERTIES

Vinyl Chloride	B.P.	-13.9°C
Cyanogen Gas	B.P.	-20.5°F
Boron Trimethyl	B.P.	-20°C
Disilane	B.P.	-14.5°C
Methyl Phosphine	B.P.	-14°C
Methyl Amine	B.P.	-6.5°C
Bromo Amine	M.P.	-7°C
1,2,3,4 Tetramethyl Benzene	M.P.	-6.25°C
Hydrogen Cyanide	M.P.	-13.4°C
Methyl Nitrite	M.P.	-17°C

were rejected as contributing to health and safety hazards towards response personnel and the general public. Pure hydrocarbons, such as the alkanes, were tentatively rejected as coolants because of their flammability. The tentative status was used since the hydrocarbons could be applicable if the use of a hydrocarbon coolant did not add to the hazard already present because of the spilled material. Because less hazardous candidate materials were found that possess a cooling capability equal to or better than that provided by hydrocarbons, the hydrocarbons were ultimately rejected.

Freons --

Freons (chlorofluorocarbons) were initially set aside in case no viable candidate coolants could be defined. Ultimately, the freons were rejected because of present concerns and litigations surrounding their impact upon the environment. The production of these chemicals may be limited and open end uses, such as would be envisioned for spill response, have been curtailed.

Commercial Refrigerants --

Commercial refrigerants, such as ammonia, methyl chloride and sulfur dioxide have been rejected as health and safety hazards. Their use as spill coolants could be considered for enclosed areas, but probably would require measures to reclaim or otherwise recover the coolant for acceptable disposal.

Miscellaneous Coolants --

Slurry mixtures of carbon dioxide particles in liquid nitrogen or argon and some procedures for producing them have been patented by Smith and Townsend (1968). The claims made for these slurries imply that they could be considered alternatives for this investigation. Action on such mixtures was deferred in this program since it would require working with patented materials and procedures.

Sulfur hexafluoride possesses favorable thermophysical properties. Although it has an identifiable toxicity, the TLV is high at 1000 ppm. After detailed consideration it was decided that the use of large quantities in a spill situation could result in unsafe downwind concentrations of the hexafluoride. This, coupled with uncertainties of availability and cost, resulted in rejection of sulfur hexafluoride from consideration.

Refrigeration Systems --

In addition to specific coolant materials, consideration was given to two approaches which fall in the category of re-

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frigeration systems. Water or ammonia absorption systems and steam-jet refrigeration units with large cooling capacities are available which provide safe, dependable cooling. They do not present environmental problems, but they are large and can require special services such as high pressure steam. Because of logistic problems, size, weight, services, etc., such systems for field operations were deemed impractical.

Acceptable Coolants

The consideration of toxicity, flammability, cooling capacity and availability already discussed in this section resulted in the elimination of most of the materials appearing in Table 1. Four candidate cooling materials remained for further evaluation: liquid nitrogen, liquid carbon dioxide, solid carbon dioxide and water.

Wet Ice --

Water is the most innocuous of all the materials considered. It should present neither health nor safety hazards as a result of its use in quantities that would cool a typical spill. Water could be used in either the liquid or solid state, but a sub-cooled solid form would be the most effective means for cooling a spill.

There are three possible problem area which can arise with the use of water as the cooling material: 1) the total liquid volume of the spill would be substantially increased, possibly causing excessive spread or overflow of containment devices, 2) the perceptible heat load could be increased by the heat capacity of the water, and 3) exothermic reaction between the water and the spilled material.

These problems could restrict the use of water ice as a coolant on some spills. Many hazardous materials are miscible with water, however. Dilution with water could offset the stated difficulties. Assessment of these effects would require experimental measurements.

Carbon Dioxide --

Carbon dioxide has acceptable thermophysical properties for the proposed application, and has the additional benefit of being a refrigerant. It could be used in either the solid or liquid state. Storage as a liquid permits the use of its refrigerant properties to minimize storage losses and allow long term storage at remote locations. Solid CO_2 is commercially available, however, in a multiplicity of locations within the U.S.

The application of large volumes of carbon dioxide to a

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spill will result in the generat on of large volumes of CO_2 gas over the spill. This can have both desirable and undesirable effects. The gas would remain close to the surface to condense the vapors of the hazardous material and would inhibit the ignition and burning of the spill vapors, if they were flammable. On the other hand the carbon dioxide vapor presents a problem for response personnel since its density could result in the formation of an obscuring and nonrespirable gas mixture in the spill vicinity. This would require the monitoring of ambient oxygen concentrations.

Liquid Nitrogen --

Liquid nitrogen has the potential to cool most low-boiling, hazardous materials below their freezing points which could facilitate their separation and removal from the ground.

Liquefied nitrogen has the unique characteristic among the candidate coolants selected for responding to accidental spills of being less dense than many of the low-boiling, hazardous materials. It would appear possible, therefore, to float this coolant on the surface of many spills and take advantage of the insulating properties of the hazardous materials to reduce heat transfer to the ground beneath the spill. The total heat load might thus be significantly reduced.

Storage and dispensing of liquefied nitrogen would present some difficulties or require some specialized equipment, but both equipment and experience are available from present commercial manufacturers.

Liquefied nitrogen has the problem of creating a nonrespirable gas mixture and obscuring cloud in the spill vicinity. Nitrogen is a simple asphyxiant and would require large volumes and poor mixing to create health hazards, but monitoring ambient oxygen concentrations would be necessary for safe operation.

EVALUATION OF COOLANT SYSTEM CHARACTERISTICS FOR SPILL APPLICATION

An outline of the factors influencing the temperature of accidentally spilled materials is presented in Figure 1. The temperature of the spilled material, which is the primary concern of this program, is shown to be directly related to its environment, its own thermophysical properties, and the amount spilled. The presence of the coolant and the ratio of the two sets of thermophysical properties and amounts determine the rate at which any temperature change occurs and the ultimate temperature which can be attained.

Factors affecting the temperature of a spilled material have been divided into two categories: 1) those which are
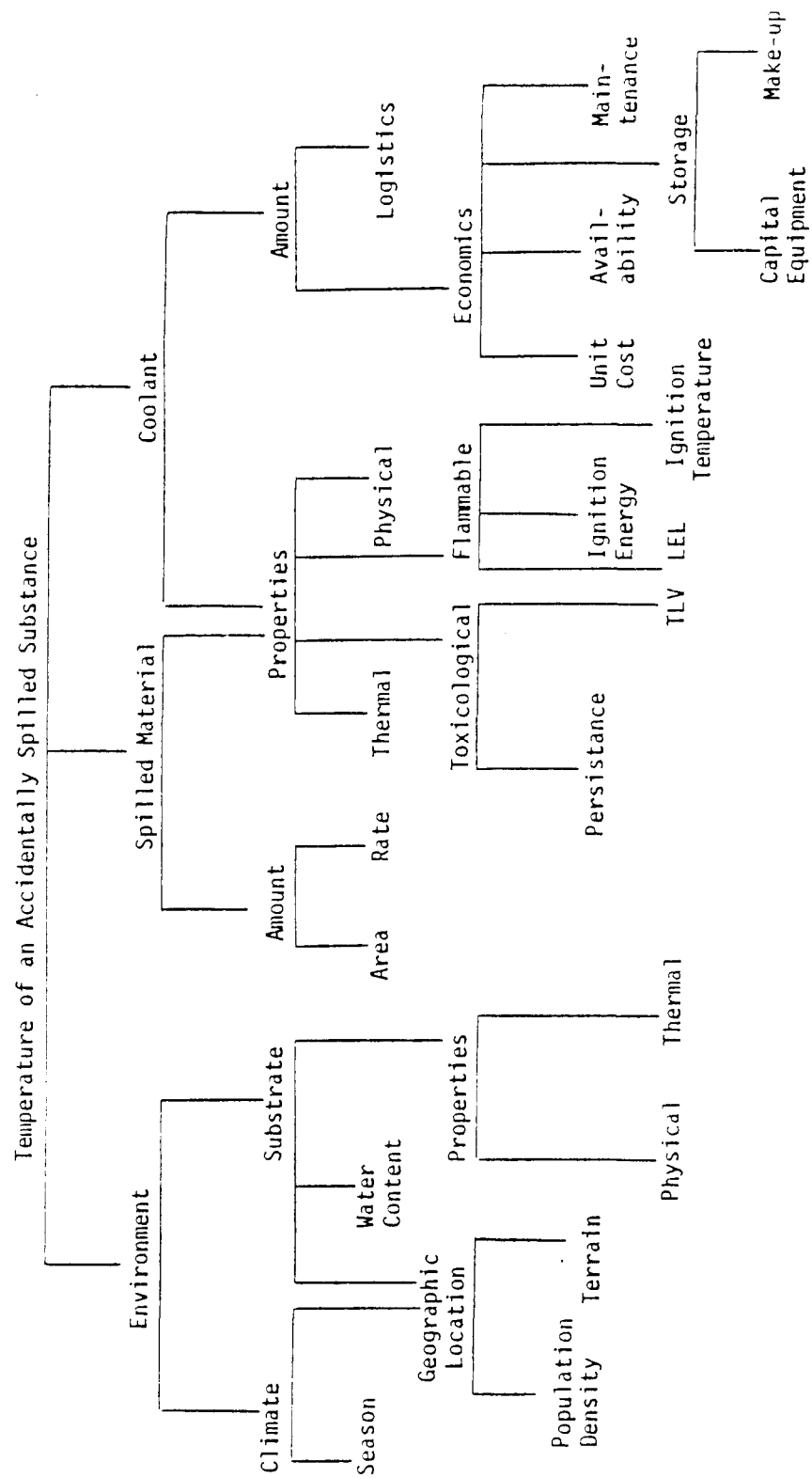
Figure 1. Factors influencing the temperature of an accidentally spilled material.

considered to be uncontrollable, and 2) those which are subject to some degree of control. The factors which are considered uncontrollable in accidental spills of low-boiling, hazardous materials include the environmental factors such as season, wind, rain, location, substrate characteristics and structure and the spill itself, including: amount, rate of spillage, vapor pressure, heat of vaporization and thermal conductivity.

Representative values were selected for these factors to establish a range of conditions under which a proposed cryogenic cooling system could be applicable.

Nine factors associated with the effectiveness of a coolant are included among those which are considered controllable. They play an integral part in selecting a cooling material. These factors include the amount of coolant, its rate and effectiveness of dispersal, phase transition temperature, latent heat of phase change, effective rate of heat transfer, liquid or vapor density and solubility or miscibility with the spilled material.

Heat Transfer Assessment

Two separate approaches may be used to define heat transfer within an accidental spill treated with a cryogen. The rate can be estimated by theoretical approximations, or it can be measured under simulated conditions. Theoretical approximations may be made with standard heat transfer equations, or more refined estimates can be made from models, such as described by Bell (1978), which require computer calculations.

Basic heat transfer calculations yield heat transfer rates of 3300 Kcal/m²hr (1230 BTU/ft²hr) during the initial cooling, and 950 Kcal/m²hr (350 BTU/ft²hr) to maintain the cooled condition.

The alternative approach for defining a typical heat load is a pragmatic evaluation of experimental data published concerning spills of cryogens. These data have been reported by Drake and Reid (1975), Kosky and Lyon (1968) and Board, et al (1971). The data reported for boiling rates have been measured in various units of heat transfer, but generally fall within the range of 2,000 to 11,000 Kcal/m²hr (740 to 4060 BTU/ft²hr).

The work published by Drake and Reid (1975) is a synopsis of experimental data obtained from spills of a liquefied natural gas on various substrates. These data are fitted to the equation:

$$q = A \, t^{1/2}$$

in which q is the heat transferred, t is the time from initial spillage in hours and A is an experimentally fitted constant. Values of A, obtained for typical substrates vary considerably,

but generally fall in the range cited above.

This extensive range of heat transfer rates indicates the variability which would occur under ambient conditions. Since the objective of this program is to establish the working parameters for candidate systems to treat accidental spills, the task of selecting a representative heat transfer rate included the selection of realistic conditions while retaining a reasonable safety factor.

The approach used an analysis of experimental data with conservative estimates where data were unavailable. A heat transfer rate of 6700 Kcal/m²hr (2460 BTU/ft²hr) was selected to apply during the first half hour and a rate of approximately 2000 Kcal/m²hr (740 BTU/ft²hr) to maintain a steady state condition, for the remaining three and one-half hours of the proposed spill response operation. These are clearly and purposely higher than the rates obtained from the calculations noted above. These were selected to insure a conservative situation.

The assessment of candidate cryogens, as cooling materials, was simplified by using two assumptions: 1) the average specific heat of the spilled hazardous material is 0.5 cal/g°C and 2) the cooling capacity of candidate cryogens will be approximated by the latent heat of the phase change with subsequent correlations of these cooling capacities by converting thermal data into cost.

Estimation of Coolant Potential

Estimations of the potential of coolants on spills of hazardous materials were made by comparing equilibrium vapor pressures at two temperatures, 0°C and 25°C (32°F and 77°F). The purpose of this exercise was to determine the degree of benefits which would accrue by cooling to 0°C (32°F) and conversely to assess the need for lower temperatures for meaningful mitigation of the vapor hazard of spilled materials. These comparisons provide a common basis from which to make general comparisons of the various cooling materials but are insufficient for estimating efficiencies or calculating vaporization rate reductions.

Representative hazardous materials were selected for this evaluation of coolants. These materials and the properties needed for estimating coolant effectiveness are presented in Table 3. Effectiveness must reference defineable end points. The flammability limits and TLV of the hazardous materials were selected as the reference points. Lower flammability limits would average about 1 percent vapor concentration, which would correspond to an equilibrium vapor pressure of approximately 7 torr. Threshold limit values are in the range of 10 to 100 ppm, which corresponds to equilibrium vapor pressures in the range of

0.01 to 0.1 torr. Assessment of the relative effectiveness of coolants is also influenced by the average vapor concentrations which would cause asphyxiation. Asphyxiation would require a coolant vapor concentration greater than 12 percent, which would correspond to a vapor pressure of approximately 90 torr.

The vapor pressure comparisons shown in Table 3 show that cooling to 0°C (32°F) can reduce the vapor levels of most materials below their lower flammable limit. There are other more universally available techniques, foam blankets and direct water dilution, which are equally effective in mitigating the flammable vapor hazard.

For cooling to be a useful mechanism of vapor control, with the anticipated difficulties of logistics and field operation along with cost, it must provide benefits beyond those of presently available techniques. It would be desirable to reduce vapor concentrations below the TLV but this may not be possible for all materials under any set of conditions.

Based upon the assessment of the coolants system requirements, it was decided that 0°C (32°F) was the maximum temperature which could be considered. The preference was for a coolant system which could produce subzero temperatures at the surface of a spilled material. This did not result in the elimination of water ice from consideration but it prejudiced the selection towards liquid nitrogen and the two forms of carbon dioxide.

LABORATORY STUDIES FOR DATA CLARIFICATION

To complete the process of selecting coolant candidates, experimental data were required. The experimental investigations undertaken had two objectives:

1) to observe the characteristics and
results of placing candidate coolants
on representative, hazardous materials

2) to provide information on the relative
effectiveness of the candidate coolants.

These investigations included the measurement of cooling and heating rates, minimum temperatures, vapor concentrations, and evaporation rates. The materials selected as hazardous spill simulants were readily available, and were considered representative of compounds which might be encountered in a typical spill response situation.

Determination of Achievable Temperatures

The first series of tests was done in the apparatus shown in Figure 2a to observe the behavior of the candidate coolants
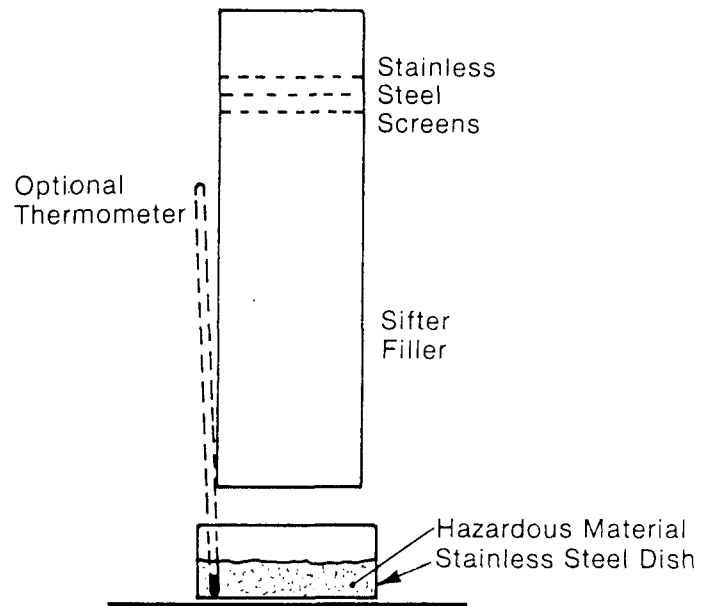
a. Time-Temperature
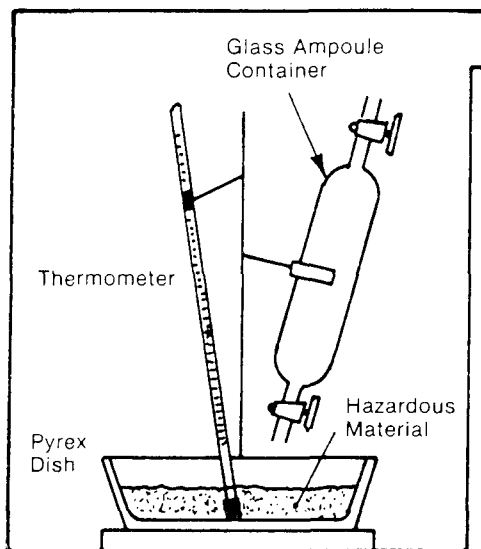
b. Vapor Concentration
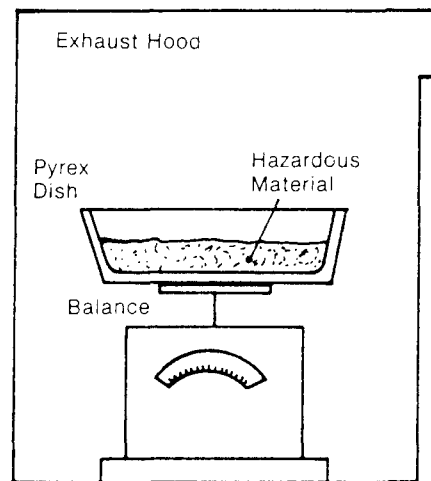
c. Evaporation Rates

Figure 2. Laboratory test apparatus.

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and the representative hazardous spill materials when they were placed in contact. One hundred milliliter (3.38 oz) samples of acetic acid, gasoline, methylene chloride, lacquer thinner, naphtha, toluene and vinyl acetate were placed in the 10 cm (3.94 in.) diameter, stainless steel dish. A 9.5 cm (3.74 in.) diameter sifter filler was positioned about 7 cm (2.76 in.) above the liquid surface to deliver a homogeneous layer of solid water or carbon dioxide particles to the liquids in the dish. Liquid nitrogen was poured over the surface from a weighed Dewar flask.

The amount of each coolant used in the tests was calculated to remove approximately 1200 Kcal/m² (135 BTU/ft²) over a 1/2 hour time span from the liquid samples in the stainless steel dish. The total amount of coolant was added within the first 1/2 to 2 minutes of the test, however. Coolant loadings used for the tests were about 1.5 g/cm² (3.1 lb/ft²) for wet ice, 1 g/cm² (2 lb/ft²) for solid carbon dioxide and 2.4 g/cm² (4.9 lb/ft²) for liquefied nitrogen.

The temperature of the spill simulant was measured with a low temperature thermometer placed at the rim of the stainless steel dish.

Minimum temperatures were achieved in approximately 5 to 8 minutes with wet ice (subcooled to -18°C [0°F]), in about 1/2 to 5 minutes with solid carbon dioxide, and in about 1 to 3 minutes with liquefied nitrogen. The observed minimum temperatures of the spill simulant differed by an order of magnitude depending on the coolant used, i.e., for wet ice -8 to -12°C (18 to 10°F), for dry ice -50 to -75°C (-58 to -105°F) and for liquefied nitrogen -150 to -180°C (-238 to -292°F). Attempts to increase the cooling rate and/or reduce the minimum temperature obtained by using salt water ice rather than subcooled ice were not beneficial. Typical time-temperature curves are shown in Figures 3,4,5 and 6.

The cooling rates observed in these tests indicate that a suitable performance level can be attained if the coolant can be dispersed evenly over the spill area. Heat transfer rates, calculated from the amount of materials used and the observed temperature changes, were in the range of 500 to 4500 Kcal/m²hr (180 to 1660 BTU/ft²hr). These rates are in the lower part of the theoretically calculated range, but were measured on small scale, experimental test units.

The minimum temperatures obtained with subcooled, wet ice were about -12°C (10°F). This would be adequate for reducing the flammability of such materials as isopropyl ether, methyl ethyl ketone and some lacquer thinners, that have flash points exceeding -12°C (10°F). This minimum temperature would not be maintained throughout the four-hour response operation and would be inadequate to reduce the flammability of materials such as

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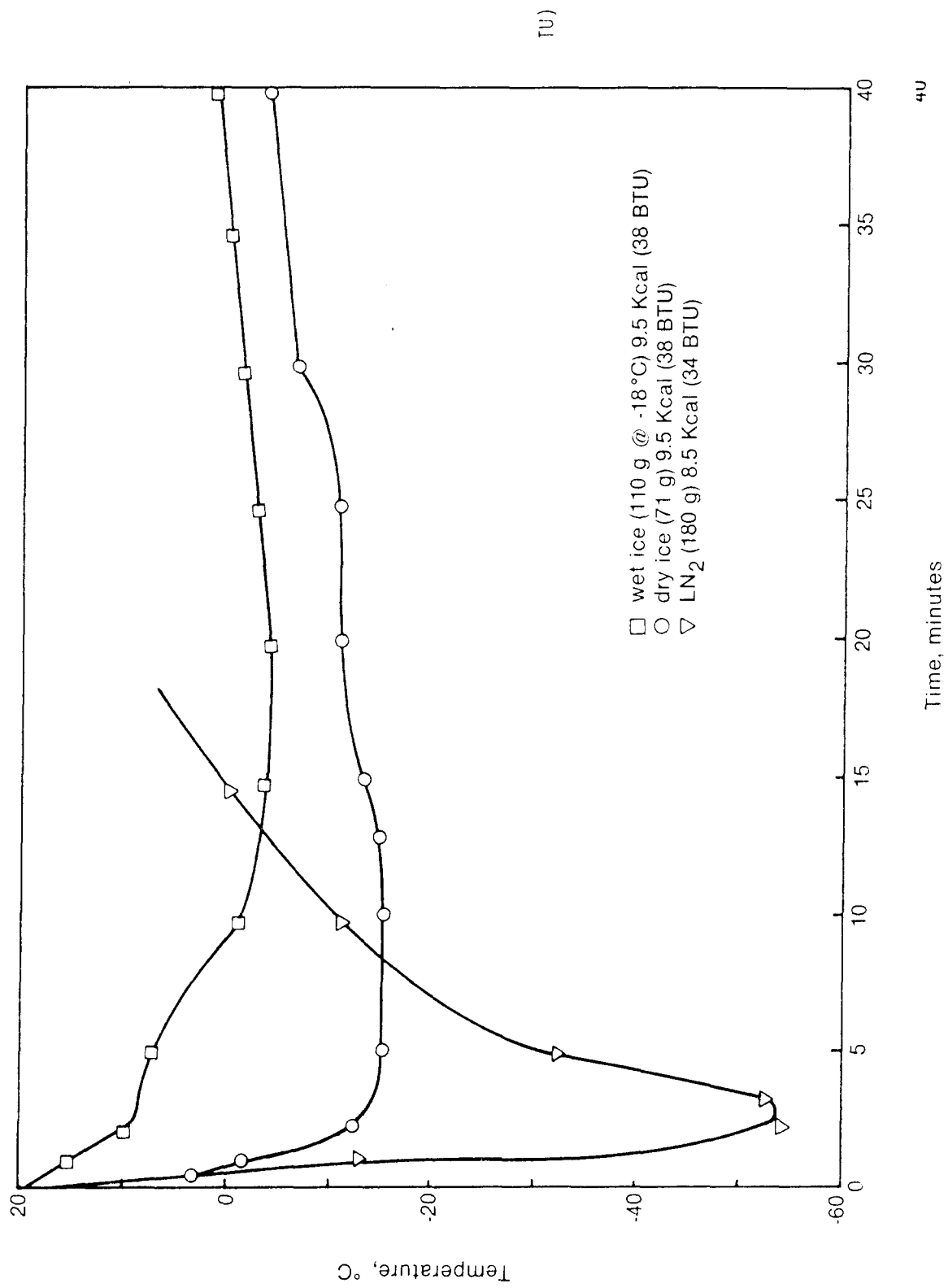
Figure 3. Candidate coolants added to 105 g glacial acetic acid.
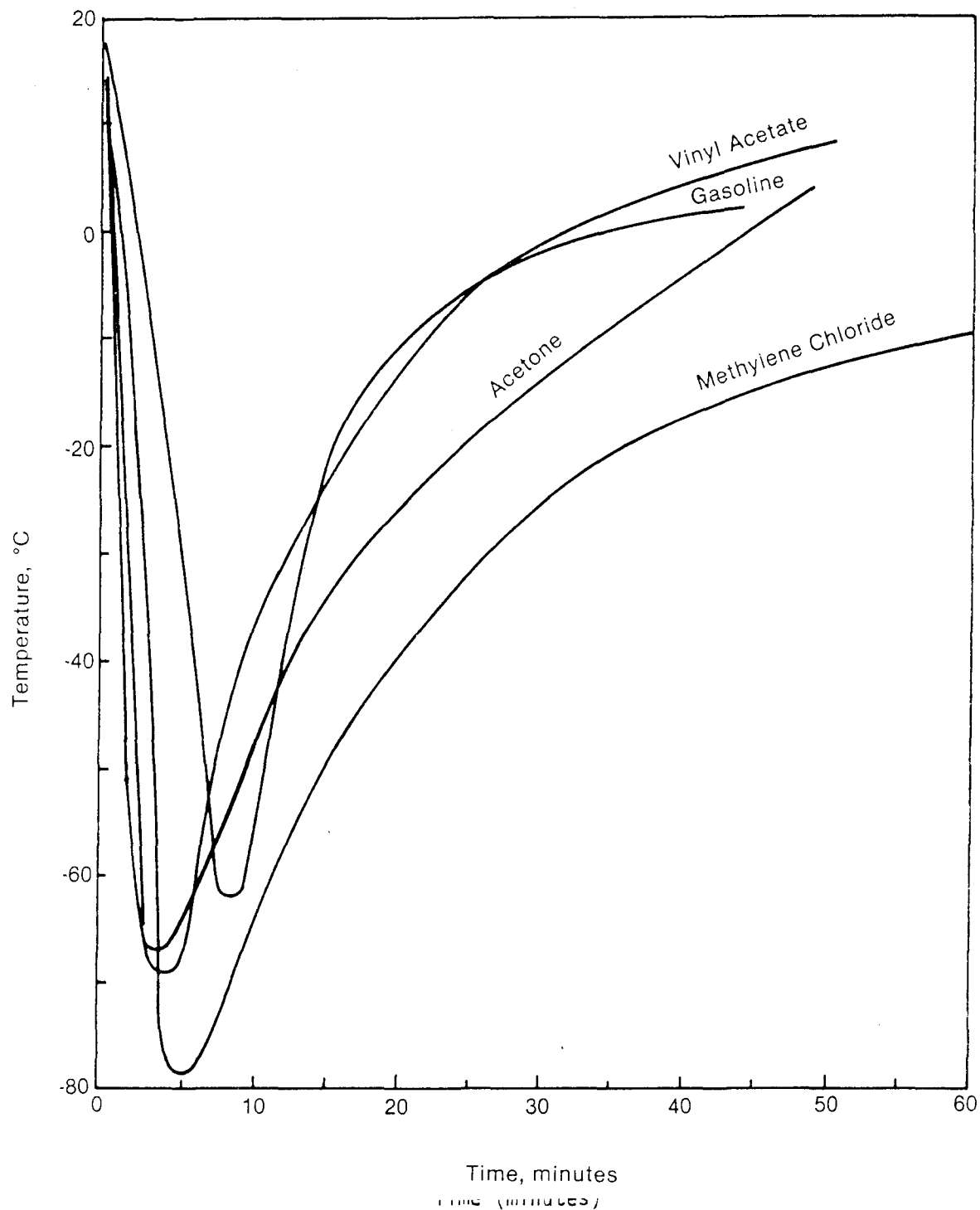
Figure 4. Time-temperature changes observed when carbon dioxide was placed on representative hazardous materials.

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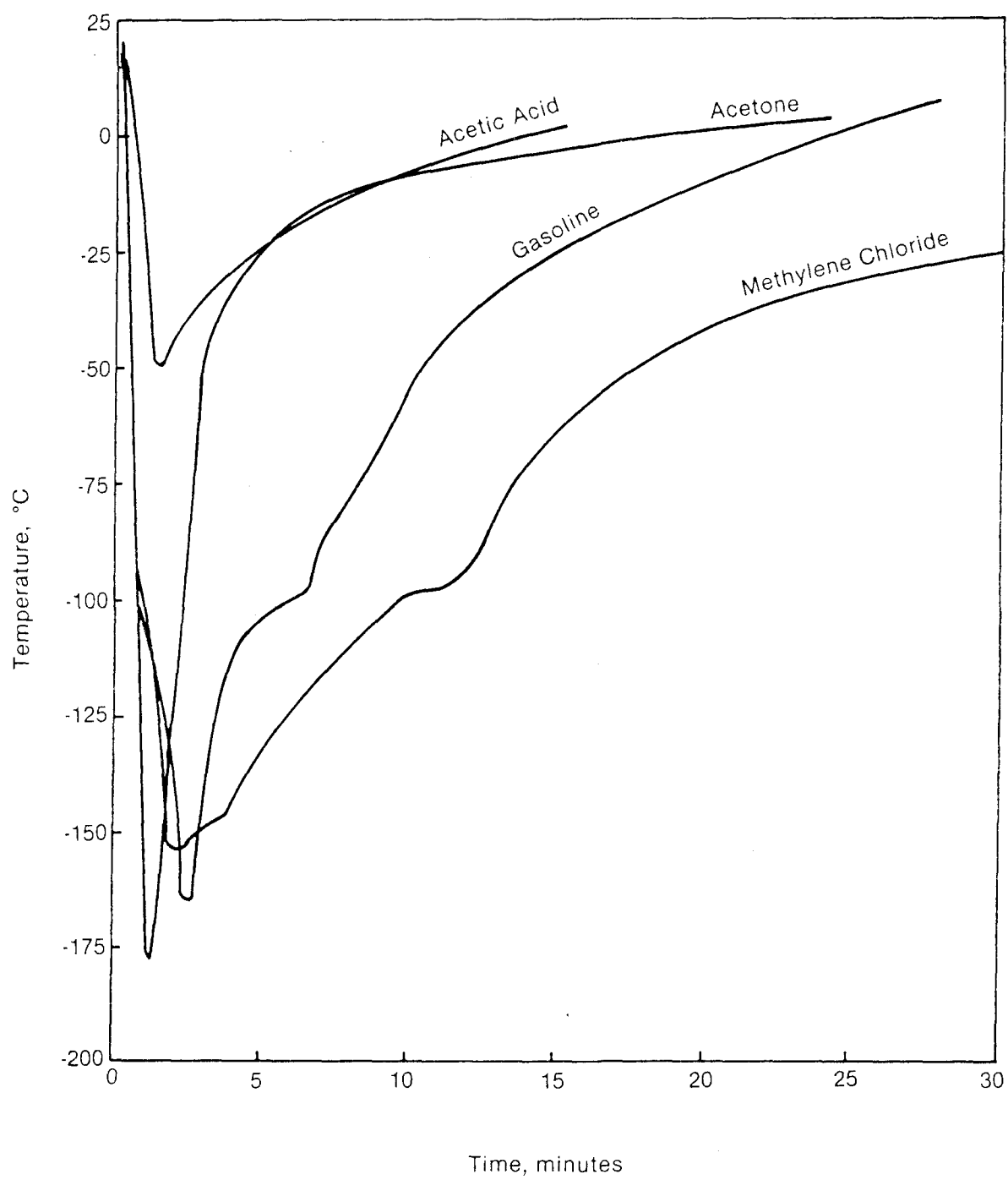
Figure 5. Time-temperature changes observed when liquefied nitrogen placed on representative hazardous materials.

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Figure 6. Candidate coolants added to acetone.

○ wet ice (375 g @ -18°C) Kcal (123 BTU)
□ dry ice (220 g) 30 Kcal (118 BTU)
▽ LN_2 (485 g) 23 Kcal (92 BTU)

Axis labels: Temperature, °C (vertical) and Time, minutes (horizontal)

acetaldehyde, acetone, isopropylamine, ethyl formate or gaso-
lines.

The minimum temperatures obtained with dry ice were near
its sublimation temperature of -78°C (-109°F). This minimum
temperature would be adequate for reducing the flammability of
most materials (gasoline -41°C [-41°F]), but would have to be
considered a diluent for liquefied fuel gases.

The minimum temperature obtainable with liquefied nitrogen
would provide the most protection against ignition and would
approach the TLV for many hazardous materials. Some uncertainty
remains regarding the reduction of the spill vapor concentration
during the initial cooling phase. Soon after the addition of
coolant to the spill simulant, the smell of the vapor from the
spill was noted to intensify. This may be attributed to the en-
trainment of droplets of spill simulant in the vigorously bubbl-
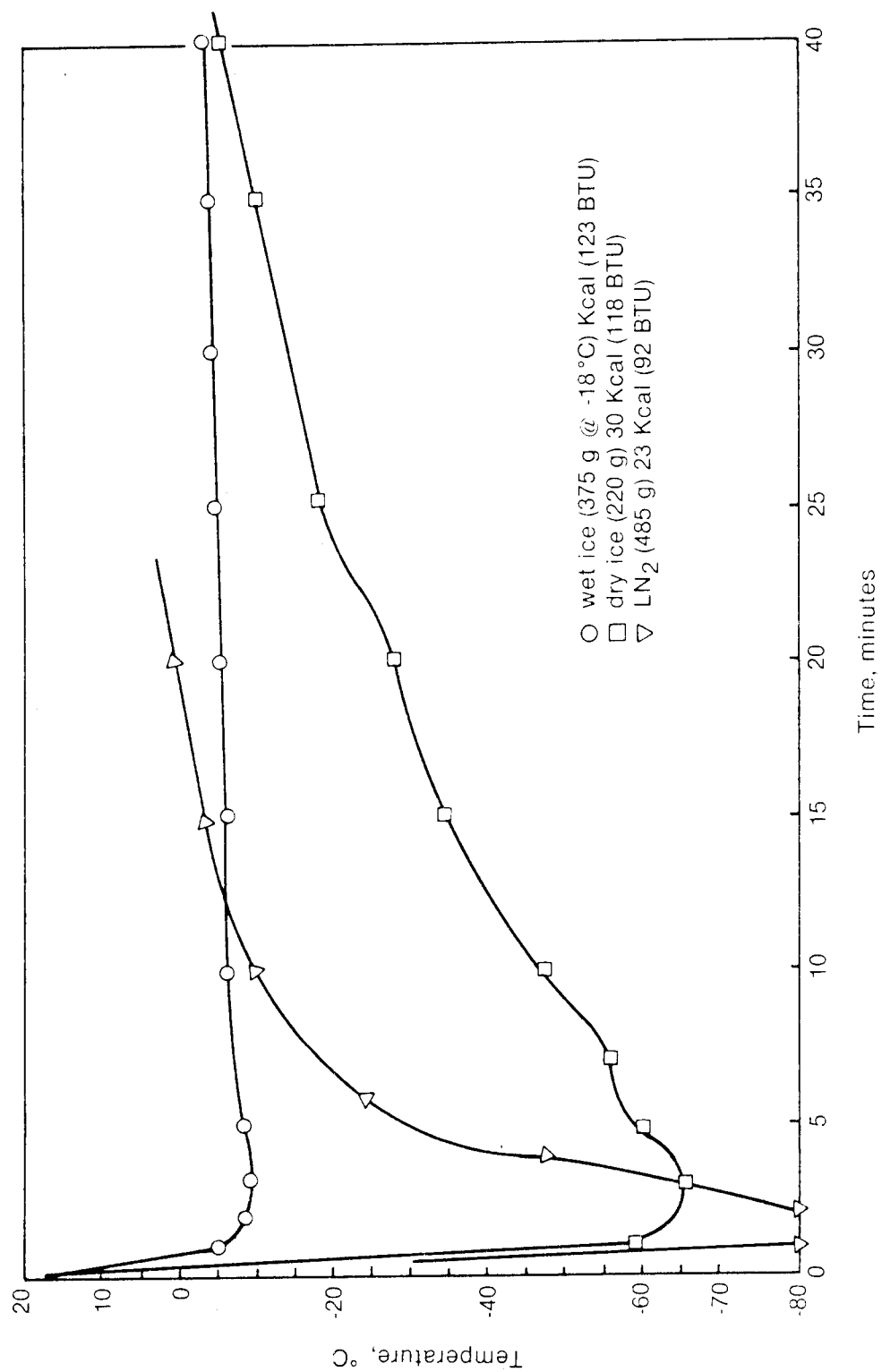ing coolant gases produced by the rapid phase-change caused by
the initially large spill-coolant temperature difference. The
general test results are compiled in Table 4.

Determination of Achievable Vapor Concentration

A series of tests was conducted with the apparatus shown in
Figure 2b, to measure the influence of candidate coolants on
vapor concentrations over a simulated spill. Acetone was se-
lected as the representative spill material, because it has an
appreciable vapor pressure (175 torr at 20°C [68°F]), a relatively
high threshold limit value (1000 ppm) and is a commonly trans-
ported solvent. The tests were beset by a number of problems;
although every effort was made to control the test variables.

The anticipated results were intended to provide indications
of the relative effectiveness of candidate coolants for suppres-
sing evaporation and to provide some measure of the reduction in
the size of the area that would be threatened by the dispersion of
a hazardous vapor cloud from the spill. While vapor concentra-
tions were consistently reduced by the addition of the coolants,
the data were incapable of quantitative interpretation.

There are three possible sources of error in these experi-
ments: 1) substrate heat content, 2) variable air velocity over
the spill, and 3) miscellaneous equipment problems. Steady
state temperatures of the spills indicated that the substrates
used in these tests did not permit adequate modeling of the heat
losses occurring from an open spill. Air velocities were
measured in the exhaust hood. The air velocity varied between
0.5 and 1 Km/hr (0.3 to 0.63 mi/hr). This may have influenced
the observed vapor concentrations.

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TABLE 4. RESULTS OF SCREENING TESTS

Representative Spill Material	Coolant	Observations
Acetic acid	water(s) carbon dioxide(s) nitrogen(l)	splashing, some of the ice floats even at first some splashing, vapor cloud formed, partial freezing vaporization and vapor cloud are slow, freezes evenly
Gasoline	water(s) carbon dioxide(s) nitrogen(l)	excessive splashing as ice goes to bottom foaming and frothing with some apparent entrainment rapid vaporization and vapor cloud with some apparent entrainment, most of liquid freezes
Lacquer thinner	water(s) carbon dioxide(s) nitrogen(l)	excessive splashing some splashing and a little frothing vapor cloud formed; apparently displaced liquid, partial freezing
Methylene chloride	water(s) carbon dioxide (s) nitrogen(l)	some splashing, ice floats on surface some splashing; particles wetted, producing rapid vaporization larger vapor cloud, does not freeze
Naphtha	water(s) carbon dioxide (s) nitrogen(l)	excessive splashing some splashing and some frothing with vapor cloud rapid vaporization and cloud formation with apparent entrainment
Toluene	water(s) carbon dioxide (s) nitrogen(l)	splashing some splashing with froth formation, rapid vaporization small vapor cloud and all liquid freezes evenly
Vinyl acetate	water(s) carbon dioxide (s) nitrogen(l)	excessive splashing some splashing; particles wetted with rapid vaporization small vapor cloud formed with some possible entrainment, portions of the liquid freezes

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Gas samples were drawn into evacuated glass containers from locations about 5 cm (2 in.) above the liquid surface. The influence of the escaping, cold vapors may have been responsible for the lack of reproducibility obtained from these samples. The glass containers were cleaned and evacuated prior to taking a sample. Some leaks were found in the stopcock seals after the tests with solid water were completed but it could not be determined if this had occurred before or after the analyses were performed.

Data from these tests are compiled in Table 5. The data clearly show that vapor concentrations can be reduced by the addition of coolants to spills of hazardous materials. Vapor concentrations were reduced to 25 percent of the untreated values by adding wet ice and to 10 percent or less of the untreated values by adding dry ice or liquefied nitrogen. It was not possible to determine the contributions of convective mixing or substrate heat transfer with this experimental arrangement, however.

Determination of Evaporation Rates

The third series of tests was performed with the apparatus shown in Figure 2c. The objective of these tests was to circumvent the experimental errors of the vapor concentration tests by a direct measurement of evaporative losses. These measurements were used to compare the relative effectiveness of each candidate coolant for reducing the hazards caused by vapors generated from accidental spills.

An accurate description of the evaporation and dispersion of vapors from an open spill requires the use of a mathematical model incorporating terms for all point sources. Several models have been developed by Sutton, Pasquill, Turner and others, referenced in a review paper by Slade (1968). Most of these models, and more recent variations, require computer calculations for solution, and were considered beyond the scope of this investigation.

All of these models rely upon the basic laws of diffusion and the interchangability of heat and mass transfer equations. Typical mass transfer equations such as,

$$dq/dt = DS \, dC/dX; \text{ and}$$

$$E = K_m P_{vap} S/F$$

where q = amount evaporated; t = time; D = diffusion coefficient; S = area of source; C = concentration of diffusion species; X = distance from source; E = evaporation rate; K_m = mass transfer coefficient; P_{vap} = vapor pressure and T = absolute temperature, are related by $K_m = D/RT$, where R = gas constant and that vapor concentrations are conveniently expressed in terms of partial

TABLE 5.   VAPOR CONCENTRATIONS MEASURED OVER A
250 cm² POOL OF ACETONE

Coolant	Acetone Concentrations @ Various Temperatures			
$H_2O(s)$	960 ppm @ 10°C (+50°F)	260 ppm @ -2°C (+28°F)	434 ppm @ -6°C (+21°F)	204 ppm @ -8°C (+17°F)
$CO_2(s)$	6520 ppm @ 12°C (+54°F)	2570 ppm @ -5°C (+23°F)	407 ppm @ -48°C (-56°F)	99 ppm @ -62°C (-80°F)
$N_2(l)$	146 ppm @ 17°C (+63°F)	88 ppm @ -8°C (+17°F)	13 ppm @ -25°C (-12°F)	39 ppm @ -140°C (-220°F)

pressures. The working equation used to correlate measurements made in these laboratory tests was:

$$E = AK_m\gamma \ln \left(\frac{P-p''}{P-p'} \right)$$

This equation represented the particular geometry and characteristics of our tests in terms of E = evaporation rate (g/sec); A = proportionality constant; K_m = mass transfer coefficient (sec/cm); γ = radius of simulated spill (cm); P = atmospheric pressure (N/m^2) and p' and p" = vapor pressures at liquid surface and far removed (representing vapor concentrations).

Similar equations can be developed, starting from the Maxwell diffusion theory, to follow the form:

$$E/S = \frac{DPM}{RTF} \ln \left(\frac{P-p'}{P-p''} \right)$$

in which the additional terms are defined as S = area of spill (cm^2); D = diffusion coefficient (cm^2/sec); P = atmospheric pressure (torr); R = gas constant (cm^3 mm Hg/mol/°K); F = film thickness (cm) and M = molecular weight of diffusing species (g/mol).

The initial tests in this series provided experimental evaporation rates for representative spill materials that could be compared with theoretical values. Glacial acetic acid, acetone, methylene chloride, and isopropanol were selected for the tests. The results of these tests are presented in Table 6.

Acetic acid and acetone were selected as the representative hazardous materials for several tests in which the evaporation rate was determined after the addition of the candidate coolants. The tests were prepared by weighing 100 g (3.5 oz) of each material into a pyrex dish with a soil interliner. The amount of coolant used was calculated to absorb approximately 30 Kcal (119 BTU). This value was calculated from heat transfer approximations of 1200 Kcal/m^2 (440 BTU/ft^2) over an area of 250 cm^2 (39 in^2).

Glacial acetic acid was selected because it would freeze at approximately 16°C (61°F), with a heat of fusion of 45.9 cal/g (82.6 BTU/lb), and pose a formidable heat load for the candidate coolants. Acetone was selected because its thermophysical properties are typical of many low-boiling, hazardous materials. The results of these tests are compiled in Table 7 for comparison.

Coolant Availability, Storage and Application

An evaluation of the cooling capabilities and other pertinent data does allow appraisal of the potential candidates, but any coolant selected must be readily available or storable and

TABLE 6.   COMPARISON OF MEASURED AND CALCULATED
EVAPORATION RATES USING DRY ICE (T = -78°C [-110°F])

Material	Calculated Stefan Equation (g/cm^2/sec)	Experimentally Determined (g/cm^2/sec)
Water	0.0003	0.000013
Acetic Acid	0.0002	0.000012
Acetone	0.0039	0.0002
i-Propyl Alcohol	0.0077	0.0004
Methylene chloride	0.0080	0.0001

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TABLE 7. COMPARISON OF EVAPORATION RATES FOR REPRESENTATIVE HAZARDOUS MATERIALS

Simulant	Evaporation Rate ($g/cm^2/sec$) for Various Coolants			
	None $T = 23°C$ $(73°F)$	$H_2O(s)$ $T = 0°C$ $(32°F)$	$CO_2(s)$ $T = -78°C$ $(-110°F)$	$N_2(l)$ $T = -195°C$ $(-319°F)$
Acetic acid				
(experimental)	1.2×10^{-4}	0.5×10^{-5}	1.2×10^{-5}	$< 2 \times 10^{-6}$
(calculated)	2×10^{-4}	3×10^{-5}	$< 3 \times 10^{-5}$	n.a.
Acetone				
(experimental)	2×10^{-4}	1.2×10^{-5}	4×10^{-5}	not meas.
(calculated)	3.9×10^{-3}	7×10^{-4}	9×10^{-5}	n.a.

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techniques must be available to apply the material to the spill in a suitable form. Some consideration of these factors has been given to potential coolants earlier in the program. An in-depth review was made of the four coolants.

As a starting point, a survey letter was sent to a cross section of companies engaged in the marketing of the coolants and/or equipment for handling the coolants. The consensus of suppliers was that CO_2 systems be used. The advantages cited for their recommendation were the related usage, ready availability, and the existence of handling equipment which could be modified for this application. Spent CO_2 gas is not considered hazardous per se. It is heavier than air and stays near ground level until gradually dispersed by wind action. Depths of cold CO_2 gas at the point of application are expected to range from 0.5 to 1 meter (1.5 to 3.0 ft) maximum. They are usually visible, because of moisture condensation from humid air. For safety, oxygen concentrations should be monitored at the spill site since high CO_2 concentrations will displace the air and could pose an asphyxiation problem to personnel.

Dry ice was suggested as a feasible alternative if a crushing operation (with related packaging disposal) and particulate dispersal equipment could be evolved. Coolant quantities and costs could be lower with a properly developed system.

Subcooled wet ice was also feasible. For mobile operation, system design would require some equipment modification for optimum field use.

Liquid N_2 was considered to be the least feasible of the three candidate coolants because of high storage losses and problems of delivery to remote spill sites. Coolant storage and typical losses for the coolants considered are presented in Table 8. A summary of selected properties for the candidate coolants is presented in Table 9.

Solid Water --

Ice is commercially made and stored in either the wet (0°C [32°F]) or cooled (-18 to -28°C [0 to -20°F]) condition in forms ranging from 45 to 150 Kg (99 to 330 lb) blocks to 1 to 6 mm (0.03 to 0.24 in.) thick flakes. When stored at 0°C (32°F) in insulated bins, ice will experience losses of 1 to 2 percent per day due to melting. Cooled ice is kept relatively dry by a refrigerated annulus in the storage bin, which keeps losses almost negligible and keeps the ice free-flowing for one to two months.

Handling equipment for high volume operation will require some special design and/or modification. Shavers or crushers with related conveyors may not be a problem. Transfer up to 150 meters (490 ft) in plants is commonly accomplished with medium pressure blowers using cooled air. Such equipment may require

TABLE 8. COOLANT STORAGE LOSSES

Coolant	Container	Coolant Loss %/24 hr Day	Remarks
L N_2	Trailer	0.8	LOX, trailer specifications
	Storage	10.0	Liquid Carbonic quotation
L CO_2	Trailer	0.3	Chemetron skid without refrigeration unit
	Skid w/reefer	0	Mechanical refrigeration used
S CO_2 dry ice	Box w/blocks	1.7	Chemetron @ 21°C (70°F)
	Box w/pellets	3.0	Est. @ 2X block rate
S H_2O wet ice	Bin w/reefer	0	Flake ice, held at -17 to -12°C (0-10°F)
	Bin, insulated	1.0	Est. @ 1/2 S CO_2 rate

TABLE 9. SELECTED PROPERTIES OF CANDIDATE COOLANTS

Candidate Coolants	Temperature (°C)	Pressure (atm)	Cooling Capacity (cal/g)	Estimated Cooling Efficiency (%)	Cost $/ton (metric)	Cost $/ton	Coolant Costs for Typical Spill ($)
Wet ice	0	1	79.7	90	88 ± 22	80 ± 20	800 to 1000
	-17.8	1	89.4	90	132 ± 22	120 ± 20	700 to 900
Dry ice	-78.5	1	136	80	231 ± 22	210 ± 20	750 to 1050
Carbon Dioxide liquid storage	-17.8	20.4	66.7	45	210 ± 22	190 ± 20	1500 to 2500
45% flashed to snow	-78.5	1	61.2	70	210 ± 22	190 ± 20	1500 to 2500
Liquid Nitrogen	-196	1	47.8	30	220 ± 22	200 ± 20	1200 to 8000

as much as 5 kg air/kg ice (5 lb air/lb ice) depending upon system characteristics. Air lock modifications at the spill dispersal point may well suggest a low pressure fan system, as used in snow blowers, highway mulchers, or silage blowers. These would discharge directly over the spill area. Sized ice could be further pulverized by a fan blade and cracking nozzle attachments. High noise levels, requiring ear protection would be expected.

The simplest ice system would use a local supply of small-sized ice, delivered to the spill site by the supplier's truck. Deliveries could be expected within 2-4 hours, under normal working conditions, but delays of 16 hours or more could occur during off hours or during weekends.

A crusher unit would permit the use of large blocks. Refinements, such as a blower unit, would be needed to increase the effectiveness of the system.

More complex and costly ice systems could be devised for 1-4 hour response time supplying cooled flake ice. Flake Ice Company has a mobile ice generating system rated at 20 tons/day (18,000 kg). Six of these systems would be required to reach 5-tons/hr (4500 kg), the initial cooling rate. They would also require electrical power and water supply accessories.

A more feasible approach may be to use a mobile cooled ice storage bin system with field cooling and dispersing accessories. The bin could be filled by local suppliers or by an ice maker at the bin storage site.

Solid Carbon Dioxide --

Dry ice is commercially available in either block (23 kg [50 lb]) or pellet (1 cm [0.39 in.] diameter) forms, usually packaged in insulated boxed containing 1100 to 1300 kg (2400 to 2900 lb). Storage of the solid form of carbon dioxide usually incurs a loss of 1.5 to 3 percent per day due to sublimation, which would suggest procurement from local suppliers when needed. Crushing or shaving operations are usually performed just prior to use; 5 to 10 percent losses are experienced by suppliers during in-plant operations.

These high sublimation losses preclude storage beyond 1 to 2 weeks and have been a major factor in the decline of distribution depots. Storage and handling now favor the "no-loss" liquid-to-snow carbon dioxide systems but delivery times may be somewhat greater than expected from solid water suppliers. Portable liquid units are still not as universally available as block ice.

Handling equipment for spill applications can be similar to that used for applying water ice. A dry ice handling system would have the versatility of being applicable with water ice.

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Production of solid carbon dioxide at the spill site does not appear to be a feasible approach. Production would best be accomplished by the conversion of liquid to snow.

Liquefied Carbon Dioxide --

Liquefied carbon dioxide is also commercially available from storage in insulated tanks, where it is held as a liquid at -18°C (0°F) and 15,200 torr (20 atmospheres) pressure. The liquid carbon dioxide can be flashed to atmospheric pressure, through expansion nozzles, to produce solid "snow"). Maximum conversion efficiency is reported as 45 ± 3 percent. Delivery times should be within 2 to 20 hours during the normal work schedule, but may become a limiting factor during off hours or weekends.

Equipment is commercially available which has been designed for analagous service and could be adapted into the proposed system for treating accidental spills with a minimum of modification. Liquefied carbon dioxide would be transported to the spill site in insulated tank trailers. These are available in 16,000 to 23,000 kg (35,000 to 51,000 lb) capacities. They meet ASME/DOT specifications (including baffles) for road service, but do not include self-refrigeration units. Filling with sub-cooled liquid and insulating with 10 to 15 cm (3.9 to 5.9 in.) of polyurethane are enough to keep losses negligible, however, for the anticipated working times. The most economical system would use the tank trailers from local suppliers to supply the distribution system manned by the spill response team.

A fast-response system would include a mobile tanker fitted with a self-refrigeration system and dispersing hoses and nozzles. A typical unit which is available is a 5-ton (4500 kg), skid-type tank fitted with a self-refrigeration unit, two 30.5 m (100 ft) reels of 3.8 cm (1.5 in.) hose and playpipe nozzles.

Liquefied Nitrogen --

Nitrogen is transported and used in the liquid state for many commercial and industrial operations. It is normally transported in vacuum-insulated tank trailers at -196°C (-320°F) with pressure relief valves set at approximately one atmosphere. These trailers have capacities of 18,000 to 21,500 kg (40,000 to 47,400 lbs) and normally carry such accessories as a pump and flexible stainless steel hose which are capable of transferring this load in approximately one hour.

Transporting and storage losses are between 0.8 and 10 percent per day, which would preclude extended storage. The more feasible approach would be to use the supplier's tank trailer as the source of coolant, and couple this to a distribution hose and dispersal accessories which are part of the spill response unit.

Liquefied nitrogen is available within 2 to 20 hours in most sections of the country. Some supply problems could arise from the quantities required for larger spills and when needed on weekends and holidays.

The dispersal equipment for liquefied nitrogen would be 30 to 150 meters (98 to 490 ft) of 5 cm (2 in.) flexible hose, with couplings. This hose is available in 4.5 to 7.6 meter (15 to 25 ft) lengths, which would weigh between 13 and 45 kg (30 to 100 lb) each. Suppliers may be able to include extra hose with the trailer, on occasion, but it would be preferable to include extra lengths of hose and couplings with the spill response unit.

During the first half hour of cooling with the liquefied nitrogen system, at least 2 to 4 operators would be needed to assemble and deploy the hoses. Subsequently, the maintenance cooling operations could be handled by 1 or 2 men.

Dispersal of liquefied nitrogen to produce a uniform cover over the hazardous, volatile spill may be difficult. The combination of very low temperature and low density should make it possible to pour the nitrogen on the surface and have it spread over the solidified spill. Pouring may not be a practical approach. It is not possible at present to determine the losses which would result if the LN_2 would be sprayed onto the surface.

The alternative systems and components available for handling the three candidate coolants have been summarized in Table 10 for comparison. The costs, compiled in the last column, are estimates of the total equipment expenditures required to prepare a system for handling a spill of 1000 kg (2200 lb) covering an area of 50 m^2 (540 ft^2).

SELECTION OF CANDIDATE COOLANTS

With the data derived from the laboratory studies combined with the basic thermophysical properties it was expected that a selection could be made of not more than two coolants to be carried forward in the program. The possibility that two cool-ants might be selected existed because of cost and availability factors. For spills of flammable materials where vapor concen-trations of 1 percent or less would be acceptable (since gen-erally this lean a mixture will be below the lower flammability limit), a coolant with a lower cooling potential could be se-lected if cost and availability were favorable. For spills of toxic materials, where vapor concentrations below 100 ppm are de-sired, cost and availability factor would be secondary to the cooling capacity.

The results of the laboratory work clearly showed that CO_2 met minimum requirements of cooling capacity. Thus, a firm com-mitment was made to proceed with CO_2. A decision could not be

TABLE 10. SPILL COOLANT SYSTEM COMPARISONS

System	Coolant/Spill Amount (tons)	Coolant/Spill Cost ($x10³)	Operators Required (No.)	Equipment Description	Equipment Cost ($x10³)	Response Time (hr)	System Cost w/Full Equipment ($x10³, Max)
(0°C)	8	0.7		Suppliers Truck		2-20	
			5-10	Manual Distribution	2		3
			6-11	Crusher	2		5
			3-5	Blower/Conveyor	8-12		17
Solid Water	7	0.9		Suppliers Truck		2-20	
			4-8	Manual Distribution	2		3
			5-9	Crusher	2		5
(-18°C)			2-4	Blower/Conveyor	8-12		17
			3-5	Add CO$_2$ Refrigeration	.2-7		24
		0.3	2-4	Mobile Ice Bin	130-250	1-4	250
			3-6	Mobile Ice Plant	400-700	2-6	700
Solid Carbon Dioxide (-78°C)	5	1.1		Suppliers Truck		2-20	
			3-6	Manual Distribution	1-2		3
			4-7	Crusher	2-3		6
			2-4	Blower/Conveyor/CO$_2$	12-24		30
Liquid Carbon Dioxide (-18°/-78°C)	13	2.5		Suppliers Tanker		2-20	
			2-4	Hose and Snow Horns	2-15		18
			2-4	Mobile Tanker Systems	50-100	1-4	110
Liquid Nitrogen -196°C	39	8.0		Suppliers Tanker		2-20	
			2-4	Hose and Fittings	5-30		38

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reached on whether CO_2 was best in liquid or solid form; that decision depended in part on methods of storage and application.

Firm decisions on liquefied nitrogen and wet ice (either at 0°C [32°F] or subcooled) could not be made without additional testing on a larger scale than was possible in the laboratory. The need for these scale-up tests reflect concerns regarding both the effective application of liquid nitrogen and the ability of wet ice to provide sufficient temperature reduction in real spill situations. Because of these uncertainties a series of scaled-up tests were conducted.

SECTION 6

SCALED UP TESTING OF SELECTED COOLANTS

The inability to select a final coolant candidate based on the review of thermophysical properties, the laboratory test data, and other relevant information, indicated that further testing and an evaluation of the logistic factors was required. Accordingly, subscale field tests were conducted to provide additional necessary information.

SCALED UP TEST DESIGN

Test Size and Configuration

The conclusion reached at the end of the prior phase of the program was that a larger sized test was necessary to obtain data on a practical scale. A test spill size of 9.3 m² (100 ft²) was selected. This was in the form of a pit 3.05 x 3.05 x 0.30 meters (10 x 10 x 1 ft) deep. The bottom was leveled with packed sand and lined with a polyethylene sheet to prevent percolation of the spilled liquid into the soil. This allowed renewal of the pit after each test by replacing the liner.

Hazardous Spill Simulant

In selecting a spill test chemical, a material with a high vapor pressure at ambient temperature appeared most desirable since cooling effects would be most significant. A review of several potential materials resulted in the selection of diethyl ether as the simulant. It is a nontoxic, volatile liquid with very limited water solubility which limits the interference in the vaporization rate caused by dilution of the spill with water from melting wet ice.

Test Measurements

The basic measurement taken in each of the subscale field tests was the temperature reduction of the spill simulant, diethyl ether. Thermocouples were located in the spilled liquid and at a depth of 0.30 meters (1 ft) in the ground below the plastic liner.

Ether vapor concentratrations were measured downwind of the

spill with combustible gas detectors. Weather instruments were installed to measure wind direction and velocity along with ambient temperature.

Oxygen indicators were installed to determine the effect of CO_2 and nitrogen application on breathability downwind of the spill.

Procedures for Coolant Application

Since these were still preliminary tests to select a candidate material, complicated equipment to apply the coolants was not justified. Both wet ice and dry ice were crushed and applied to the diethyl ether pool as particles using hand shovels. The particle size distribution was not measured for either wet ice or dry ice.

Liquid carbon dioxide from portable tanks was discharged through snow horns. This resulted in a combined discharge of solid CO_2 snow and CO_2 vapor.

Liquefied nitrogen was applied to the spill as a liquid spray. The liquid was delivered to the test site in a tank truck. A 3.8 cm (1-1/2 in.) stainless steel hose connected to the tanker was used for delivery of the nitrogen to the spill surface.

COOLANT TESTS

All coolant tests were run with 208 liters (55 gallons) of ether in the pit giving an average depth of 2.5 cm (1 in.). Discussions of results for each test are given in the following sections. The results of the tests are plotted in Figure 7.

Wet Ice

For the wet ice tests, 380 kg (850 lbs) of ice was applied manually. The crushed ice was evenly distributed to give a visible ice layer over the spill surface. The spill temperature reduction was fairly rapid from 27°C to -5.5°C (80°F to 22°F).

The test duration was four hours. Over this time the temperature of the spill remained fairly constant and there was no need to add additional ice. In going from 27°C to -5.5°C (80°F to 22°F) the equilibrium vapor pressure was reduced from 580 torr to 150 torr. The measured vapor concentrations were in line with the equilibrium vapor pressure. Initial vapor concentrations were in the range of 5 percent. Some variation was observed which appeared to be caused by wind fluctuations. After the ice was applied, the vapor concentration declined to between 1 and 2 percent. This is close to the lower flammable limit of 1.85 percent for diethyl ether. It would be expected that vapor
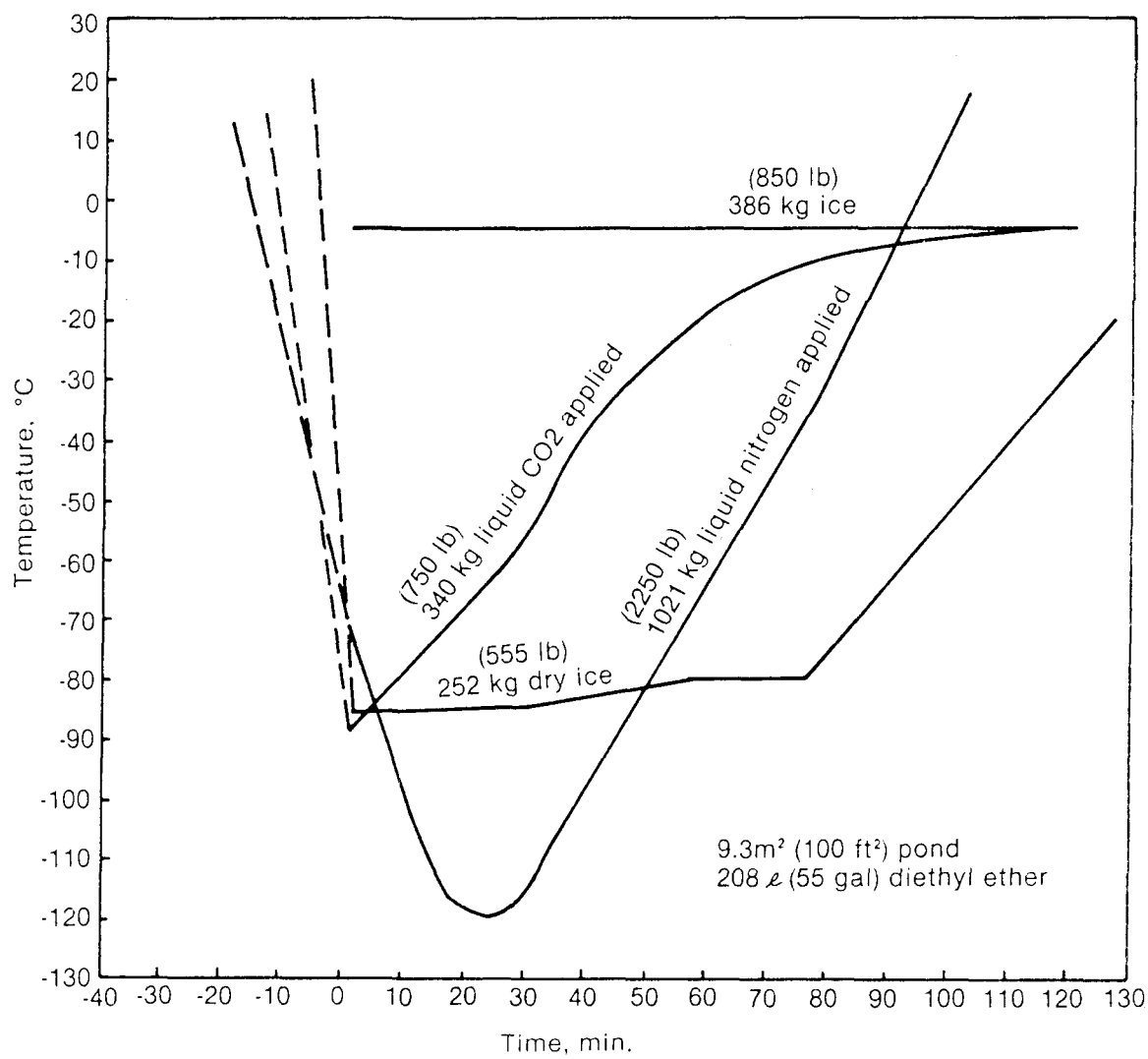
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Figure 7. Subscale field test results with ethyl ether.

concentrations would be well bel w the lower flammable limit down-
wind of the spill.

After the addition of ice the vapor level was still well
above the TLV of 400 ppm. Some reduction in the area downwind
of the spill wherein the vapor concentration exceeded the TLV of
400 ppm would be expected.

Dry Ice

In the dry ice tests, 252 kg (555 lbs) of crushed dry ice
was added manually to the diethyl ether pool. Efficiency of
application was about 90 percent with most losses occurring
through sublimation. Temperature reduction was from 20°C to
-85°C (68°F to -120°F). This is equivalent to a reduction in
vapor pressure from 442 torr to 0.45 torr.

No meaningful diethyl ether vapor measurements were ob-
tained. The CO_2 interfered with the combustion type gas de-
tectors. Estimates of the diethyl ether concentration based on
equilibrium vapor pressure put the level in the range of 600 ppm
by volume but this value is not consistent with values measured
in subsequent tests. The values obtained during the liquid CO_2
coolant tests were eventually used as a reference.

The 252 kg (555 lbs) of dry ice maintained the spill temp-
erature between -80°C to -85°C (-110°F to -120°F) for 1.3 hours.
At that point the spill began a slow increase in temperature,
reaching -20°C (-4°F) in fifty minutes. At this point the test
was terminated.

Liquid Nitrogen

Approximately 1020 kg (2250 lbs) of liquid nitrogen was
dispersed onto the spill from the tank truck. The application
of the cryogen to the spill surface resulted in intense boiling
and the formation of a condensed moisture fog that obscured the
test pit and made visual observations impossible. For this
reason the discharge was terminated after twenty minutes to ob-
tain a view of the spill. After the coolant discharge was term-
inated, several minutes elapsed before the fog dissipated suf-
ficiently to permit observation of the pit. At that time it
was clear that the diethyl ether had been frozen. No additional
liquid nitrogen was applied.

The temperature at the beginning of the test was 13°C (55°F).
Unlike the wet ice and dry ice tests, the spill temperature con-
tinued to decrease after termination of coolant application. The
minimum temperature recorded, -120°C (-184°F), occurred twenty-
five minutes after coolant application had ceased.

There was no leveling off of the spill temperature as was

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observed in tests with wet ice a d dry ice. After reaching a
minimum, the temperature immediately began to increase. It pass-
ed through the -85°C (68°F) range achieved with the dry ice less
than one hour into the test, and returned to ambient temperature
less than two hours into the test.

The equilibrium vapor pressure of diethyl ether at -120°C
(-184°F) is about 0.01 torr. Due to the inability to use com-
bustible gas detection in the dry ice tests, gas samples were
taken during this test and analyzed on a chromatograph. In the
downwind direction the pretest diethyl ether concentration was
9.3 percent. As the spill passed through the temperature mini-
mum, a downwind level of 116 ppm was measured. This is well be-
low the TLV but still above the odor threshold. Maintenance of
vapor concentrations below the TLV would require continued appli-
cation of LN_2. The 1020 kg (2250 lbs) of LN_2 added to the spill
in this test held the diethyl ether concentration below the TLV
for no more than 40 minutes.

Liquid Carbon Dioxide

Liquid carbon dioxide was discharged to the spill through
a snow horn. Three hundred forty kilograms (750 lbs) of CO_2,
the volume of the storage unit, were discharged at a rate of
90.7 kg (200 lbs) per minute. Expansion through snow horns con-
verts the pressurized, refrigerated liquid to a combination of
vapor and solid particles. Conversion efficiencies to particles
as high as 50 percent have been reported but in these tests the
conversion efficiency appeared to be no better than 15 percent.

It was subsequently confirmed that the observed 15 percent
conversion is consistent with the type of snow horns normally
available. Their purpose is fire extinguishment where the vapor
is the effective material. Snow formation is used as a means to
project the CO_2 beyond the reach of plain vapor discharge. Higher
conversion efficiencies are achievable only with special snow
horn designs.

The spill temperature achieved by the addition of dry ice
formed from liquid CO_2 by a snow horn approximated that attained
with the crushed dry ice. There was no maintenance of the low
temperature, however. Almost immediately upon conclusion of
solid CO_2 snow addition, the spill temperature began to increase.
This is attributable to the poor conversion to snow (15 percent)
which is the only effective coolant form.

Like the nitrogen application, the use of liquid CO_2 pro-
duced a heavy obscuring vapor cloud above the spill. Gas samples
taken downwind of the spill and analyzed on a chromatograph gave
a pretest diethyl ether value of 8300 ppm and a post application
value of 96 ppm. Both of these values are lower than those ob-
served in the liquid nitrogen coolant tests. The lower diethyl

ether concentrations were probab y caused by differences in ambient conditions -- wind speed, wind direction and air temperature. The significant feature in these test sequences is the ratio of the vapor concentration before and after treatment of the spill with coolant.

Since similar low temperatures were recorded in both the dry ice and liquid CO_2 tests, the vapor concentration measurements obtained are probably applicable to the dry ice test also.

COOLANT SELECTION

The basic importance of the data from the subscale tests is the difference in temperature achieved in the ether by each coolant and the maintenance of that temperature after application was stopped. On the basis of these data, crushed dry ice would be judged the superior spill coolant. Other factors need to be considered, however. A complete review of the four coolant candidates was made and a summary of the advantages and disadvantages of each is presented in Table 11.

Analysis of the total data clearly showed that liquid CO_2 was the least desirable of the four materials. The poor conversion efficiency and obscuring gas cloud are serious impediments when equivalent temperatures can be achieved with dry ice without those difficulties. Efforts were made to identify and obtain snow horns of better efficiency. Although the CO_2 industry quotes higher efficiencies, none were able or willing to provide MSA with either a price of equipment or a design to build to.

Choosing one from the other three coolants required assessing advantages and disadvantages. These are summarized for each coolant in Table 11. Wet ice was finally eliminated basically because of its limited temperature reduction. There were very few hazardous volatile materials with vapor concentrations that could be reduced below the TLV by cooling to near 0°C (32°F). Concentrations might be reduced below LELs but other more readily available techniques such as foam application can also provide such reductions.

The use of liquid nitrogen can result in the greatest reduction in spill temperature and for highly toxic materials with low TLVs, it may be the only coolant which would be effective. The problems of logistics, the need for large quantities, and the poor persistance of temperature reduction led to the selection of dry ice as the best all around coolant material.

Dry ice was chosen as the optimum material. It is applicable to the broadest range of volatile chemicals readily available in a suitable form, and with the least complications. This selection does not indicate that the other coolants are unsuit-

TABLE 11. CRYOGEN COMPARISONS

Cryogen	Advantages	Disadvantages
Liquefied Nitrogen	1. Cheaper than CO_2 on per pound basis 2. Extremely low temperatures possible	1. Vapor losses on storage 2. N_2 cloud significantly reduces visibility and oxygen levels in vicinity of spill 3. Larger quantities needed to cool spill than solid CO_2 4. Not as cost effective as solid CO_2 5. Possible entrainment of hazardous liquid by N_2 vapors
Liquefied Carbon Dioxide	1. No storage losses 2. Reasonable temperature reduction of spill	1. Higher liquid CO_2 losses upon application to the spill 2. CO_2 cloud significantly reduces visibility and oxygen levels in vicinity of spill 3. More expensive than solid CO_2 on the basis of amount actually applied to the spill
Solid Carbon Dioxide	1. Better cost advantage than liquid CO_2 or liquefied N_2 2. Less application losses than with LN_2 or liquid CO_2 3. Rapid cooling of spill 4. No problems with CO_2 cloud 5. Can be projected over distances 6. Readily available 7. Safer than liquefied N_2 or liquefied CO_2 to handle	1. Storage losses 2. Grinding necessary before application
Ice	1. Safest to use 2. Most readily available 3. Can be projected	1. Temperature of the spill is not reduced sufficiently 2. Increases the liquid volume of spill when the ice melts

able. In certain spill scenario: the cooling capability of wet ice might be adequate or the extremely low temperature capability of liquid nitrogen might be required.

SECTION 7

EQUIPMENT DEVELOPMENT

The selection of dry ice as the prime coolant brought with it a need for equipment to crush the commercially available 23 kg (50 lb) blocks to a suitable particle size, and to dispense the particles over the spill surface. Since this was primarily a feasibility study, extensive development of sophisticated optimized equipment was not warranted. This phase was constrained by directions to develop a prototype unit to allow the demonstration of feasibility using existing commercially available equipment to the greatest extent possible. The evolution of the necessary equipment for the dry ice distribution system was conducted within those guidelines.

REVIEW AND EVALUATION OF COMMERCIAL EQUIPMENT

Two basic components were defined for the desired system: a crusher and a conveyor. Certain auxiliary equipment could also be identified; these were primarily power train items whose selection was secondary to the two major components.

Crushers, Choppers, Hammermills, etc.

To provide a list of equipment types to be examined, a questionnaire was sent to a broad cross section of manufacturers of crushing, grinding, shredding and chopping equipment including those concerned with the generation of dry ice crystals for cloud seeding and fog dispersal. The majority of commercial equipment available (hammermills, soil and mineral grinders, and wood chippers), readily converted dry ice blocks into fine particles. The problem was that these devices produced a particle size distribution that contained far too many very small particles. This resulted in high coolant losses from sublimation and also severely limited the ability to project the crushed dry ice.

The basic design of equipment classified as shredders or chippers allowed modifications both of the speed (rpm) of operation and the number and spacing of tines. Through variation of these features, significant changes could be made in the size distribution of the dry ice particles. A number of modifications were tested with a wood chipper and a compost shredder. The initial effort was concentrated on the wood chipper since it contained an integral blower. Ultimately, however, the shredder was

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found to be capable of producing a more desirable size distribution and it was selected as the crusher portion of the system.

The unit selected was a Model 4G Shredder/Grinder manufactured by the W.W. Grinder Company, Wichita, Kansas. This model was chosen because it was the smallest unit of that design which would accept 25.4 cm (10 in.) cubes of dry ice. The crushed dry ice is discharged by gravity through a screen and down a chute located beneath the rotating tines. The dimensions and pertinent features of the unit are given in Table 12.

TABLE 12. SHREDDER/GRINDER (W.W. Grinder Co.,Model 4-G)

Power Train	0.67 KW (9 HP) at 3200 rpm
Hopper Size - Mill	43.2 x 43.2 cm (17 in. x 17 in.)
- Top	89 x 91.5 cm (35 x 36 in.)
Screen Opening	5.1 cm (2 in.)
Mill Speed	Max. - 2500 rpm Min. - 600 rpm

Conveyors, Blowers, etc.

A device was needed that could take the crushed material from the shredder and distribute it over the spill. The equipment compatible with most of the crushing units that were investigated involved blower mechanisms. In some cases mechanical conveyors (belts, buckets and the like) were available. Pneumatic conveying, where particles are blended with a carrier air stream rather than distributed by simply blowing, was an alternate mechanism.

Mechanical conveyors were deemed unsuitable since they could not project the dry ice particles over the spill area. Only minimal consideration was given to this approach.

While pneumatic conveying had certain advantages in mobility and flexibility of the discharge port, it was anticipated that excessive dry ice sublimation losses would result. The blowers appeared to have more potential as a dry ice dispersion mechanism than did pneumatic conveyors.

A number of blower types were evaluated and the simple snow blower design appeared to be the best for this application. Forage blowers and similar units that were considered could project crushed materials for greater distances. The snow blower was considered to be adequate for the spill size to be employed in the

demonstration phase of this progam. In addition, the snow blower incorporated an auger mechanism to feed the snow to the blower whereas the forage blowers did not. In this application it was believed that the auger feed would simplify mating the blower unit to the dry ice crusher.

The initial selection of a snow blower was based upon the mechanical needs of the ultimate equipment, but it was in-fluenced by a desire to make the equipment as simple as possible while utilizing existing commercial items. The snow blower appeared to provide both a pick-up and distribution capability.

INTEGRATE AND TEST PROTOTYPE

It was reasonably clear that even though the blower could project the dry ice particles over some distance, manipulation and movement of the equipment at the test site would be necessary. The crusher came mounted on a four wheeled frame to provide mo-bility. Integration of the snow blower into that frame would facilitate simultaneous movement of the two components. With that accomplished, testing of the unit could be conducted.

Component Integration

The crusher placement on the wheeled frame was such that a large open area existed below the discharge screen. A receiving tray was built into that area, which was closed on the bottom and three sides. The open side faced out from the crusher. The blower was mated to the crusher so that the auger pick up pro-truded into the tray and the blower body provided closure of the fourth side.

In operation, the crushed dry ice was fed by gravity into the tray where it was picked up by the auger, fed to the blower and discharged through a port at the top of the snow blower. A flexible hood was attached to the discharge port to allow some variation in the direction of discharge without moving the en-tire crusher-snow blower unit.

The snow blower frame was attached to the crusher frame. The method of attachment raised the blower so that its wheeled chassis was clear of the ground. Movement of the crusher frame thus moved the total unit.

Preliminary tests with this unit indicated certain other refinements were needed. An inclined baffle was incorporated into the crusher discharge to better direct the dry ice to the pick-up auger of the snow blower. The discharge port of the snow blower was moved from the top to the side of the unit to eliminate the bends in the discharge path. This benefited the discharge pattern and the throw distance.

Tests with dry ice blocks revealed two deficiencies. The crusher could process dry ice blocks faster than the snow blower could discharge the dry ice particles and the discharge pattern was not uniform. It was decided that for the feasibility study a slower feed rate into the crusher would be acceptable, with the understanding that the equipment could be optimized if the test results were negative.

The uneven dry ice discharge pattern from the snow blower reflected the particle size range. The larger particles could be projected several feet. The majority of the dry ice was discharged in the form of fine particles and the distance was a maximum of 3 meters (10 ft). For the feasibility tests this also was held to be adequate although well short of that necessary for a practical system. During these tests single blocks were fed through and the output collected. Weighing the output showed an average recovery of 75 percent.

The unit, comprised of the crusher/snow blower combination, is shown in two views in Figure 8.

Preliminary Field Tests

To further evaluate the unit assembled in the prior phase, a field test was conducted. The test parameters were based upon an enlargement of the 9.3 m² (100 ft²) subscale tests previously conducted.

The test impoundment was a 46 m² (500 ft²) steel pan, lined with polyethylene. Due to environmental decisions by local authorities, the test had to be conducted in a remote area even though the only consideration outside of the immediate test area was the odor. In retrospect this resulted in the test being performed in terrain and under conditions that might be more typical of an actual spill site.

A diagram of the test impoundment showing the location of gas samplers and the wind direction is given in Figure 9.

To conduct the test 1630 kg (3000 lbs) of ether were poured into the test impoundment. Air samples were taken to characterize the vapor concentration at five points around the spill impoundment area (Figure 9) during unrestricted evaporation before the application of dry ice. The samplers draw 1 liter (0.26 gallon) per minute through a 250 ml (0.07 gallon) sample bottle. The samplers were operated for 5 minutes to insure a representative sample. At that time they were sealed off and the entrapped material analyzed by gas chromatography.

After the first set of gas samples were taken, dry ice particles were added to the spill using the crusher-blower. The crusher was initially fed the commercially available 23 kg (50 lb)
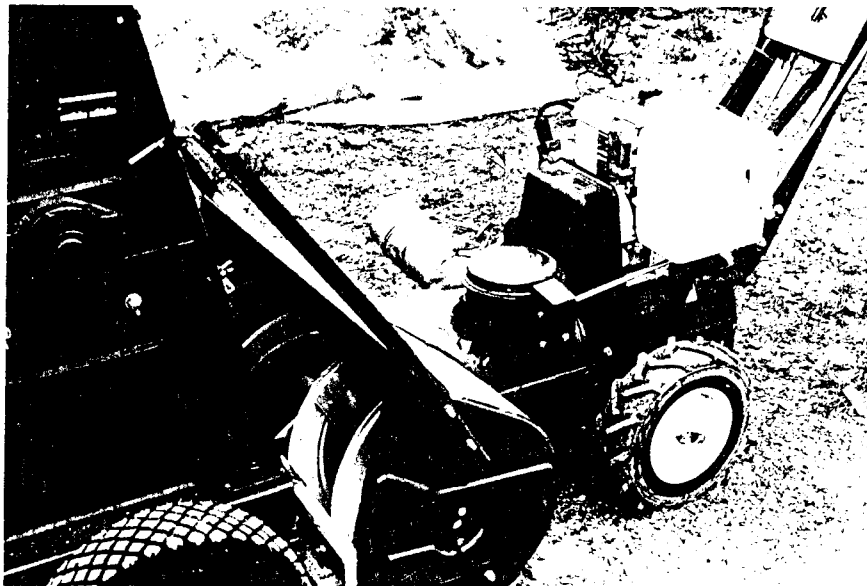
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Figure 8. Crusher/snow blower combination.

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Positions of sampling tubes
labelled 1 through 5
Wind predominantly from east
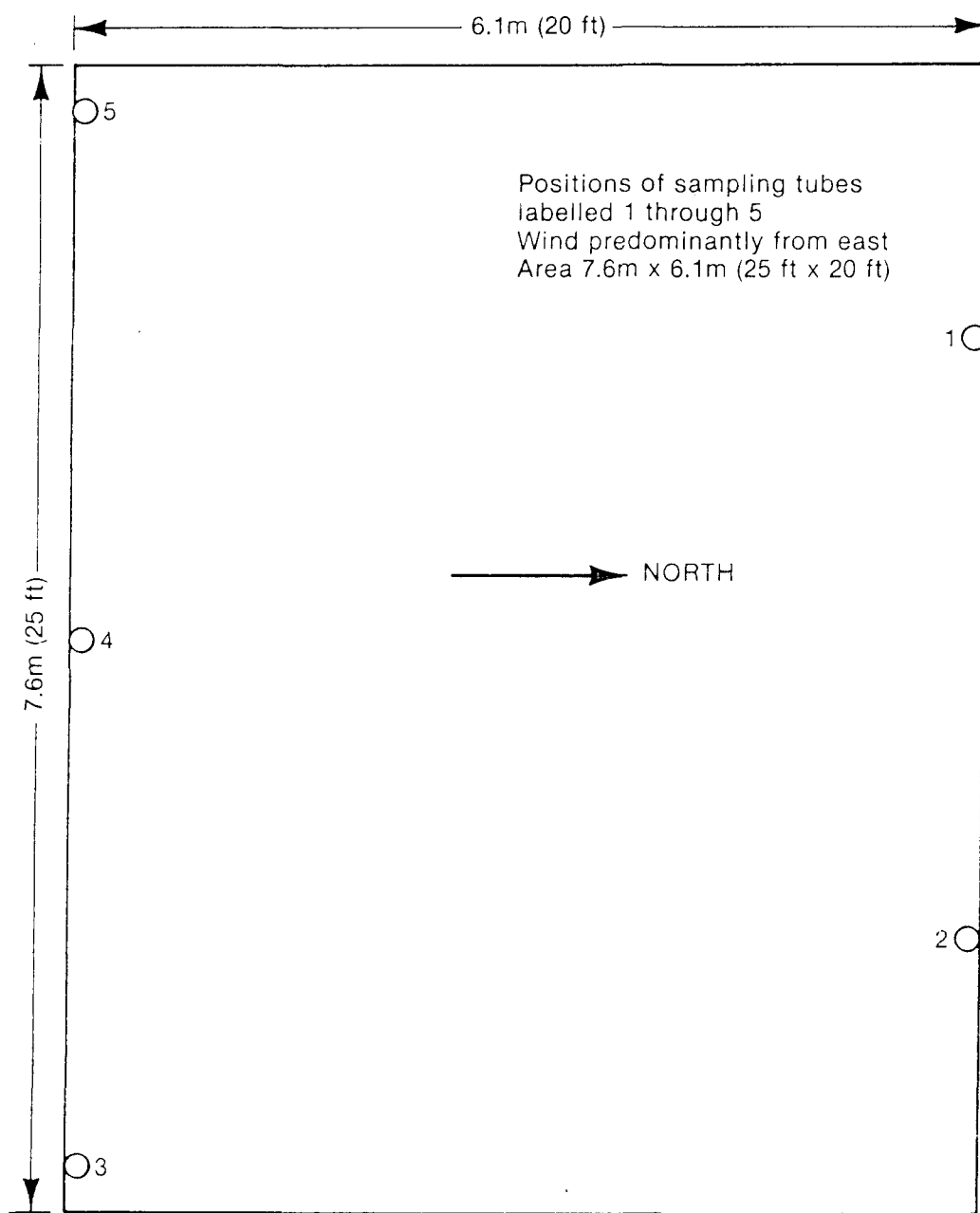Area 7.6m x 6.1m (25 ft x 20 ft)

Figure 9.   Diagram of spill impoundment area.

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dry ice blocks. As noted earlier, the crusher capacity is well in excess of that of the snow blower, and the intermittent feeding of the dry ice tended to stall the snow blower. To provide a more uniform feed, the blocks were manually broken into smaller pieces which were then fed to the crusher.

The short projection distance of the snow blower along with wind changes forced excessive movement and manipulation of the distribution system. The nature of the ground made this action more difficult than had been anticipated. The low oxygen created by the CO_2 vapor caused stalling of the gasoline driven engine of the blower.

The mating of the two components had used a simple design. It was inadequate for the conditions encountered and the linkages failed. During the latter half of the test, the crushed dry ice had to be applied to the spill manually.

The test was carried to completion even with these difficulties since the test data, spill temperature and vapor concentration measurements were felt to be meaningful. Seventy four blocks of dry ice were added (1680 kg [3700 lbs]) to the spill over a 35 minute period. Assuming an efficiency of 75 percent per prior measurements the effective application was 1270 kg (2800 lbs). Weather conditions at the site were clear with a light variable wind and an ambient temperature of 27°C (80°F).

The temperature of the spill pool was rapidly decreased from 20°C (68°F) to -63°C (-81°F). The lowest spill temperature recorded was -67°C (-89°F).

The vapor samples taken at various points around the spill gave significant values for four positions both before and after the dry ice application. Sample 2 was lost in the pretest sequences and Sample 1 was lost in the post test sequence. The results are given in Table 13. Samples 1 and 2 were taken downwind of the spill and Samples 3, 4 and 5 were taken upwind as shown in Figure 9. The upwind-downwind status is somewhat questionable since the wind was light and variable and all of the sample ports were 30.5 cm (12 in.) above the spill surface.

The reduction in the vapor concentration brought about by cooling the spill was significant, but the lowest diethylene concentration found was still about an order of magnitude greater than the TLV. Although the test could be considered successful in terms of the ability of dry ice to reduce the vapor hazard from the diethyl ether, it was a failure as far as the equipment design and performance was concerned.

EQUIPMENT REDESIGN

The analysis of the preliminary field test results concluded that the crusher portion of the equipment was satisfactory.

TABLE 13. DIETHYL ETHER VAPOR CONCENTRATION BEFORE
AND AFTER APPLICATION OF DRY ICE

Sample Location No. (see Fig. 9)	Before	After
1	13.9% (139,000 ppm)	lost cap
2	lost cap	0.5% (5,000 ppm)
3	11.7% (117,000 ppm)	0.9% (9,000 ppm)
4	8.3% (83,000 ppm)	0.3% (3,000 ppm)
5	40.2% (402,000 ppm)	0.8% (8,000 ppm)

Some optimization might be possible with tine size, shape, spacing, rotation, etc., but the existing design appeared adequate for the objectives of this program.

The dispensing portion of the unit was the problem area. Reconsideration was given to the two alternatives, mechanical conveying and pneumatic conveying. Mechanical conveying was ruled out. Its projection problems were considered to be worse than those encountered with the blower and of sufficient magnitude that they were not offset by a potential of uniform distribution of dry ice independent of particle size range.

This left pneumatic delivery as the only viable alternative. The existing technology would indicate that such delivery is feasible and that commercial equipment existed which could be adapted to this application. The drawback came from anticipated sublimation losses due to high air to particle volume ratios and long flow paths in hoses. In the absence of any other viable alternative, it was decided to test a pneumatic delivery system in combination with the crusher.

Selection and Adaptation of a Pneumatic Conveyor

As part of its mining equipment line, MSA markets a pneumatic conveyor system designed for crushed limestone. This unit, termed a "rockduster" consists of a blower, a hopper, an auger feed screw and a hose discharge. It is driven by an electric motor in an explosion-proof housing meeting Bureau of Mines standards.

A small unit with a capacity of 540 kg (1200 lbs) per minute throughput was available. In the interest of time as well as cost along with the availability of engineers familiar with the unit and spare parts and optional equipment, a decision was reached to use this unit for the evaluation of pneumatic conveying.

Some investigative tests were run by abutting the two units. In the first run about 68 kg (150 lbs) of dry ice was fed through the crusher-duster. About 65 percent of the charged material was delivered as particles. This was a greater sublimation loss than with prior combinations but was considered to be acceptable.

Using 30.5 m (100 ft) of hose it was possible to reach the far side of the 7.6 m (25 ft) wide test pit from the near side. Particulate distribution was uneven as anticipated ranging from 0.32 cm to 2.54 cm (1/8 in. to 1 in.) in diameter. Only the larger dry ice particles could be projected to the far side.

As with the snow blower, the capacity of the crusher is significantly greater than the capacity of the pneumatic unit.

Excessive feed through the crusher results in a build up of dry ice particles in the hopper. The particles bridge and weld, shutting off feed to the auger at the bottom of the hopper. This bridging is easily broken up mechanically but it is not an acceptable situation.

Several modifications were made in the rockduster in an attempt to alleviate the bridging. The sides of the hopper were made as smooth as possible but the reverse slope of the walls, the main factor, could not be readily changed. Some air from the blower was diverted back into the hopper to create agitation in that area. It was beneficial but not a total answer.

The major modification was increasing the size of the auger for a faster solids throughput. This provided some improvement of throughput but resulted in some cases in plugging at the nozzle-auger interface. This appeared to be due to the decreasing distance between flights along the length of the auger. This tended to compact the solids as they move through the auger section. Because of the nature of the dry ice, the particles self weld and agglomerate.

The size of the auger is 42.9 cm (16 7/8 in.) long with the flights in the hopper being 8.9 cm (3 1/2 in.) diameter decreasing to 4.8 cm (1 7/8 in.) diameter in the feed tube extending off the hopper. Plugging resulted because the 4.8 cm (1 7/8 in.) diameter section had flights decreasing from 5.1 cm (2 in.) pitch spacing to 3.8 cm (1 1/2 in.) spacing. Another auger of the same size was installed with 5.1 cm (2 in.) pitch spacing on all the flights. This eliminated the compacting effect of the decreasing pitch of the flights and the plugging at the end of the auger.

To minimize back pressure the standard 3.8 cm (1 1/2 in.) hose was replaced with a 5.1 cm (2 in.) inside diameter hose. Broadcasting distance was not appreciably affected and large particles were discharged a distance of 15-23 meters (50-75 ft). To minimize fines production, crusher speed was reduced from about 900 rpm to 600 rpm by pulley wheel change and an increase in the size of the integral screen. These had some influence but it was small. Any significant improvement in the operating characteristics appeared to lie with major changes in crusher and/or conveyor design.

After completing modifications, the unit was operated continuously for approximately 19-20 minutes with a throughput of 260 kg (575 lb) dry ice or a rate of about 13.6 kg (30 lb)/minute. Dry ice blocks used were 25.4 cm (10 in.) square by about 2.54 cm (1 in.) thick (2.40 kg [5.3 lb]/ea) fed at a rate of one block about each 10 seconds. Measurement of dry ice input to dry ice output from the discharge hose indicated about a 50 percent conversion. The basic limitation was a dry ice feed of about

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13.6 kg (30 lbs) per minute. For the field demonstration to be conducted, this was deemed adequate.

Two further modifications were made in this combination of units which had no relation to system capacity or efficiency. One modification mated the two units into a single entity and the other unified the power source.

The rockduster comes mounted on a three-wheeled frame. To make the dry ice distribution system, the crusher was removed from its wheeled frame and mounted above the hopper of the rockduster so that both units were not supported by the three-wheeled frame.

The rockduster is driven by an explosion-proof electric motor but the crusher has a gasoline engine. The engine can be compromised by the presence of CO_2 vapor and it could be a source of ignition of flammable material spills such as the diethyl ether test spill liquid. To simplify the system, the gasoline engine was replaced with an explosion-proof electric motor. Both motors could be driven by a remote diesel/electric generator.

The final unit as deployed for the field demonstration is shown in three views in Figure 10, with an isometric schematic drawing shown in Figure 11.
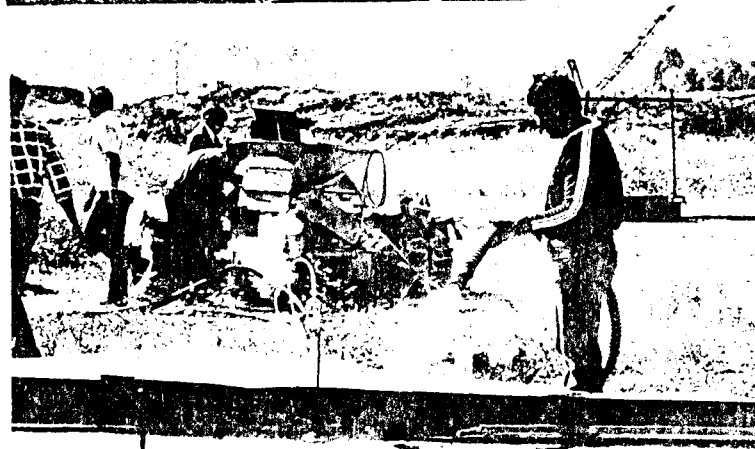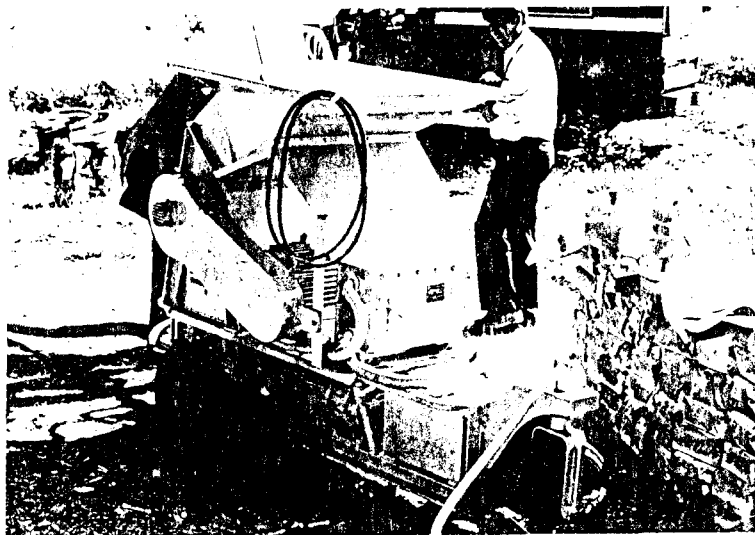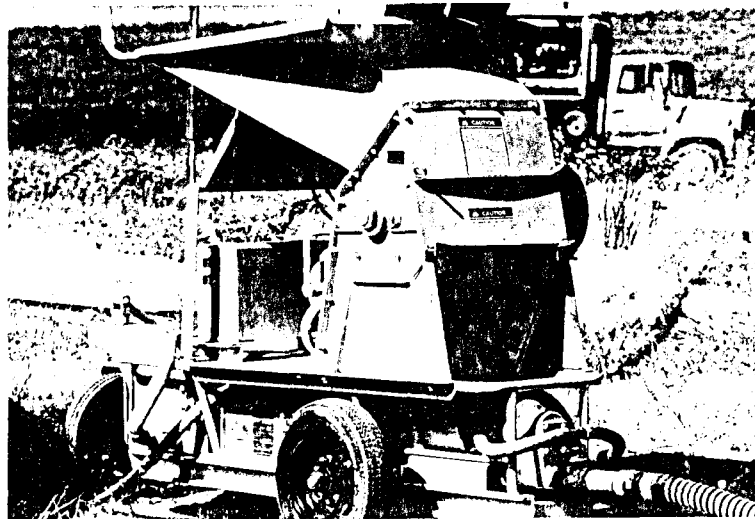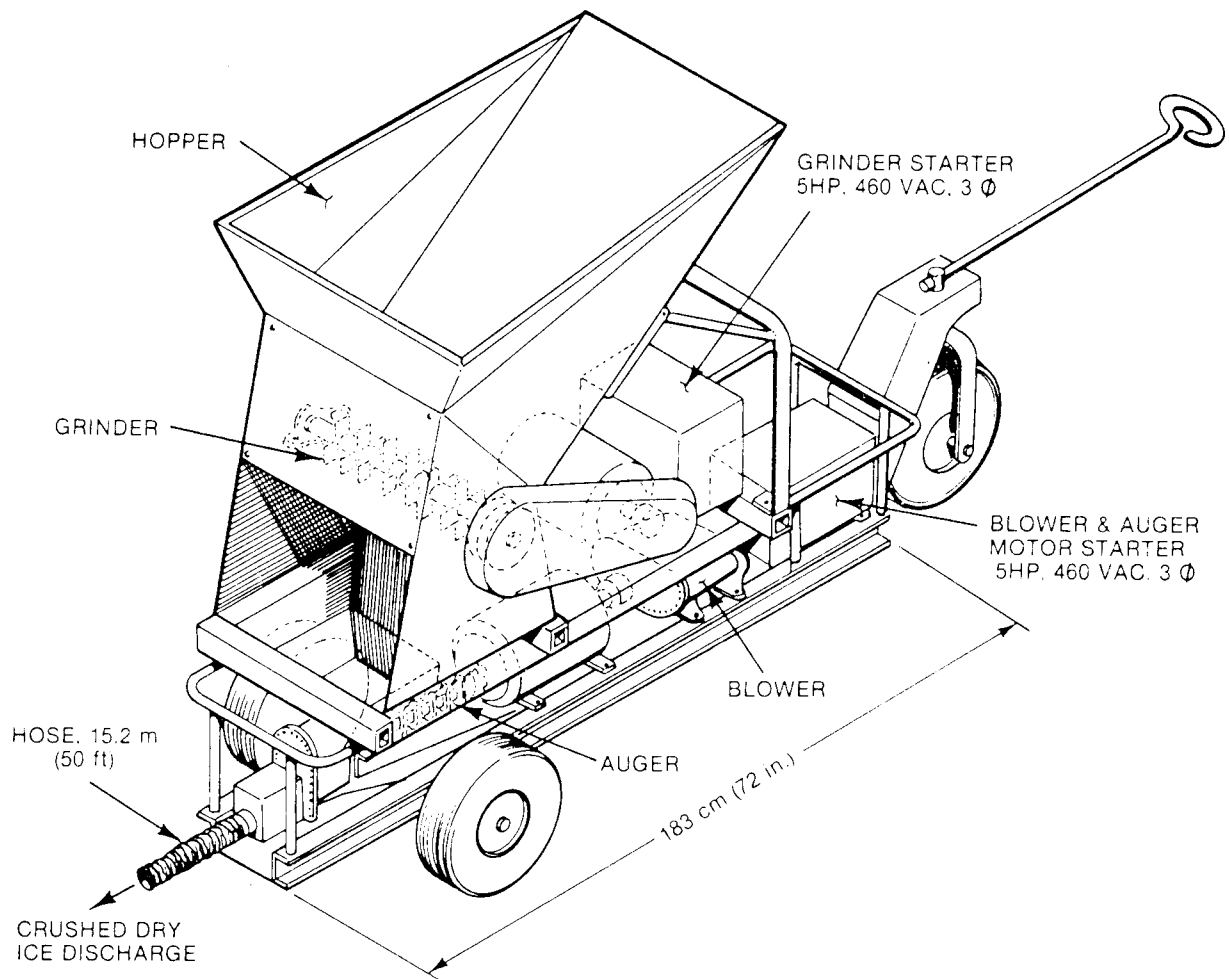
Figure 10. Field demonstration unit.

HOPPER

GRINDER STARTER
5HP, 460 VAC, 3 Ø

GRINDER

BLOWER & AUGER
MOTOR STARTER
5HP, 460 VAC, 3 Ø

BLOWER

HOSE, 15.2 m
(50 ft)

AUGER

183 cm (72 in.)

CRUSHED DRY
ICE DISCHARGE

Figure 11. Dry ice distributor.

SECTION 8

FIELD DEMONSTRATION

The final phase of the program was the conduct of a demonstration of the feasibility of cooling as a technique to control the vapor hazard from spilled volatile chemicals. This demonstration was designed to use the crusher-pneumatic unit evolved in prior phases of the program.

DEMONSTRATION TEST DESIGN

The final demonstration test design paralleled that previously used to evaluate the crusher-snow blower combination. The test involved a spill area of 46.5 m² (500 ft²) in the form of a polyethylene-lined steel pan 7.6 x 6.1 x 0.3 m (25 x 20 x 1 ft) deep. The impoundment was set up in the same manner and same area of the prior field test.

Diethylether was chosen as the spill simulant for reasons previously described; it is a highly volatile, essentially non-toxic and basically nonwater soluble liquid. Seven hundred fifty-seven liters (200 gallons) of ether was set as the spill volume. Eight hundred sixteen kilograms (1800 lbs) of dry ice coolant in the form of 25.4 x 25.4 x 2.54 cm (10 x 10 x 1 in.) slabs was available for the test.

The spill site was monitored at five points around the periphery of the test pit using gas samplers. The samplers draw one liter (0.26 gallon) per minute through a 250 ml (0.066 gallon) sample bottle. Samples were designed to be taken after charging the ether to the test pit and again after maximum temperature reduction was achieved.

In addition to gas samples, spill temperature measurements were also planned. Weather instruments were incorporated into the test plan to measure wind direction and speed along with ambient temperatures.

FIELD TEST OPERATIONS

The field test was conducted on a clear day with an ambient temperature of 21°C (69.8°F). Wind speed averaged 32.2 kph (20 mph). Due to unevenness of the test site, difficulty was experienced in leveling the test pan. This caused an uneven dis-

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tribution of the ether in the tray. The ether was restricted to
the upwind end of the tray covering an area 7.6 x 3.05 meters
(25 x 10 ft). This caused the sensors on the downwind side of
the tray to be about 3.05 meters (10 ft) away from the edge of
the spill rather than at the edge.

After initial vapor concentration samples were taken, dry
ice was applied to the liquid in the tray using the crusher-
pneumatic conveyor system developed during the program. The
crusher-pneumatic system was located about 25 meters (80 ft) up-
wind of the spill area. A diesel generator set located about
152 meters (500 ft) from the dry ice unit provided power to the
two electric motors.

Thirty and a half meters (100 ft) of hose was connected to
the discharge port of the pneumatic unit. Dry ice blocks were
fed to the crusher at an average rate of 13.6 kg (30 lbs) per
minute. The crushed dry ice particles were discharged through
the hose onto the spill surfaces using 2.3 m^3/min (80 ft^3/min)
of air at 31.5 m/sec (100 ft/sec) using a 3.8 cm (1.5 in.)
diameter hose. Preliminary tests had given an application effic-
iency of 50 percent for a 6.8 kg (15 lbs) per minute application
of dry ice.

The temperature of the spill pool was monitored during dry
ice application and for an extended period after application
was terminated. A maximum temperature reduction of -65°C (-85°F)
was achieved after 20 minutes of discharge. The method of appli-
cation used to distribute the CO_2 over the spill surface required
continuous movement of the discharge across the spill surface.
The maximum of -65°C (-85°F) was achieved during the time of
direct dry ice application to that area where temperature was
being monitored. As the discharge is moved over the surface of
the spill the time interval between discharge at a specific
point and the return of the discharge to that point was of the
order of two to three minutes. In that interval temperature
variations of as much as 10°C (18°F) were observed. Thus, the
avarage temperature at any point in the spill pool was about
-60°C (-76°F). Dry ice was discharged for 30 minutes, consuming
408 kg (900 lbs). Because of sublimation the amount actually
applied to the spill is estimated at 50 percent of that quantity
or 204 kg (450 lbs).

When dry ice discharge was stopped the temperature of the
pool increased within 30 minutes to -30°C (-22°F). The rate of
rise slowed with time as would be expected. It leveled off to a
slow rate of rise above -20°C (4°F) and was still below -10°C
(14°F) after two hours. A plot of the temperature-time profile
is given in Figure 12.

Ether vapor concentrations were measured before dry ice dis-
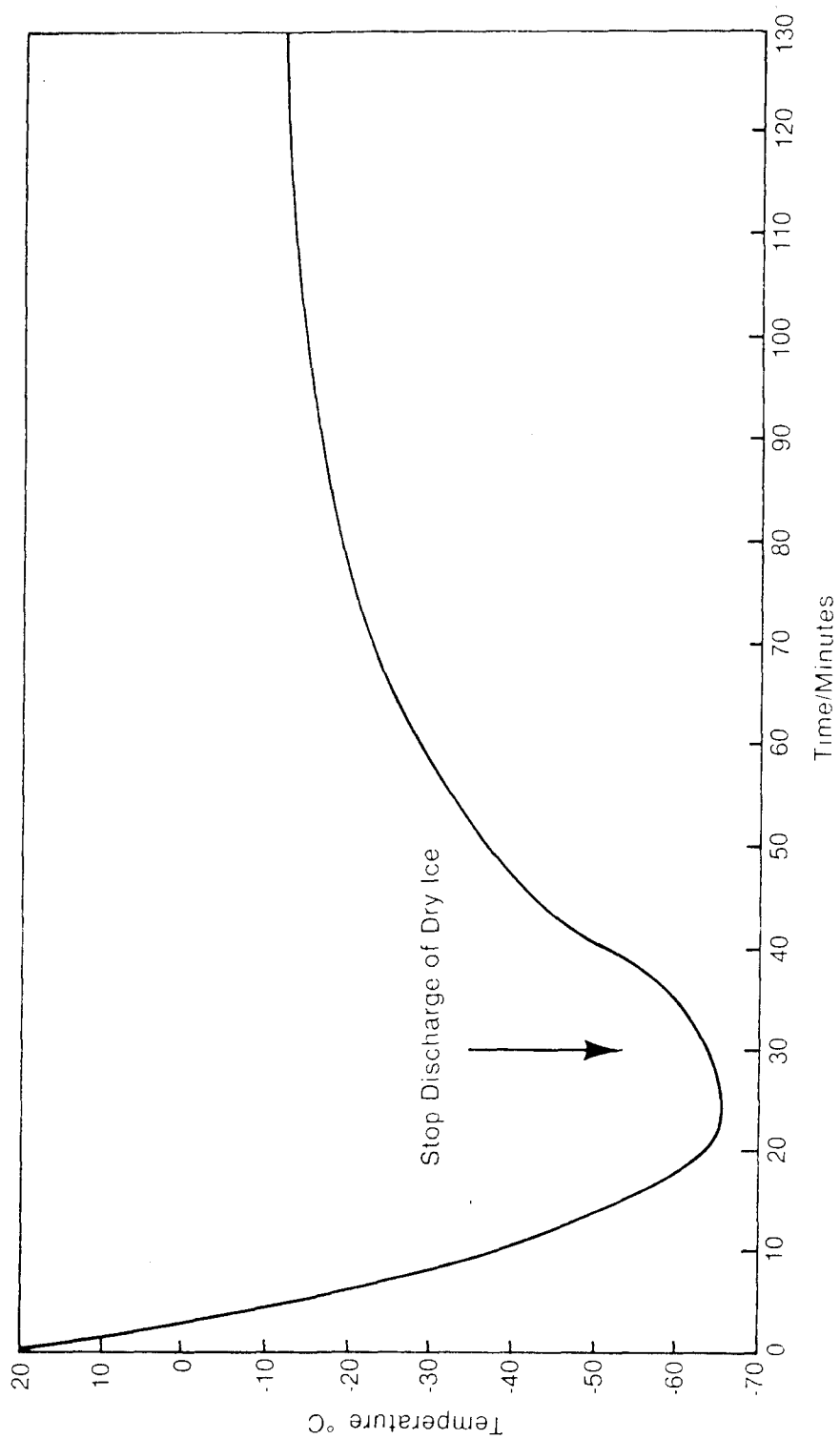charge was initiated and again after 30 minutes of application.

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Figure 12. Cooling rate vs time for dry ice treated ethyl ether pool.

The values obtained vary as a result of location and wind effects. Thus the observed vapor concentrations provide only a relative measure of effectiveness.

Sample stations 1 and 2 were located at the upwind edge of the spill pool and locations 3, 4 and 5 were at the downwind edge of the impoundment which was approximately 3 meters (10 ft) downwind from the edge of the spill pool as previously noted.

The analysis of the samples gave the following results in ppm:

Sample Station	Before Dry Ice	After Dry Ice
1	6,400	80
2	10,800	350
3	3,800	80
4	2,100	430
5	2,300	540

The scatter is too great for any absolute quantitative analysis but it is clear that the cooling has markedly reduced the rate of vapor release from the ether. The sublimation of the dry ice causes surface agitation which probably exaggerates t he vapor release. The temperature reduction decreased the equilibrium vapor pressure from 535 torr at 20°C (68°F) to 4 torr at -60°C (-76°F).

SPILL SCENE CLEAN UP

The final task of the program concerned an appraisal of the clean up procedures which would be appropriate for the cooled fluid and those interferences which might occur. For the situation where the cooled spill remains liquid, such as with the diethyl ether, the benefit of the coolant is to slow materials loss to the environment through vaporization. This does allow evaporation of the spill at a rate which would be slow enough that the TLV would not be exceeded for the life of the spill or would be exceeded only at the immediate spill area.

The number of materials which might be treated in the above manner is probably small. It is also probable that only small spills could be allowed to evaporate although spills in remote or difficulty accessible areas might be best dissipated through slow evaporation.

The obvious course of action is to pick up the spill or chemically treat it in place. The cooling process should not interfere with pickup by vacuum trucks, the EPA Emergency Collection System or similar procedures using collection tanks or bags. The

dry ice particles that might be entrained in the spill are small enough to pass through hoses and valves. CO_2 release within the container may necessitate procedures for venting over pressure and/or limit the volume which could be drawn into a given container size.

Chemical treatment needs to be addressed on an individual basis. Chemical reactions which are exothermic would be counter productive to the cooling process. Such action would need to be evaluated with reference to the benefits of chemical treatment.

Since CO_2 is not highly soluble in most of the materials to which the cooling process might be applied, there should be little retention to interfere with ultimate disposal procedures such as containment or incineration.

If coolant application would convert the liquid to a solid, clean up procedures would change. If the temperature of the spilled material is decreased well below its freezing point, it would be possible to pick up the material mechanically as a solid. Except for small spills where shoveling by individuals could be employed, mechanical pick up may be problematic. Heavy equipment is not designed to skim materials nor to work rapidly.

Solid to solid heat transfer is considerably slower than solid to liquid and in practice it may be difficult to subcool the spill very far. If subcooling is difficult, cooling could be used to hold the spill in a frozen condition until clean up equipment adaptable to a liquid is in place. At that time, cooling would be discontinued. As the spill warms and melts the cold liquid can be picked up and transferred to temporary containment or treated chemically if that is advisable.

In terms of clean up and/or recovery of a spilled chemical, the presence of the coolant does not appear to offer any serious interference. It must be constantly recognized, however, that the carbon dioxide can pose a life hazard to personnel in the spill area due to oxygen displacement. All personnel working directly on the spill would probably require some sort of breathing protection due to the nature of the spill. Self-contained breathing apparatus would be preferred to canister gas masks. Canister units cannot protect against the aphyxiation hazard of high CO_2-low oxygen atmospheres. The spill area atmosphere should be continuous monitored. The spill area must always be considered dangerous. Impairment of work skills or conscious processes due to reduced oxygen levels can have dramatic consequences.

EVALUATION OF COOLING AS A MECHANISM OF VAPOR HAZARD CONTROL

The work which has been conducted during this project has well established the feasibility of cooling to reduce the vapor

hazard from spilled volatile chemicals.   There are some areas where improvements could be made in the dispensing equipment but these are not beyond technology.   The question which remains un-answered concerns the practicability of the coolant system.   A series of questions need to be answered in assessing practic-ability:

- To how many spills would the cooling technique be applicable?

- Of these, what number could be treated by an alternate procedure?

- Do the alternate procedures give commensurate results or do they possess advantages in terms of logistics, deployment or application which would justify some reduction in efficiency?

The answers to these questions allows determination of the number of spills for which cooling would be chosen as the most effective procedure.   This gives a base to establish the de-sirability of investment in the equipment necessary to effectively utilize the coolant technology.   The technology is completely de-pendent on the ready availability of both coolant and equipment and the ability to deploy and use it at the spill site.   Until these factors are established, any evaluation will be incomplete.

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16. ABSTRACT

Spilled chemicals that pose a hazard to the land and water ecosystems can also provide a significant vapor hazard. Although the vapors released by such chemicals may ultimately be dispersed in the environment with little long-term effects, they do pose a hazard to life and property downwind of the spill.

Among the vapor amelioration techniques that have been considered is the use of a coolant to lower the temperature of a spill and reduce its equilibrium vapor pressure. This program has been conducted as a feasibility study of that mechanism.

Four potential coolants were examined: water ice, dry ice, liquid carbon dioxide, and liquid nitrogen. Further evaluation based on laboratory studies and limited scaled-up tests established dry ice as the most versatile coolant choice.

Water ice does not cool sufficiently. Liquid nitrogen and carbon dioxide require large quantities of material, and produce a dense obscuring cloud that has some adverse implications.

Dry ice avoids the problems presented by the other coolants and is readily available at a reasonable cost, but a method is required for crushing and distributing the dry ice to the spill. A prototype unit was developed consisting of a crusher and a pneumatic conveyor to perform these functions.

A pool of diethyl ether with 2.23 m^2 (250 sq ft) of surface was cooled to -60°C (-76°F) using 408 kg (900 lb) of dry ice fed at a rate of 13.6 kg (30 lb) per minute. A measurable reduction in downwind vapor concentration was realized. Pool temperature was still below -10°C (14°F) 2 hours after dry ice discharge was terminated.

This program has established feasibility of the mechanism, but additional work is necessary to establish practicality, define materials to which cooling is applicable, and optimize the dispensing equipment.

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