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CHLORINE HAZARD EVALUATION FOR THE ZINC-CHLORINE
ELECTRIC VEHICLE BATTERY

Final Technical Report

By
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April 1980

Work Performed Under Contract No. AC02-78ET25405

Factory Mutual Research Corporation
Norwood, Massachusetts

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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ABSTRACT

This report presents an evaluation of the hazards associated with conceivable accidental chlorine releases from zinc-chlorine electric vehicle batteries. Since commercial batteries are not yet available, this hazard assessment is based both on theoretical chlorine dispersion models and small-scale and large-scale spill tests with chlorine hydrate (which is the form of chlorine storage in the charged battery). Six spill tests involving the chlorine hydrate equivalent of a 50 Kwhr battery indicate that the danger zone in which chlorine vapor concentrations intermittently exceed 100 ppm extends at least 23 m directly downwind of a spill onto a warm (30-38°C) road surface. Other accidental chlorine release scenarios may also cause some distress but are not expected to produce the type of life-threatening chlorine exposures that can result from large hydrate spills. Chlorine concentration data from the hydrate spill tests compare favorably with calculations based on a quasi-steady area source dispersion model and empirical estimates of the hydrate decomposition rate. The theoretical dispersion model has been combined with assumed hydrate spill probabilities and current motor vehicle accident statistics in order to project expected chlorine-induced fatality rates. These calculations indicate that expected chlorine fatality rates are several times higher in a city such as Los Angeles with a warm and calm climate than in a colder and windier city such as Boston. Calculated chlorine-induced fatality rate projections for various climates are presented as a function of hydrate spill probability in order to illustrate the degree of vehicle/battery crashworthiness required to maintain chlorine-induced fatality rates below current vehicle fatality rates due to fires and asphyxiations.

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Several members of the staff of Energy Development Associates (EDA) also provided technical assistance essential to the successful completion of the project. This assistance included responding to numerous questions about the zinc-chlorine battery design and operation and potential accident scenarios, providing advice on the synthesis of chlorine hydrate, and supplying Factory Mutual with apparatus for synthesizing hydrate for the large-scale spill tests. The authors are particularly grateful to Dr. Chen Chi, Mr. Peter Carr, Mr. Harry Bjorkman, Mr. John Schramm, and Dr. Satya Kodali of EDA for this assistance.

A key contribution to this study was made by the National Highway Traffic Safety Administration's Center for Statistics and Analyses, which provided relevant vehicle accident statistics. It should be noted that Factory Mutual Research extrapolated some of the Center's National Crash Severity Study Statistics without NHTSA endorsement and, therefore, the conclusions concerning casualty projections are those of Factory Mutual only.

Another contribution the authors wish to acknowledge is the representative insurance industry reaction provided by Mr. Carl Stidsen and others at Allendale Mutual Insurance Company and by Dr. Nathaniel Pulling of Liberty Mutual Insurance Company.

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I

INTRODUCTION

The zinc-chlorine battery currently being developed by Energy Development Associates (EDA) with Department of Energy (DOE) financial support is one of the leading candidate advanced electric vehicle batteries^{*}. Reported design specifications⁽¹⁾ for the first commercial EDA electric vehicle battery approach or exceed the 11 DOE performance and cost goals⁽²⁾ for advanced electric vehicle batteries. EDA is aiming to produce commercial electric vehicle batteries in the early 1980's, several years ahead of DOE expectations.

Besides satisfying performance and cost criteria, a commercially successful zinc-chlorine electric vehicle battery must be sufficiently safe to be driven on public roadways. The safety question is particularly interesting for the zinc-chlorine battery because chlorine is stored in the form of solid chlorine hydrate as opposed to the more conventional and more volatile liquid chlorine. A major emphasis in the study reported here has been to assess the chlorine toxicity hazard associated with the chlorine hydrate in the EDA battery.

A preliminary safety and environmental assessment of zinc-chlorine electric vehicle batteries has been performed previously by EDA⁽³⁾. In the previous study, Kodali, et al performed theoretical calculations of chlorine vaporization and dispersal following various hypothesized mishaps involving chlorine hydrate. Although their calculations indicated only a small danger zone downwind of the hypothesized mishaps, they acknowledged that more extensive analyses, together with experimental verification, are required to fully explore the zinc-chlorine battery safety question. The Factory Mutual study described in this report was motivated by the need for a more rigorous and independent assessment of the chlorine hazard.

The approach followed in the present investigation has been: 1) to identify worst-case accident scenarios which are expected to result in potentially hazardous chlorine releases; 2) to acquire experimental data on chlorine hydrate decomposition and chlorine vapor dispersal in these accident scenarios; 3) to conduct theoretical modeling to generalize, extend, and supplement the experimental results; and 4) to assess the implications of the chlorine hazard. The

* Another version of the zinc-chlorine battery is being developed by EDA with DOE and Electric Power Research Institute financial support for electric utility load-leveling applications.

major part of the effort was on the chlorine hydrate experiments described in Sections VI and VII. Relevant battery accident scenarios are defined in Section III. Theoretical models of chlorine dispersal are presented in Section IV for outdoor roadway scenarios, and in Section V for road tunnel mishaps. Insurance industry reactions to chlorine hazard are documented in Section VIII, and casualty projections are reported in Section IX. Before presentation of the hazard assessment, the battery itself is described in the following section.

II

BATTERY DESCRIPTION

2.1 BATTERY DESIGN AND OPERATION

The Energy Development Associates zinc-chlorine battery is based on the following two reversible reactions:

where the value of x in the second reaction ranges from 6 to 10. During charge, electrolytic decomposition of the aqueous zinc chloride electrolyte (first reaction) causes zinc to be plated onto one (high-density graphite) electrode while gaseous chlorine is liberated at the other (porous graphite) electrode. The chlorine liberated during charge is pumped to a refrigerated battery store compartment where the exothermic (18.6 Kcal/g-mole for $x = 8$) chlorine hydrate formation reaction occurs. During discharge, both reactions proceed in the reverse direction, with warm electrolyte (30°C) providing the heat required to decompose the cold chlorine hydrate (nominally at 9.6°C and atmospheric pressure) in the battery store.

Figure 2-1 is a flow schematic illustrating how the EDA electric vehicle battery operates. Electrolysis occurs in the cell stack as the electrolyte is pumped through the stack and into a sump at the bottom of the battery. As indicated in Figure 2-1, some electrolyte is also pumped to the hydrate store after flowing through a chiller and the chlorine gas pump. On charge, most of the chlorine hydrate actually forms in the three-phase-flow gas pump as chilled electrolyte at 0°C mixes with chlorine gas coming from the stack. The hydrate is filtered in the insulated store and cold electrolyte is returned to the sump via an intermediate heat exchanger in which there is some heat transfer from the warm electrolyte flowing in the opposite direction. Refrigerated coolant flow to and from the electrolyte chiller on charge is supplied from an external source not carried on the vehicle.

FIGURE 2-1 FLOW SCHEMATIC OF EDA ELECTRIC VEHICLE BATTERY
(reproduced with permission from reference 1)

During discharge, flow directions remain the same, but the electrolyte chiller is not operated. Thus, warm electrolyte is pumped into the hydrate store to decompose the hydrate at a rate dictated by the chlorine demand of the reverse electrolysis reaction in the cell stack. The liberated chlorine gas is injected into the electrolyte on the pressurized side of the electrolyte pump. As discharge proceeds, the zinc chloride concentration of the aqueous electrolyte continually increases to a maximum value of about 20% at the fully discharged state.

Control of electrolyte and coolant flow rates is accomplished by a pressure sensor located in the stack gas space (along with a back-up sensor in the store) and wired to solenoid valves in the flow lines. The stack pressure is less than atmospheric pressure in order to maintain a low level of dissolved chlorine and thereby improve cell electrochemical efficiency. Store compartment pressure is nominally 5 psig (34.5 kPa) above stack pressure to facilitate electrolyte and chlorine gas return to the stack. Store pressures and chlorine gas flow rates during charge and discharge are given in Table 2-1 for an electric vehicle battery with a 50 kWh output capacity. Battery compartment sizes are also listed in Table 2-1. More detailed design and operating specifications are available in the various EDA reports.^(3,4,5)

The EDA electric vehicle battery hardware configuration available as of this writing is shown in Figure 2-2. The actual commercial battery configuration will depend on the specific vehicle in which it is to be installed. The 50.4 kWh battery shown in Figure 2-2 has overall length x width x height dimensions of 53 x 21 x 21 in. (1.53 x 0.53 x 0.53 m) and weighs approximately 500 Kg. The hydrate store compartment is a separate sealed container inside the polyvinyl chloride lined fiberglass battery case. Under normal operation, no chlorine should be emitted from the battery. The external connections indicated in Figure 2-2 refer to electrical connections and coolant flow connections during battery charge.

The EDA preliminary safety report⁽³⁾ described several special safety features and interlocks which are proposed for the commercial battery configuration. For example, the battery is supposed to be embedded into a foam layer in the vehicle chassis. Chlorine absorbent (perhaps some type of caustic agent) will be distributed within this foam layer to absorb chlorine inadvertently

TABLE 2-1

50.4 kWh BATTERY DESIGN PARAMETERS
RELEVANT TO CHLORINE MANAGEMENT

TOTAL CHLORINE CONTENT	41 Kg	
HYDRATE STORE VOLUME	126 liter	
VAPOR SPACE IN CELL STACK	28 liter	
VAPOR SPACE IN STORE	4 liter	
PARAMETER	CHARGE	DISCHARGE
CHLORINE HYDRATE MASS ($\text{Cl}_2 \cdot 8\text{H}_2\text{O}$)	124 Kg	0
STORE PRESSURE	0 psig	2 1/2 psig
CHLORINE GAS FLOW RATE (STP)	28 l/min	40 l/min

FIGURE 2-2 EDA ELECTRIC VEHICLE BATTERY CONFIGURATION
(reproduced with permission from reference 1)

released from the battery case during some mishap. Of course, the effectiveness of the foam absorbent will depend on the rate of chlorine release as well as the specific type and concentration of absorbent. Since absorbent specifications remain to be determined, chlorine dispersion calculations in this report ignore its presence.

Another proposed safety feature is a 5-10 psig (34.5-69 kPa) rupture disc in the battery case. This rupture disc (which is not shown in Figure 2-2 because its size is yet to be determined) is intended as a final contingency to prevent battery case rupture due to uncontrolled pressurization. Chlorine released from the rupture disc would presumably be partially absorbed by the surrounding foam layer.

One additional battery component that is relevant to safety considerations is the use of a hydrogen-chlorine recombination reactor for the hydrogen gas that is generated from the aqueous electrolyte during the latter stages of charge. A fluorescent light photochemical reactor has been employed in the battery stack for this purpose, but a different passive reactor is also being considered by EDA.

2.2 CHLORINE HYDRATE

Since chlorine hydrate has apparently not been used in any other commercial product, its properties relevant to battery safety are briefly reviewed here. More complete property data are available in the chemical literature⁽⁶⁾ and in published (Ref 5, Section 18) and unpublished⁽⁷⁾ form from EDA.

Chlorine hydrate is a pale yellow, ice-like solid which forms at low temperatures at water/chlorine mole ratios of 6-10. The hydrate formation temperature in the EDA battery depends on the absolute pressure and the concentration of the zinc chloride aqueous solution. At atmospheric pressure, the equilibrium hydrate formation temperature from pure water is 9.6°C (49.3°F), and from a 16% zinc chloride solution is about 4°C (Ref 5, Figure 18-2). These temperatures are significantly higher than the boiling point of liquid chlorine -34°C. Chlorine hydrate's exothermic heat of formation with water is 18.6 kcal per mole of chlorine. Since this value is almost four times as high as the latent of vaporization of liquid chlorine (4.88 kcal/mole), chlorine hydrate is inherently more stable (less volatile) than liquid chlorine.

The hydrate itself is a solid crystalline structure with a specific gravity of 1.23 (for $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$). In the battery store, hydrate forms as particles which agglomerate and pack as the state of charge increases. Pressure filtration in the electric vehicle battery store is designed to produce a volumetric packing ratio of about two thirds solid hydrate and one third aqueous solution at a full state of charge.

Hydrate morphology in the battery depends strongly on the solid/liquid ratio, i.e., on the battery state of charge. In the early stages of hydrate formation and battery charging, the store contains a relatively thin hydrate slurry. As charging continues, the hydrate slurry gradually thickens into a slush and finally into a thick filter cake. However, even in the fully charged state, there is some liquid content in the store. Photographs of the chlorine hydrate synthesized during the experimental tasks in this investigation are shown in Sections VI and VII. The morphology and physical appearance of the spilled hydrate is discussed in those sections.

III

ACCIDENT SCENARIOS

Accident scenarios of primary concern here involve inadvertent releases of chlorine or chlorine hydrate. Our objective in identifying such scenarios is to determine the quantity and rate of release and the external environments in which such releases represent a hazard. The exact sequence of events preceding the release is left unspecified because it is difficult, if not impossible, to determine at this stage of zinc-chlorine electric vehicle battery evolution. As battery design and testing continue and future markets are better defined (in terms of vehicle configuration, charging procedure, driving mission, etc.), more detailed scenario descriptions will be possible.

A summary of the important accidental chlorine release scenarios is given in Table 3-1, while Table 3-2 lists the various possible release environments. Internal and external mishaps causing these chlorine release scenarios are discussed below.

Chlorine vapor toxicity effects and miscellaneous battery hazards not related to chlorine release are also briefly discussed in subsection 3.3.

3.1 INTERNAL MALFUNCTION SCENARIOS

Internal battery malfunctions will lead to a chlorine release only if the battery case is breached from an uncontrolled pressure increase or (much less likely) from thermal or chemical degradation. Gradual pressure increases should not result in battery case breaching unless the pressure activated battery controlled shutdown system is inoperable. Upon sensing an abnormal pressure increase, the control system is designed to self discharge the battery by allowing chlorine hydrate in the store to slowly decompose. The evolved chlorine gas would then flow to the cell stack where it is electrochemically converted to chlorine ions in the zinc chloride electrolyte. It is conceivable that this self discharge sequence can be interrupted by component malfunctions such as blocked or corroded tubing and/or valves between the store and the stack. The latter situation would eventually lead to battery case breaching, but the subsequent rate of chlorine release would depend upon the rate of heat transfer into the battery store and the size of the battery case opening. Unless the

TABLE 3-1
ACCIDENTAL CHLORINE RELEASE SCENARIOS

Scenario	Cause	Quantity/Rate Chlorine Released	FMRC Treatment
1. Hydrate Spill	Case and store wall ruptured from collision, piercing, or uncontrollable pressure increase	Depends on spill size, state of charge, and ambient conditions	Extensive testing and mathematical modeling
2. Direct Chlorine Vapor Release	Same as 1, but less violent	2a. Instantaneous 28 liter release* 2b. Maximum continuous release rate = 40, 28 l/min during discharge, charge**	Mathematical dispersion modeling
3. Hydrate Decomposition within Breached Battery	Same as 2	Worst case is equivalent to 40 l/min during discharge	Treated as for 2b
4. Hydrogen-Chlorine Explosion	Recombination reactor fails temporarily	Depends on extent of blast damage and state of charge	Dispersion calculation for extreme case of a 41-Kg release
5. Fire Exposure	Electrical fire, gasoline or diesel fuel fire, etc. near battery	Unknown	Postponed until fire tests can be conducted

* In the 28 liter instantaneous release, the cell stack would have to be slightly above atmospheric pressure.

** The 40 and 28 l/min release rates assume that the pumps continue to operate after the battery case is breached.

TABLE 3-2

CHLORINE RELEASE ENVIRONMENTS

ENVIRONMENT	LIKELIHOOD	FMRC TREATMENT
Outdoor road	Inevitable	Field tests and detailed Mathematical Dispersion Model
Road tunnel	Relatively low frequency	Simple Mathematical Dispersion Model
Garage	Relatively low frequency	None
Vehicle passenger compartment	Depends on vehicle ventilation design	None

battery case rupture occurs at a high pressure or results in a hydrate spill, it is unlikely that this self discharge malfunction scenario would cause as large and rapid a chlorine release as the other scenarios discussed in this section.

Rapid pressure excursions beyond the capability of the battery deactivation system are highly unlikely in all but one scenario. Common transients such as short circuits and high charging rates are probably not a hazard in the zinc-chlorine battery because the effective internal charging rate is limited by the electrolyte pumping capacity. On the other hand, the possibility of hydrogen-chlorine explosions remains a serious concern. An explosion could result if the recombination reactor failed temporarily and allowed hydrogen to accumulate to a concentration above the lower explosive limit of 4-6% by volume. Restarting the reactor would then trigger an explosion. The peak pressure generated by such an explosion depends on the hydrogen concentration. It is conceivable that the explosion pressure would rupture the battery case and store wall and violently disperse hydrate. If the ambient temperature were above 10°C when this scenario occurred, the violently dispersed hydrate would rapidly decompose releasing chlorine vapor. Chlorine dispersion in this scenario is discussed in Section 4.2.

It is not yet clear whether the hydrogen-chlorine explosion scenario and other internal malfunctions are far-fetched possibilities or highly probable occurrences. A detailed Failure Modes and Effects Analysis for the battery^{*} and component reliability data would help resolve this uncertainty.

Scenarios involving slow chlorine release rates are not of concern unless the release occurs in a confined environment where the chlorine can accumulate. As Table 3-2 indicates, road tunnels, garages, and the vehicle passenger compartments are three examples of confined environments. Gradual chlorine accumulations in these enclosures would probably be detected by smell or by chlorine analyzers. The need for chlorine analyzers and special ventilation systems in vehicle passenger compartments could eventually be determined by conducting gas mixing tests in typical electric vehicles. Similar tests for hydrogen and methane fueled vehicles have already been conducted.⁽⁹⁾

* At this writing, a Failure Modes and Effects Analysis (FMEA) has not been performed for the zinc-chlorine electric vehicle battery but a preliminary FMEA is available⁽⁸⁾ for the load-leveling version of the battery.

3.2 EXTERNALLY INFLICTED MISHAPS.

The most obvious externally inflicted accident scenario is a vehicle collision resulting in battery case rupture. The size and location of the rupture will determine whether hydrate is spilled. Since hydrate spills during violent collisions are inevitable, a major effort during this project has been devoted to both small-scale and large-scale spill tests. These tests are described in Sections VI and VII.

The other externally inflicted scenario listed in Table 3-2 is fire exposure. Heat transfer from the fire would cause hydrate to rapidly decompose and the accompanying chlorine vapor pressure rise would probably rupture the store wall and battery case. Since chlorine is an oxidant, the fire could conceivably intensify. On the other hand, the aqueous zinc chloride solution could partially suppress the fire. Even if the fire is unaffected by the chlorine hydrate and electrolyte spill, the fire-plume-dominated dispersion of chlorine vapor is difficult to predict. All these uncertainties suggest that a fire test on an actual battery would be needed to accurately evaluate the fire exposure hazard scenario.

3.3 CHLORINE TOXICITY

Chlorine is a respiratory irritant that produces physiological reactions ranging from mild discomfort to death, depending on concentration and duration of exposure. Reactions to a given exposure depend strongly on the condition of the respiratory system. As indicated in Table 3-3, the reported odor threshold varies from a low of 0.02 ppm for people with a keen olfactory response to a high of 3.5 ppm for people with a congested respiratory system. The severest physiological reactions to high concentrations are experienced when there are chronic respiratory problems such as emphysema and asthma.

The often quoted physiological response data of Fieldner et al⁽¹¹⁾ are included here in Table 3-3 to aid interpretation of the chlorine concentration data presented in Sections IV-VII of this report. ICI Ltd⁽¹²⁾ has used these data together with chlorine toxicity data from other published and private sources to construct the physiological response curves shown in Figure 3-1; these curves are useful in assessing typical physiological effects expected from transient exposures to chlorine concentrations ranging from 1-1,000 ppm.

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TABLE 3-3
PHYSIOLOGICAL EFFECTS OF EXPOSURE TO CHLORINE*

EFFECT	CHLORINE CONCENTRATION (ppm)
Slight irritation after long exposure (also OSHA TLV and ceiling limit)**	1.0
Odor detectable ⁽¹⁰⁾	0.02 - 3.5
Noxiousness, impossible to breathe several minutes	5
Throat irritation	3-6 ⁽¹³⁾ 15.0
Coughing	30.2
Dangerous in 30 min	40-60
Unbearable in 1 min	100
Fatal for cats after 30 min ⁽¹³⁾	300
Fatal for most animals after a few deep breaths	1,000

* Unless otherwise noted by superscript reference numbers, the data is from Fieldner et al⁽¹¹⁾.

**Federal Register 44, p 41427, July 17, 1979

FIGURE 3-1 EFFECTS OF TRANSIENT EXPOSURE TO CHLORINE
(Reproduced from reference 12)

The available physiological data, reported in the literature and subjectively observed in the present spill test program, indicate that chlorine presents two types of potential hazards in the electric vehicle battery application. The first hazard is the bona fide risk of casualties incurred during major accidental chlorine releases. The second hazard is the perceived risk often encountered with minor accidental releases producing low, albeit detectable, levels of chlorine vapor. The present research project has produced results which can be more easily used in evaluating the first hazard. An evaluation of the perceived risk problem should become clearer as battery reliability and road test data are acquired, and the commercialization process reaches the marketing stage.

3.4 MISCELLANEOUS HAZARDS

There are several miscellaneous hazards associated with the zinc-chlorine battery (as with virtually all industrial products) that are not directly attributable to chlorine or chlorine hydrate. One of these hazards is the potential for electric shocks during charging mishaps. The electric shock hazard is common to all electric vehicle batteries with the voltages (0-120 volts) and power requirements (57-113 kW) anticipated for typical electric van driving. Another related battery hazard, which is common to all electric vehicle batteries, is the potential for electrical fires. Both these hazards are currently being reviewed by battery manufacturers and regulatory authorities and are not discussed further in this report.

One additional zinc-chlorine battery hazard that should be documented is the toxicity and corrosivity of the zinc chloride electrolyte. Exposure to zinc chloride fumes can cause damage to the respiratory tract, and skin contact with concentrated zinc chloride solution can produce severe irritation, eczematous dermatosis, and ulcerations.⁽¹⁴⁾ The authors' experiences with zinc chloride in this test program indicate that the skin irritation problem, which seems to be more of a hazard than the fume problem, can be alleviated through standard chemical laboratory precautions, such as wearing long rubber gloves and washing immediately after contact. Parenthetically, it should be noted that chlorine hydrate skin contact did not produce any of these dermatological effects.

IV

CHLORINE DISPERSION CALCULATIONS FOR OUTDOOR RELEASES

An assortment of chlorine dispersion models is available for calculating downwind chlorine vapor concentrations for the outdoor roadway accident scenarios described in Section III. The range of validity and accuracy of the various dispersion models has been investigated in a concurrent Factory Mutual Research study⁽¹⁵⁾ geared toward zinc-chlorine load-leveling battery hazards. Calculations described in the present report are based on conventional and modified Gaussian Plume Dispersion Models previously recommended for atmospheric releases of chlorine⁽¹⁶⁻¹⁸⁾ and other heavier-than-air vapors.⁽¹⁹⁾ Comparisons⁽¹⁵⁾ between calculated and measured chlorine concentrations in the range 1-100 ppm indicate that these models are typically accurate within a factor of 2-3 for chlorine vapor releases in a relatively open area on level terrain. This level of accuracy should be acceptable in view of uncertainties about chlorine release rates, physiological effects, and meteorological and topographical conditions at potential accident sites.

4.1 CONTINUOUS CHLORINE VAPOR RELEASES

Here, we consider accident scenarios in which chlorine vapor is emitted continuously through an opening in the battery case. If the size of the opening and the rate of chlorine release are sufficiently small (as expected in scenarios 2 and 3 in Table 3-1), the standard Gaussian Plume Model equation should be applicable in the far field where chlorine concentrations are under 100 ppm. Thus, the volumetric concentration distribution downwind from a ground level point source is given by (Ref 17, eq (1)):

$$\bar{\chi}(x,y,z) = \frac{\dot{Q}}{\pi \sigma_y \sigma_z \bar{U}} \exp \left\{ -\frac{1}{2} \left(\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2} \right) \right\} \quad (4-1)$$

- where $\bar{\chi}$ = time-averaged chlorine vapor concentration (vol or mole fraction)
- $\dot{Q}$ = volumetric vapor release rate (m³/sec)
- $\bar{U}$ = mean wind speed (m/sec)
- $\sigma_y(x), \sigma_z(x)$ = plume crosswind width and height, respectively (m)
- x, y, z = downwind, crosswind, and vertical distances from release point (m).

The values of $\sigma_y(x)$ and $\sigma_z(x)$ in eq (4-1) are strongly dependent upon atmospheric conditions and are usually specified in terms of atmospheric stability, i.e., gustiness categories. A variety of empirical prescriptions for $\sigma_y(x)$ and $\sigma_z(x)$ have been employed in previous chlorine dispersion calculations. Calculations presented here were obtained using the Simmons et al⁽¹⁸⁾ curve fits to the Pasquill-Gifford empirical correlations for $\sigma_y(x)$, as follows:

Category	Equivalent Pasquill-Gifford Category	$\frac{\sigma_y(m)}{x^{.91}}$
Unstable	A-B-C (average)	0.20
Neutral	D	0.13
Stable	E-F (average)	0.077

A prescription adopted here for the vertical dispersion coefficient, $\sigma_z(x)$ is

$$\sigma_z(x) = 0.20 \sigma_y(x) \quad (4-2)$$

for all three atmospheric stability categories. The Bureau of Mines⁽¹⁷⁾ and Simmons et al⁽¹⁸⁾ have recommended using eq (4-2) as a means of modeling the negative buoyancy effects of chlorine dispersion due to its heavier-than-air molecular weight. On the other hand, Howerton⁽¹⁶⁾, Kodali et al⁽³⁾, and Sellers⁽¹²⁾ have employed the conventional Pasquill-Gifford or Smith-Singer correlations⁽²⁰⁾ for $\sigma_z(x)$ based on data in the air pollution literature for trace quantities of neutrally buoyant vapors. The FMRC comparison⁽¹⁵⁾ between computed concentrations and experimental data for continuous chlorine vapor releases indicated that the use of eq (4-2) produced slightly better agreement with the data than the other available correlations for $\sigma_z(x)$.

Inversion of eq (4-1) produces the following equations for chlorine isopleths, i.e., constant concentration contours, for a particular concentration, $\bar{\chi}$.

$$\text{Along } z=0, \quad Y(x) = \sigma_y [2 \ln (\dot{Q}/\bar{\chi}\pi\sigma_y\sigma_z\bar{U})]^{1/2} \quad (4-3)$$

$$\text{Along } y=0, \quad Z(x) = \sigma_z [2 \ln (\dot{Q}/\bar{\chi}\pi\sigma_y\sigma_z\bar{U})]^{1/2} \quad (4-4)$$

Calculated 3.5 ppm and 100 ppm isopleths based on eqs (4-3) and (4-4) are shown in Figures 4-1 and 4-2 for a 40 l/min chlorine vapor release (scenarios 2b and 3 in Table 3-1). The isopleths in Figure 4-1 are for an unstable atmosphere with a mean wind speed of 5 m/sec. It is evident from Figure 4-1 that the 100-ppm isopleth under these atmospheric conditions is too small to expose bystanders to any potentially dangerous concentrations of this magnitude. The 3.5-ppm isopleth in Figure 4-1 is also sufficiently close to the ground (maximum height is less than 1 m) to avoid distressing erect adult bystanders downwind of the release. However, some irritating effects may be experienced by children, seated adults, etc. and also as a result of wind gusts momentarily transporting higher fluctuating chlorine concentrations toward downwind observers.

The isopleths shown in Figure 4-2 are for a stable atmosphere with a representative wind speed of 2 m/sec. The isopleths under these conditions extend considerably further downwind than those for the unstable atmosphere corresponding to Figure 4-1. Moreover, the 3.5-ppm isopleth in Figure 4-2 has a maximum elevation of about 1.5 m, indicating there is a greater likelihood that downwind bystanders as far as 180 m from the release site will inhale objectionable chlorine concentrations. These calculations indicate that the continuous vapor release scenarios from a damaged battery may, depending on atmospheric conditions, expose bystanders to objectionable concentrations but should not produce serious injuries.

The preceding calculations were also conducted with the traditional Pasquill-Gifford correlations for $\sigma_z(x)$. The resulting isopleths were somewhat higher, but narrower in crosswind width and shorter in downwind extent than those shown in Figures 4-1 and 4-2. The conclusion about possible objections but no injuries remains as stated previously.

4.2 INSTANTANEOUS RELEASE OF CHLORINE VAPOR

Instantaneous chlorine vapor releases can be caused by hydrogen-chlorine explosions and other accident scenarios in which the vapor space of the battery stack or store is pressurized at the time the case is opened or breached, e.g., via the rupture disc. In these situations, downwind transient concentrations are computed with the "expanding puff" atmospheric dispersion model. According to the expanding puff model, the chlorine cloud is diluted via air entrainment

CHLORINE ISOPLETHS

VAPOR RELEASE RATE .00067 CUM/S

WIND VELOCITY 5 M/S

UNSTABLE ATMOSPHERE ($\sigma_z = 0.2\sigma_y$)

FIGURE 4-1 CHLORINE ISOPLETHS - UNSTABLE ATMOSPHERE

Elevation (X,Z) contours for the 3.5 and 100ppm isopleths are shown above the X-axis, and plan view (X,Y) contours are shown below the X axis.

CHLORINE ISOPLETHS

VAPOR RELEASE RATE .00067 CUM/S

WIND VELOCITY 2 M/S

STABLE ATMOSPHERE ($\sigma_z = 0.2\sigma_y$)

FIGURE 4-2 CHLORINE ISOPLETHS - STABLE ATMOSPHERE

Elevation (X,Z) contours for the 3.5 and 100ppm isopleths are shown above the X axis, and plan view (X,Y) contours are shown below the X axis.

as it is convected downwind at the wind velocity. The instantaneous chlorine concentration, χ , at location x, y, z is given by⁽²⁰⁾

$$\chi = \frac{Q}{\sqrt{2\pi}^{3/2} \sigma_{xi} \sigma_{yi} \sigma_{zi}} \exp \left\{ -\frac{1}{2} \left[\frac{(x - \bar{U}t)^2}{\sigma_{xi}^2} + \frac{y^2}{\sigma_{yi}^2} \right] \right\} \quad (4-5)$$

where Q = volume of chlorine released (m^3),
 $\bar{U}$ = wind speed (m/sec)
 t = time after release (sec)
 $\sigma_{xi}, \sigma_{yi}, \sigma_{zi}$ = downwind, crosswind, and vertical standard deviations of concentration distribution in puff (m).

The dispersion coefficients, $\sigma_{xi}, \sigma_{yi}, \sigma_{zi}$, for the puff model are not necessarily the same as those for the steady point source (eq (4-1)). It is common to invoke the assumption of isotropic horizontal direction turbulence, such that $\sigma_{xi} = \sigma_{yi}$. Here, we also invoke the time variation assumption used in the Bureau of Mines chlorine report⁽²⁰⁾, namely:

$$\frac{\sigma_{xi}}{\bar{\sigma}_x} = \frac{\sigma_{yi}}{\bar{\sigma}_y} = \frac{\sigma_{zi}}{\bar{\sigma}_z} = \left(\frac{t}{10 \text{ min}} \right)^{0.2} \quad (4-6)$$

for time intervals less than 10 min after the release. The values of $\bar{\sigma}_y$ ($= \bar{\sigma}_x$) and $\bar{\sigma}_z$ depend upon atmospheric stability conditions. The following Smith-Singer correlations for $\bar{\sigma}_y$ together with the previous assumption for $\bar{\sigma}_z$ to simulate negative buoyancy effects have been used for these calculations.

Atmosphere	$\bar{\sigma}_x = \bar{\sigma}_y$	$\bar{\sigma}_z$
Unstable	$0.36 x^{.86}$	$0.20 \bar{\sigma}_y$
Stable	$0.31 x^{.71}$	$0.20 \bar{\sigma}_y$

Calculations using the puff model have been conducted for values of the chlorine release quantity, Q , corresponding to accident scenarios 2a and 4 in Table 3-1. In scenario 2a, Q is set equal to the cell stack vapor space volume of 28ℓ (1 ft³). The downwind drifting 100 ppm and 1,000 ppm isopleths for this release scenario in a stable atmosphere with $\bar{U} = 2$ m/sec are shown in Figure 4-3. The 1,000-ppm isopleth develops a maximum horizontal diameter of about 6 m at 10 sec, while the 100-ppm isopleth persists at about 12 m in size for somewhat longer than 1 min. The duration of exposure for a bystander in

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Stable Atmosphere

FIGURE 4-3 CHLORINE ISOPLETHS DOWNWIND OF A 1-FT³ INSTANTANEOUS RELEASE

the path of the puff would be about 6 sec for concentrations in excess of 100 ppm. According to Figure 3-1, this brief exposure to concentrations of 100 ppm and slightly higher is not likely to produce serious injury, but may induce distress, coughing, etc., in the vicinity of the release.

The 28ℓ puff release calculations were also conducted for unstable atmospheric conditions. The results for the unstable atmosphere indicated that there would not be any dangerous concentrations at distances of more than a few meters from the release.

A hydrogen-chlorine explosion (or a blast of external origin) will produce a chlorine vapor puff volume that depends on the extent of fragmentation of the battery case and the ejected chlorine hydrate. A lower bound of chlorine puff size would be the 28ℓ instantaneous release described previously. An upper bound, for the case of a violent external explosion triggered deliberately or accidentally, would be the instantaneous dissemination and vaporization of hydrate such that the entire chlorine content of the battery forms the initial "puff". The following calculations describe the downwind diffusion of a 41-kg (12.8 m^3) instantaneous release corresponding to such an extreme explosion. Although the credibility of this scenario may be debatable, the calculated results are presented in the spirit of "let's see what could happen if ...".

We assume in this calculation that the blast wave traveling ahead of the puff does not produce any residual disturbance in the ambient wind patterns conveying the puff downwind. Thus, eq (4-5) is applicable for computing the downwind chlorine vapor concentration distribution in space and time.

The 50-ppm isopleths resulting from a 41-kg release in an unstable atmosphere with a 5 m/sec wind are shown in Figure 4-4. The 50-ppm isopleth envelope representing the maximum crosswind vertical and axial distances at which transient concentrations may exceed 50 ppm is also shown in Figure 4-4. As ambient air is entrained into the chlorine cloud, the 50-ppm isopleth grows to a maximum horizontal diameter of 57 m at approximately 1 min after the explosion. After this time, the entrained air continues to dilute the cloud and reduce the size of the 50-ppm isopleth, until it disappears entirely at 103 sec (516 m downwind) after the explosion. the longest exposure to concentrations in excess of 50 ppm would be 17 sec for someone situated about 300 m directly downwind of the battery.

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FIGURE 4-4 50-PPM ISOPLETHS DOWNWIND FROM A 41-KG(12.8m^3) CHLORINE RELEASE IN AN UNSTABLE ATMOSPHERE WITH A 5-m/s WIND

According to Figure 3-1, this exposure may be expected to induce coughing and some distress, but no permanent injuries or fatalities.

The same type of catastrophic release during stable atmospheric conditions (2 m/sec wind) would produce potentially injurious chlorine concentrations over a much larger area as indicated by the isopleths in Figure 4-5. Transient concentrations of 50 ppm or higher in this case would extend to a maximum distance of about 2,000 m directly downwind and about 73 m crosswind. Someone situated about 1200 m directly downwind would be exposed to 50 ppm or higher concentrations for a duration of about 70 sec. Figure 3-1 indicates this exposure time is close to the danger threshold. Exposure to detectable and potentially irritating concentrations in excess of 3.5 ppm would be considerably longer as indicated by the larger size of the 3.5-ppm isopleth in Figure 4-5.

4.3 HYDRATE SPILL SCENARIOS

Chlorine hydrate spills from a breached battery will result in hydrate decomposition and chlorine vapor release at a rate that depends upon battery state of charge, atmospheric and substrate temperatures, and the size of the spill. The chlorine hydrate spill tests and heat conduction model described in Section VI indicate that the chlorine release rate decreases as a function of time after the spill. Therefore, neither the steady vapor release dispersion model (eq (4-1)), nor the instantaneous vapor release model (eq (4-5)) are directly applicable to the hydrate spill scenario. Instead, a quasi-steady area-source dispersion model described as follows will be used for predicting chlorine vapor concentrations downwind of a hydrate spill. This model has previously been employed by Welker⁽²¹⁾ and by Zalosh⁽²²⁾ for cryogenic liquid spills.

In the quasi-steady dispersion model, the instantaneous downwind dispersion pattern is assumed to have a spatial distribution given by eq (4-1), but the vapor release rate, $\dot{Q}$, is allowed to vary with time. Since the vapor is assumed to travel downwind at the wind velocity, the release rate used to calculate the concentration at time t at a distance x downwind is the release rate at time $t - x/\bar{U}$. Thus, the chlorine concentration χ is given by:

$$\chi(x, y, z, t) = \frac{\dot{Q}(t - x/\bar{U})}{\pi \sigma_y \sigma_z \bar{U}} \exp \left(-\frac{y^2}{2\sigma_y^2} - \frac{z^2}{2\sigma_z^2} \right) \quad (4-7)$$

FIGURE 4-5 CHLORINE ISOPLETHS DOWNWIND FROM AN INSTANTANEOUS RELEASE OF THE CHLORINE IN A 50 kWh MODULE, DURING STABLE ATMOSPHERIC CONDITIONS

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The release rate used in subsequent calculations with eq (4-7) is assumed to be of the form

$$\dot{Q} = B \hat{t}^{-n} \quad (4-8)$$

where $\hat{t} = t - x/\bar{U}$ and B and n are both empirically prescribed values that depend on spill conditions.

As in the previous dispersion models, the crosswind and vertical dispersion coefficients, σ_y and σ_z in eq (4-7) are functions of downwind distance. However, the distance used in these correlations is now adjusted to account for the finite size of the source, i.e., the spill. A virtual point source is assumed to be located a distance x_v upwind of the center of the "area source" and the distance x' used in eq (4-7) is:

$$x' = x + x_v \quad (4-9)$$

The virtual source distance, x_v , can be calculated (Ref 19, p 106) by effectively treating the area source as a crosswind line source of width proportional to the spill diameter, D. The prescription used here (and by several others as explained in Ref 19) is

$$\sigma_{y0} = D/4.3 \quad (4-10)$$

where σ_{y0} is the crosswind standard deviation at the spill site. The dispersion coefficient is assumed to be a power function of the virtual downwind distance, x' , such that

$$\sigma_y = a_y x'^{b_y} \quad (4-11a)$$

$$\sigma_z = a_z x'^{b_z} \quad (4-11b)$$

and

$$\sigma_{y0} = a_y x_v^{b_y} \quad (4-11c)$$

where a_y , b_y , a_z , b_z are constants that depend upon the atmospheric stability category. Combining eqs (4-10) and 4-11c), we obtain the following equation for the virtual distance, x_v :

$$x_v = (D/4.3 a_y)^{1/b_y} \quad (4-12)$$

Vapor concentrations calculated with this virtual point source model differ significantly from those computed with a point source model (origin at center of spill) when the downwind distance is less than about ten times the spill diameter. Since potentially injurious or fatal chlorine concentrations may exist as far as ten spill diameters downwind if the spill is sufficiently large, use of the more complicated quasi-steady area source model is warranted.

Calculated results obtained with this area-source quasi-steady dispersion model are presented in Section VII in comparison to spill test data. Calculations for more general spill conditions are described in Section IX.

V

CHLORINE DISPERSION CALCULATIONS FOR ROAD TUNNEL ACCIDENTS

5.1 VENTILATION SYSTEMS

Accidental chlorine releases in a confined location may result in potentially injurious vapor concentrations unless the forced ventilation rate is sufficiently high to dilute the chlorine to tolerable concentrations. Ventilation rates in road tunnels and garages are currently designed to dilute internal combustion engine emissions to safe levels. In this section, the dispersion of accidentally released chlorine in conventionally ventilated road tunnels is discussed to evaluate the suitability of existing ventilation rates for zinc-chlorine electric vehicles. Potential accidents in parking garages are not treated here because garage ventilation patterns are more difficult to calculate, and because garages probably represent a less severe hazard than tunnels due to the generally larger open areas and potential escape routes in garages.

As illustrated in Figure 5-1, the three generic types of ventilation systems employed in vehicle tunnels are 1) longitudinal ventilation systems, 2) semi-transverse systems, and 3) fully transverse systems. In longitudinally ventilated tunnels, fresh air enters at one end (either via booster fans or via entrainment due to entering vehicles) and travels to the other end where it exits as vitiated air. In semi-transverse systems, fresh air flows in a duct under or alongside the roadway, enters the roadway via portals, and then travels along the tunnel to the exhaust shafts. In fully transverse systems, stale air as well as fresh air flow in separate ducts above and below the roadway. For a nominal ventilation rate, longitudinal ventilation systems are usually less efficient than the transverse systems and are usually restricted to relatively short tunnels (often for congested urban traffic), not exceeding 1,000 m (3,300 ft).

All three types of tunnel ventilation systems are usually designed to maintain carbon monoxide concentrations under 250 ppm (Ref 23, p 20). Assuming cars spaced at 50 ft (15 m) emit an average of 1.5 cfm ($7 \times 10^{-4} \text{ m}^3/\text{sec}$), a transverse ventilation rate of 120 cfm per lane-ft ($0.18 \text{ m}^3/\text{sec/m}$) is required. In longitudinally ventilated tunnels, this ventilation requirement is usually achieved with an average air velocity of 3-7 m/sec (Ref 23, p 30), depending on tunnel length.

Air travels along
tunnel from portal
to portal

Longitudinal Ventilation (Short Tunnel)

Semi Transverse System

Fully Transverse System
(Long Tunnel)

FIGURE 5-1 MECHANICAL VENTILATION SYSTEMS FOR VEHICLE TUNNELS

Carbon monoxide detectors and annunciators are often linked to the ventilation control room in large tunnels. These detectors could be supplemented or replaced with chlorine detectors to accommodate zinc-chlorine battery powered vehicles. However, the major question is whether or not the existing fan capacities are adequate to safely dilute the chlorine, regardless of whether or not it is automatically detected. The following dispersion calculations address this question.

5.2 DISPERSION CALCULATIONS

We seek first to calculate the average chlorine concentration due to a continuous chlorine release in a longitudinally ventilated vehicle tunnel. The relevant equation for this simple mixing problem is:

$$\bar{C} = \frac{S}{UA} \quad (5-1)$$

where $\bar{C}$ = tunnel cross-section averaged chlorine concentration;

S = chlorine release rate;

U = tunnel ventilation velocity;

A = tunnel cross-sectional area.

Calculated values of $\bar{C}$ from eq (5-1) are shown in Table 5-1 for a 25-ft (7.5-m) diameter tunnel with a ventilation velocity 1) of 6 m/sec and 2) of 3 m/sec. For direct chlorine vapor release accident scenarios, chlorine release rates for calculation purposes are postulated to be 28 l/min (1 cfm) and 40 l/min, the nominal chlorine flow rates during battery charge and discharge, respectively. For hydrate spill scenarios, nominal chlorine vapor release rates of 143 l/min (5 cfm) and 9.7 l/min (0.34 cfm) corresponding to large and small spills, are postulated. The latter values are based on extrapolation techniques (constant hydrate thickness scaling and geometric similarity scaling) applied to the small-scale hydrate spill test data (Section VI), but are merely meant to be representative of various spill configurations.

The highest concentration in Table 5-1 is 19 ppm for the large hydrate spill scenario with a ventilation velocity of 3 m/sec. This concentration would produce severe discomfort but no permanent injuries if exposure is limited to a few minutes. With a 6-m/sec ventilation velocity, the average concentration would be reduced to 9.5 ppm, below the danger level for less than 200-min

TABLE 5-1

CHLORINE RELEASE RATES AND AVERAGE CONCENTRATIONS
FOR ACCIDENT SCENARIOS IN A LONGITUDINALLY VENTILATED TUNNEL

Scenario	Volumetric Release Rate (ℓ /min)	Average Concentration (ppm)	
		For U = 6 m/sec	For U = 3 m/sec
Hydrate Spill			
- Large Spill	143	9.5	19
- Small Spill	9.7	0.6	1.2
Chlorine Flow Line Rupture			
- during discharge	40	2.4	4.9
- during charge	28	1.7	3.5

exposures (Figure 3-1). For the direct chlorine vapor release scenarios, the average concentrations, as shown in Table 5-1, are all under 5 ppm.

Another aspect of the tunnel dispersion problem is the need to determine the longitudinal extent of the mixing region in which local chlorine concentrations can be significantly higher than the average values shown in Table 5-1. In order to assess this aspect, we invoke the following additional assumptions:

- 1) The chlorine is released from a point source away from the tunnel floor and walls;
- 2) Turbulent diffusion in the tunnel satisfies empirical relations obtained for turbulent pipe flow; and
- 3) Chlorine vapor gravitational spreading effects are negligible.

The solution to the turbulent diffusion equation under these assumptions is (Hinze⁽²⁴⁾, p 428):

$$c = \frac{S}{4\pi\epsilon|x|} \exp \left(-U \frac{(y^2 + z^2)}{4\epsilon|x|} \right) \quad (5-2)$$

where ϵ = turbulent diffusivity (assumed constant);

x = distance along tunnel axis;

y, z = rectangular coordinates in plane of tunnel cross-section;

and $y^2 + z^2 \ll x^2$.

The empirical relationship given by Hinze⁽²⁴⁾ (p 448) for the turbulent diffusivity, ϵ , associated with solute dispersion in turbulent pipe flow is:

$$\epsilon = 0.02 UD\sqrt{f} \quad (5-3)$$

where D = pipe (tunnel) diameter; and

f = friction factor for turbulent pipe flow.

Strictly speaking, eq (5-2) is applicable to an unbounded flow field with a uniform velocity, U . However, it is often applied to pipe diffusion situations in the region where the diffusing gas has not yet reached the pipe wall. If the gas is released near the pipe/tunnel centerline, the criterion implies that the gas concentration at the pipe wall ($y^2 + z^2 = D^2/4$) is small in comparison to the centerline concentration. From the exponential in eq (5-2)

$$\frac{UD^2}{16\epsilon x} \gg 1,$$

or, using eq (5-2) $x \ll \frac{D}{0.32\sqrt{f}}$.

For $D = 7.6$ m, and $f \approx 0.01$ (from the Moody diagram for a flow velocity of 3-6 m/sec in a concrete tunnel), $x \ll 230$ m.

Within this maximum range of applicability of eq (5-2), the peak chlorine concentration, $C_{\max}$, along the centerline of the release is given by

$$C_{\max} = \frac{S}{.08 \pi UDx\sqrt{f}} \quad (5-4)$$

Equation (5-4) can be used to estimate the distance, L , downstream from the release at which the centerline concentration approaches the fully mixed concentration given by eq (5-1). Thus, L can be determined from:

$$\frac{4S}{U\pi D^2} \approx \frac{S}{.08 \pi UDL\sqrt{f}} \quad (5-5)$$

or, upon simplifying,

$$L \approx \frac{D}{0.32\sqrt{f}} \quad (5-6)$$

Coincidentally, this is the limit of applicability of eq (5-2), as derived previously. Within this distance of about 200 m from the release site, local concentrations within a portion of the tunnel cross-section may be significantly higher than those given in Table 5-1. Within this region, people who are not sufficiently mobile to walk, run, or drive out of the high chlorine concentration zone may suffer some distress. Hopefully, there is only a remote possibility of someone being immobilized within the relatively small zone in which chlorine concentrations are distressingly high. Calculations of the analogous probability for outdoor roadway mishaps are presented in Section IX.

Transverse ventilation systems would probably result in lower concentrations than calculated for longitudinal ventilation throughout most of the tunnel because the chlorine could be removed via the vitiated air ducts instead of relying on diffusion from the tunnel exit or exhaust shaft. Dispersion calculations for transversely ventilated tunnels could be performed by network computations similar to those currently used in ventilation system design.⁽²³⁾

VI

LABORATORY-SCALE CHLORINE HYDRATE DECOMPOSITION TESTS

Thirteen laboratory-scale chlorine hydrate decomposition tests were conducted to measure the rate of chlorine evolution following a spill onto a warm simulated concrete road surface. The first seven decomposition tests involved hydrate synthesized in the laboratory with the apparatus described in Section 6.1. The last six decomposition tests involved samples of hydrate synthesized for the large-scale field spill tests described in Section VII. Experimental apparatus, test procedures, test data, and data analyses for all 13 decomposition experiments are described in this section.

6.1 LABORATORY HYDRATE PRODUCTION APPARATUS

Laboratory-scale production of chlorine hydrate was carried out in the specially fabricated synthesis column shown in Figure 6-1. The hydrate synthesis column is a 61-cm long concentric Pyrex glass cylindrical structure with inner and outer internal diameters of 7.3 cm and 10.5 cm respectively. The ends of the cylinders are seated in grooves on Kynar plates and are reinforced with General Electric RTV 106 silicone sealant to isolate the inner tube and annulus spaces. Appropriate fittings and accessories for hydrate column coolant circulation, thermocouple mounting, zinc-chloride solution filling in the column, chlorine transfer to the solution, and hydrate removal are provided on the Kynar support plates.

The temperature of zinc chloride solution in the hydrate column was monitored using a chromel-alumel thermocouple. The thermocouple bead was protected against chlorine corrosion by sheathing it in a titanium tube. The temperature of zinc chloride solution in the column was controlled at the desired value by circulating a 50:50 mixture of Prestone antifreeze automobile coolant and water maintained at the set temperature by a Neslab RTE-8 temperature control bath.

To form chlorine hydrate, a metered stream of chlorine gas was bubbled through the zinc chloride solution,^{*} using a fritted glass tube, at a rate of

* A two-percent (by weight) zinc chloride solution was used in five tests to simulate the EDA load-leveling battery store, and a 12 percent solution was used in the other two laboratory tests to simulate an electric vehicle battery store.

FIGURE 6-1 CHLORINE HYDRATE SYNTHESIS APPARATUS

approximately 2 liters per min. A few minutes after bubbling of chlorine, chlorine hydrate crystals could be seen settling at the bottom of the hydrate synthesis column. Formation of chlorine hydrate was accompanied with considerable frothiness at the top of the zinc chloride solution. The froth was the slurry of chlorine hydrate crystals in zinc chloride solution and trapped bubbles of chlorine. The frothy suspension would occasionally break loose from the upper section of the synthesis column and settle to the bottom. Excess chlorine not bonded with water molecules to form chlorine hydrate was vented to an exhaust system equipped with a chlorine absorber.*

Chlorine hydrate, settled as a light yellow slurry in the lower section of the synthesis column (Figure 6-2), was collected in a beaker by opening the drain plug. The chlorine hydrate slurry collected in the beaker was manually filtered over a polyethylene funnel equipped with fine mesh stainless steel cloth as the filtering medium. Filtering of hydrate slurry thus removed a significant quantity of the aqueous zinc chloride solution but the liquid-to-solid-hydrate ratio could not be quantitatively determined. The consistency of filtrate (i.e., filtered chlorine hydrate) was qualitatively noted for each batch. In most tests, the hydrate had the consistency of fine wet sand. The wetness of the hydrate was due to the aqueous zinc chloride solution. The filtered chlorine hydrate was then ready for measuring its decomposition rate at the desired temperatures of the concrete slab and environmental conditions.

6.2 CHLORINE HYDRATE DECOMPOSITION APPARATUS

The decomposition rate of chlorine hydrate in all 13 tests was measured in terms of weight loss in a specially fabricated apparatus shown in Figure 6-3. Each component of the apparatus is identified in the figure and is described in the following discussion.

Plexiglas Housing (1)

The housing measuring 46 cm (i.d.) and 38 cm long is a cylindrical structure made of clear Plexiglas. The function of the housing is: 1) to contain and prevent the chlorine vapors emitted during hydrate decomposition experiment

* Ventsorb Canister - a caustic impregnated charcoal adsorption unit made by Calgon Corporation.

FIGURE 6-2 CHLORINE HYDRATE FORMATION IN SYNTHESIS COLUMN

① Plexiglass Housing	⑫ Thomson Ball Bearing
② Heating Lamp	⑬ Bearing and Shaft Support Column
③ Polypropylene Foam Container	⑭ Hex Nut with Ball Bearing
④ Chlorine Hydrate	⑮ Load Plate
⑤ Concrete Platform	⑯ Load Plate and Transducer Support
⑥ Zinc Chloride Solution (Substrate)	⑰ Transducer
⑦ Aluminum Support Pan	⑱ Signal Wire
⑧ Nut	⑲ Plexiglass Housing
⑨ Air-diffuser Pipe	⑳ Tripod (Support Legs)
⑩ Hardened SS Load bearing Shaft	㉑ Thermocouples
⑪ Oil Seal	

FIGURE 6-3 CHLORINE HYDRATE DECOMPOSITION APPARATUS

from spreading throughout the hood space and to guide the chlorine vapor to the vent in an orderly fashion; 2) to allow generation of controlled ambient air conditions during hydrate decomposition.

Heating Lamp (2)

The lamp is a 100-watt light bulb mounted on the removable lid of the Plexiglas housing. The lamp looks down at the concrete slab and heats it to the desired temperature prior to deposition of chlorine hydrate on the slab. The lamp heat emission is controlled by a 100-volt variable transformer.

Polypropylene Foam Container (3)

This container is machined from a hard polypropylene foam block to the desired shape as shown. This container serves 1) to support and insulate the concrete slab used as the chlorine hydrate decomposition platform, and 2) to collect aqueous zinc chloride solution obtained following the hydrate decomposition.

Concrete Slab (5)

The concrete platform is a 25.4-cm diameter, 1.27 cm thick circular disk molded from a mixture of cement and gravel mixed in 1:3 ratio. The slab weighs approximately 1.35 kg after drying. The slab is provided with two holes midway through the thickness dimension. These holes reached approximately 6.25 cm to the center of the disk and supported two chromel-alumel thermocouples. These thermocouples recorded temperature of the slab halfway through the entire thickness.

Air Diffuser Tube (9)

To remove the chlorine gas evolved during the hydrate decomposition from the Plexiglas housing, air flow at the rate of 6 liters per minute was provided through the housing. Air diffused through a large number of 1.6-mm dia holes drilled on a 5-mm polyvinyl chloride tubing. The tubing was mounted on the floor of the Plexiglas housing in a circular perimeter.

Load Monitor And Auxiliary Components (15,15)

The composite mass of the chlorine hydrate decomposition platform including the hydrate and the hardened steel shaft bearing this load, is supported over a 4.5-kg load plate Statham Model UC4. The load plate is a mechanical interface that permits only a maximum allowable deflection of transducer cell and thus prevents accidental damage to the cell. The load plate also extends the operating force range of the transducer cell.

Transducer Cell (17)

The transducer cell is a load sensing device of the resistive strain-gage bridge type. A Statham Model UC3-Gold Cell was used for the weight loss measurements in our experiments.

Load-Bearing Shaft (13)

The load-bearing shaft is a 1.25-cm dia and 15-cm long hardened stainless steel shaft. The shaft is plated with chrome to create a frictionless surface and is held in upright position by two Thomson ball bearings as shown. The lower end of the shaft rests on a 5-mm bearing inserted between a stainless steel hex nut to assure point contact. The hex nut is then coupled to the load plate.

The upper part of the shaft is coupled to the decomposition platform. With this arrangement the hydrate decomposition measurement platform assembly (called the tare weight) rests over the transducer cell.

Oil Seal (11)

The oil seal is fabricated from polyethylene stock and mounted on the load-bearing shaft using General Electric RTV106 silicone rubber. Refined mineral oil (available from drug stores) was found to be an effective barrier and sealant against chlorine vapors that can corrode the surfaces of the load carrier shaft bearings, load plate, and the transducer cell assembly. The load plate transducer cell, part of the load-bearing shaft and the support assembly, are enclosed inside a Plexiglas cylindrical housing to protect against chlorine exposure.

6.3 LOAD CELL SIGNAL PROCESSING AND RECORDING

The concrete slab, aluminum support plate and the load support shaft combined together form the tare weight amounting to approximately 2 kg. To this tare weight is added a sample of chlorine hydrate weighing approximately one kilogram or less and containing 3-33% chlorine by weight. A Calex Model 165 bridge sensor transducer signal processing system was used to resolve chlorine mass losses of approximately one gram with this apparatus. The transducer signal is fed to a differential amplifier where it is algebraically added to an offset signal. The offset signal is derived from the same stable reference source as the transducer excitation voltage. The offset voltage is adjustable by an external potentiometer to permit cancellation of the tare load signal. The result of the algebraic summing process is fed to a variable gain amplifier; this result is then a millivolt signal representing the weight of chlorine hydrate. When amplified by a gain of 40 to 1000, a signal suitable for recording on a strip chart recorder is available. Thus, small chlorine hydrate weight losses due to release of chlorine were measured as a function of time after the hydrate spill.

Although the load cell and signal processing system had a combined accuracy of about 0.2% of the initial hydrate mass, there was another source of experimental error. Vibrations and other disturbances generated by the opening and closing of the laboratory fume hood/cabinet and other doors in the laboratory produced small discontinuities in the load cell output. Although we tried to remove these discontinuities in analyzing the load cell output, there is probably an error of 1-2% due to these disturbances. If additional tests of this type are to be conducted in the future, it would be desirable to eliminate this source of error by mounting the decomposition apparatus on a vibration isolation platform.

6.4 HYDRATE DECOMPOSITION TESTS: EXPERIMENTAL PROCEDURES AND OBSERVATIONS

After instrumentation calibration, the filtered or unfiltered hydrate^{*} was gently placed and evenly distributed over the concrete surface. As the decomposition of the hydrate proceeded, 35 mm photographs were taken to define

* Laboratory synthesized hydrate was manually filtered, whereas hydrate synthesized for the field tests was pressure filtered in the EDA apparatus.

the recession boundary of the decomposing hydrate as shown in Figure 6-4). The transient weight loss of hydrate and transient temperatures of the concrete slab were the principal data measured during the test.

A typical visual observation common to all tests was that, as the hydrate was deposited on the concrete slab, rapid bubbling of chlorine vapor appeared throughout the hydrate sample. Bubbling subsided after several minutes even though hydrate was still slowly decomposing on the slab. The rapid chlorine evolution early in the tests produced a light yellow chlorine cloud hanging low over the decomposition platform. This cloud disappeared after several minutes into the test.

Test conditions and representative mass loss data for all 13 hydrate decomposition tests are shown in Table 6-1*. Independent test parameters include the ambient air temperature, slab surface temperature, initial hydrate mass, zinc chloride solution concentration used to synthesize hydrate, and the extent of hydrate filtering. The latter two parameters characterize the equivalent state of charge of the battery store. Representative test results shown in Table 6-1 are the mass vaporized after 15 min, and the final mass vaporized after all the hydrate decomposed or the test was terminated because of an instrumentation problem. Regression analyses and discussion of the 15-min and final mass vaporization data are presented in Section 6.6.

Transient mass loss and slab temperature data for all 13 tests are presented in Appendix A. Typical mass loss curves are shown in Figures 6-5 and 6-6 for Tests 6 and 13, respectively. These figures indicate that the initial mass vaporization rates of 6-9 gm/min rapidly decrease to less than 1 gm/min within about 15 min. The time at which the mass loss rate levels off is also the approximate time at which the minimum slab surface temperature occurs. During this interval, heat conduction from the slab is the dominant heat transfer mode to the decomposing hydrate. The mass loss and slab temperature curves in Appendix A for the other tests indicate that this heat conduction dominated period occurs for 5-20 min after these small-scale spills. The residual hydrate decomposition after this period is apparently driven by convective heat transfer from the ambient air and by thermal radiation from the sun (in the field tests) or from the light bulb simulating the sun (in some of the laboratory tests). A theoretical heat conduction model to calculate vaporization rates before convection and radiation become important is presented in Section 6.5.

* Page 57

A. (t=1 min)

B. (t=10 min)

C. (t=20 min)

D. (t=40 min)

FIGURE 6-4 HYDRATE DECOMPOSING DURING LABORATORY SPILL TEST 13
(Hydrate sample from last field test)

CHLORINE HYDRATE TEST #6

FIGURE 6-5 MASS LOSS DURING LABORATORY HYDRATE SPILL TEST 6

CHLORINE HYDRATE TEST # 13

FIGURE 6-6 MASS LOSS DURING LABORATORY HYDRATE SPILL TEST 13

6.5 DATA COMPARISON WITH THEORETICAL HEAT CONDUCTION MODEL PREDICTIONS

Our objective here is to formulate a simple theoretical heat transfer model that will provide reasonable agreement with the test data and can be applied to predict hydrate decomposition rates under arbitrarily prescribed spill conditions. Kodali at EDA has previously conducted this type of heat transfer calculation^(3,5) for several chlorine hydrate spill scenarios. Similar, but more elaborate, calculations have also been conducted for cryogenic liquid spills.⁽²⁵⁾ These existing models show that conduction heat transfer rates are much larger than convective and solar radiative heat transfer rates for spills onto concrete or asphalt slabs with negligibly small wind velocities, as was the case in the present spill tests. The previously cited relationship between slab temperature and hydrate vaporization data also indicates that conduction is the dominant mode until the vaporization rates drop off by almost an order of magnitude from their initial values. Therefore, we postulate an analytical heat conduction model, based on the following assumptions:

- 1) The hydrate-slab interfacial area is an empirically prescribed decreasing function of time.
- 2) The slab is infinitely thick and initially at a uniform temperature, T_o .
- 3) Heat conduction through the slab is in the vertical direction only.
- 4) Chlorine hydrate heat of decomposition is 18.6 kcal per gm-mole of chlorine.
- 5) Water (more precisely, aqueous zinc chloride solution) and chlorine vapor released during hydrate decomposition do not provide any thermal resistance.
- 6) Convective and radiative heat transfer are negligible during the times of interest, i.e., during the initial period after the spill while vaporization rates are high.

Under these assumptions, the classical semi-infinite slab one-dimensional transient heat conduction solution for the heat flux, q , to the hydrate is⁽²⁶⁾:

$$q = \frac{k (T_o - T_h)}{\sqrt{\pi \alpha t}} \quad (6-1)$$

where k = thermal conductivity of concrete slab, (W/m°C)

T_o = initial slab temperature (°C)

T_h = hydrate temperature

α = thermal diffusivity of concrete slab (m²/min)

t = time following spill (min)

The mass rate of hydrate vaporization, $\dot{M}$, is

$$\dot{M} = \frac{qA}{h_{fg}} \quad (6-2)$$

where A is the slab-hydrate contact area, h_{fg} is the heat of hydrate decomposition per unit mass of chlorine, and q is the heat conduction rate given by eq (6-1).

Kadali (Ref 3, Appendix A) calculated the contact area A in eq (6-2) by assuming the electric vehicle battery hydrate spilled as a rigid cube equal in volume and shape to the battery store. More recently, he modeled the same hydrate spill configuration for the utility load-leveling version of the EDA battery (Ref 5, p 9-4). The more recent configuration models a slurried hydrate (corresponding to a 30% state of charge) spill as a segment of a sphere with a 45° contact angle and an assumed density of 0.8 gm/cm³. The contact area was assumed to be constant in time in both of Kadali's assumed hydrate configurations.

As Figure 6-4 illustrates, the hydrate-slab contact area actually shrinks as the hydrate decomposes. Estimates of the shrinking area from photograph sequences in several tests indicate that the instantaneous contact area A at time t satisfies the empirical relation*

$$A = A'_o e^{-mt} \quad (6-3)$$

where A'_o and m are calculated from linear regression curve fits to the area data.

* Several other analytical curve fit functions were investigated, but the decaying exponential function produced, by far, the best data correlations.

Substitution of eqs (6-1) and (6-3) into eq (6-2) yields:

$$\dot{M} = \frac{A'_o k (T_o - T_h) \exp(-mt)}{\sqrt{\pi \alpha t} h_{fg}} \quad (6-4)$$

for the instantaneous chlorine vaporization rate. Equation (6-4) can be used to calculate hydrate decomposition rates under more general conditions provided that empirical estimates are available for the parameters A'_o and m . Values of A'_o and m for the small-scale spill tests are reported here, and for the large-scale spill tests in Section 6.6.

Equation (6-4) can be integrated analytically to derive an equation for the cumulative mass, M , vaporized as a function of time following the spill. The result is:

$$M = \frac{A'_o k (T_o - T_h)}{h_{fg} \sqrt{\alpha m}} \operatorname{erf}(\sqrt{mt}) \quad (6-5)$$

where erf is the error function for which tabulated values are available in standard mathematical tables and handbooks.

Calculations based on eq (6-5) have been compared to the measured mass loss curves for three small-scale spill tests in which there were sufficient photographic data to determine the values of A'_o and m . These values and the other relevant test parameters are listed in the following tabulation.

Test No.	T_o (°C)	T_h (°C)	A_o (m ²)	A'_o (m ²)	m (min ⁻¹)
6	40	2	0.047	0.040	0.094
12 (F.T. 5)	27	6	0.048	0.039	0.056
13 (F.T. 6)	30	6	0.034	0.042	0.059

Note that the values of A'_o obtained from the curve fits differ slightly from the actual initial hydrate area, denoted by A_o in the tabulation. Concrete thermal property data used in the calculations are ⁽²⁷⁾ $k = 1.21 \text{ W/m}^\circ\text{C}$ and $\alpha = 0.00232 \text{ m}^2/\text{hr}$.

The comparisons between the calculated and measured chlorine mass loss curves for these three tests are shown in Figures 6-7, 6-8, and 6-9. In the latter two figures, there is excellent agreement, i.e., within 15%, during the first 5 min after the spill. The final mass vaporized at the end of the test is underestimated by the calculation by about 16% in Figure 6-8 and by about

FIGURE 6-7 COMPARISON BETWEEN CALCULATED AND MEASURED CHLORINE MASS LOSS FOR HYDRATE SPILL TEST 6

FIGURE 6-8 COMPARISON BETWEEN CALCULATED AND MEASURED MASS LOSS
FOR HYDRATE SPILL TEST 12 (Field Test 5)

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FIGURE 6-9 COMPARISON BETWEEN CALCULATED AND MEASURED MASS LOSS FOR HYDRATE SPILL TEST 13 (FIELD TEST 6)

40% in Figure 6-9. In Figure 6-7, the calculated mass loss exceeds the data by as much as 100% until about 70 min after the spill.

The indicated differences between the calculated and measured mass losses are understandable in view of the mathematical model assumptions. None of the assumptions are rigorously valid, and their validity decreases in the latter stages of the tests. For example, lateral heat conduction within the slab must become important as the hydrate shrinks and portions of the slab surface are exposed. Furthermore, there is clear evidence of a thin water (or zinc chloride solution) film on the slab as the hydrate decomposes; this film must influence the heat transfer from the slab to the hydrate. The effects of lateral heat conduction and water film thermal resistance would cause the calculated vaporization rates to be somewhat high, as in Figure 6-7. On the other hand, neglect of convective and radiative heat transfer effects would cause the calculated vaporization rates to be somewhat low, as in Figures 6-8 and 6-9.

It is possible to extend the heat conduction model presented here to include water film thermal resistance, forced or natural convective heating, and thermal radiation effects. Kodali et al have incorporated most of these effects into their hydrate heat transfer model.^(3,5) However, these effects are probably not as important as the need for a generalized prescription of the time-dependent hydrate-slab contact area as given by eq (6-3). It is essential to obtain additional information on the appropriate values of the parameters A'_0 and m for different spill sizes and hydrate states of charge, if theoretical heat transfer models are to be used to predict chlorine evolution rates in different hydrate spill scenarios. Calculations of this type are described in Sections 7.4 and 9.2.

6.6 REGRESSION ANALYSES OF SMALL-SCALE SPILL TEST DATA*

Two distinct stepwise regression analyses were performed on the small-scale chlorine hydrate spill test data. The first used the mass vaporized (grams) in the first 15 min following the spill as the dependent variable, while the second used the mass vaporized during small increments of time throughout the duration of the tests.

*Work described in this section was conducted by Paul Marlin, FMRC Applied Research Department

6.6.1 Mass Vaporization During First 15 Minutes

The following variables were recorded for each of 12 tests (Table 4-1, Tests 1-3, 5-13):

1. MV15 : mass vaporized in 15 min (grams)
2. MO : initial mass (grams)
3. ZNCL : ZnCl concentration (%)
4. TO : initial slab temperature - 9.6°
5. F = : 1, if filtered
0, otherwise

Thirty observations on each variable were recorded. Separate stepwise regressions were run for MV15 and $\ln(MV15)$, denoted Model 1 and Model 2 respectively, with an F value of 2.0 to enter or leave (very liberal from the standpoint of allowing variables to enter). In each case variables 2-5 and their logs were candidates for entry.

The computed equations obtained for Model 1 and Model 2 are as follows:

Model 1:

$$MV15 = -13.273 + .1916 MO - 64.37 \ln MO + 19.47 F \quad (1)$$

Model 2:

$$MV15 = 4.91 \times 10^{-4} \times MO^{1.689} \times 1.630^F \quad (2)$$

The complete regression results are shown in Appendix B.

The standardized residuals (residual $\div$ standard error of the estimate) were:

<u>Test No.</u>	<u>Model 1</u>	<u>Model 2</u>
1	-.52	-.88
2	+.69	+.22
3	-.57 z	-.86
5	1.68	+1.58
6	-1.10	-1.11
7	+.35	+1.55
8	+.63	+.20
9	-.69	+.10
10	-.95	-.91
11	+.68	+.64
12	-.16	-.09
13	+.20	-.05 ,

TABLE 6-1

CHLORINE HYDRATE VAPORIZATION DATA SUMMARY

Test No.	Hydrate Mass (g)	Ambient Temp (°C)	Surface Temp (°C)	Mass Vaporized in 15 min		Final Mass (%)	Final Time (min)	Heater (Lab Tests)	ZnCl ₂ Conc (%)	Filtered
				(g)	(%)					
1	243	22	20	4	1.7	3.3	62	off	2	no
2	434	23	50	15	3.5	6.9	105	on	2	no
3	600	34	45	32	5.3	10.0	120	on	2	yes
4	323	32	40	47	14.6	34.4	74	off	2	part
5	504	28	36	48	9.6	17.2	75	off	2	part
6	562	24	40	26	4.6	10.7	118	off	12	yes
7	384	21	40	28	7.3	15.1	35	off	12	yes
8*	1,034	28	45	93	9.0	11.4		<u>Charge Time</u> 5 hr	20	<u>Structure</u> Thick
9*	1,105	28	43	71	6.4	7.5	39	2 hr	15	Loose
10*	683	33	52	36	5.3	6.8	35	2.3 hr	5	Thick
11*	1,057	28	45	77	7.3	8.7	37	3.4 hr	4.6	Thin
12*	822	25	27	40	4.9	5.0	34	2.6 hr	6	Thin
13*	730	28	30	48	6.5	10.1	36	5 hr	5	Thick

* Samples obtained from hydrate in field tests.

giving no indication of outliers or departure from normality. Thus, eqs (1) and (2) both provide an accurate representation of the 15-min vaporization data.

6.6.2 Mass Vaporized During A Small-time Increment

In this formulation, the time, t , following the spill was incorporated into the dependent variables, and the cumulative mass vaporized at time, t , was the dependent variable. For each of the 13 tests, observations were recorded at time points $\{t_i\}$.

Define:

$M(t_i)$ = cumulative mass vaporized at t_i

$dt_i = t_{i+1} - t_i$

$MV_i \equiv MV(dt_i) = M(t_{i+1}) - M(t_i)$,

and

TO = initial temperature - 9.6°

$F_{Med} = 1$, if filtering is medium
 $F_{Med} = 0$, otherwise

$F_{Thin} = 1$, if filtering is thin
 $F_{Thin} = 0$, otherwise.

The slab temperature decrease following the spill was accounted for by assuming that it could be described by an exponential decreasing function of time as predicted by the heat conduction model described in Section 4.5.

The following model was postulated:

$$MV_i = C_0 \cdot M(t_i)^{C_1} \cdot dt_i^{C_2} \cdot TO^{C_3} \cdot e^{-C_4 t_i} \cdot C_5^{F_{Med}} \cdot C_6^{F_{Thin}} \quad (3)$$

or its linearized form for the regression:

$$\begin{aligned} \ln MV = & \ln C_0 + C_1 \ln M(t) \\ & + C_2 \ln dt + C_3 \ln TO \\ & - C_4 t_i + \ln C_5^{F_{Med}} + \ln C_6^{F_{Thin}} \end{aligned} \quad (4)$$

The resulting equation is:

Model 3:

$$MV(dt) = 6.7 \times 10^{-5} \cdot M(t)^{1.673} \cdot dt^{1.097} \cdot e^{-0.0306t} \cdot 2.265^{F_{Med}} \cdot .531^{F_{Thin}} \quad (5)$$

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The complete stepwise regression (Model 3) with an F value to enter or leave the equation of 2 is shown in Appendix B (p 140-141) (enclosure 3). A Kolmogorov-Smernov test indicated that the hypothesis that the standardized residuals were normally distributed with mean zero and standard deviation one could be rejected with a probability of .54 of being incorrect. Thus, the hypothesis that the residuals are normal is not rejected.

The residuals were found to be uncorrelated with any independent variable.

There was indication of autocorrelation between successive residuals from the same test ($\rho_{e_t, e_{t-1}} = .52$). This could be due to correlation between successive measurement errors. In this case the basic model would not be invalidated.

A separate regression (Model 4) with F_{Med} and F_{Thin} removed was run; the complete regression is shown in Appendix B and the resulting equation is:

Model 4:

$$MV(dt) = 1.31 \cdot 10^{-4} \cdot M(t)^{1.209} \cdot dt^{1.138} (T_o - 9.6)^{0.0660} e^{-.0334t} \quad (6)$$

In this case the term $\ln (T_o - 9.6)$ appeared, but a comparison of the coefficients of determination, standard errors of the estimate, and t-statistics for the individual coefficients indicate that Model 3 is superior.

Statistics from the data base upon which Models 3 and 4 are based are also shown in Appendix B.

6.6.3 Discussion of Regression Results

The regression results, as represented by eq (2) (Model 2) and eq 5 (Model 3), contain two unexpected features. One surprise is the absence of the initial slab temperature, T_o , in these equations. The theoretical heat conduction model described in Section 4.3 predicts a linear variation of vaporization rate with slab temperature. This variation with slab temperature may have been obscured by the effect of filtration, (F), in the data correlations. However, even when filtration effects are suppressed as in Model 4 (eq 6), the variation with T_o is not quite as strong as expected from heat transfer considerations (a linear variation with T_o is barely within the 2σ limit of the computed exponent).

The second surprise in the data correlations is the unexpectedly strong positive effect of the initial hydrate mass (M_0 in eq (2) and $M(t)$ in eq (5)).

In both correlations, the mass vaporized varies as the 1.7 power of the initial hydrate mass. In other words, the fraction of mass vaporized (MV/MO) increases with the 0.7 power of initial mass. This unexpected result is only limited to the relatively narrow range of initial mass used in the small-scale tests. In the large-scale field tests described in Section VI, the small sample of hydrate often vaporized before the bulk of the hydrate on the spill pad. Therefore, the data correlations presented in this section should not be extrapolated to spill sizes much greater than about one kilogram, which is the largest size in the small-scale tests.

VII

CHLORINE HYDRATE FIELD SPILL TESTS

7.1 TEST SITE AND APPARATUS

Six full-scale hydrate spill tests were conducted during July 1979 at the Factory Mutual Test Center in West Glocester, R.I. The test site was a 61 m x 61 m open area located at the north end of the lake at the Test Center as shown in Figure 7-1. The site was provided with two 1.5-m x 1.5-m heated concrete spill pads (to accommodate different wind directions) and an instrumentation trailer. Two portable gasoline powered generators supplied electrical power.

Chlorine hydrate for the spill tests was manufactured on site using apparatus designed by EDA to simulate the hydrate formation process in the battery store. EDA provided the chlorine hydrate synthesis equipment to FMRC and assisted FMRC personnel operating the equipment. With an adequate coolant supply, the equipment might have been capable of simulating a complete charging half cycle of the 128-liter hydrate store in the battery. The coolant supply available at the field test site, however, limited the manufacture of hydrate to an equivalent of about 50% of full charge, i.e., about 62 kg of hydrate, during an eight-hour synthesis period prior to the spill. The 50% charge may indeed be close to a worst-case configuration, because this hydrate is more fluid and can spread over a larger area than the hydrate in a fully charged battery. The hydrate synthesis apparatus and manufacturing procedure is described in Appendix C.

When a sufficient amount of hydrate was formed, the hydrate store was disconnected from the synthesis equipment and wheeled onto the test pad. Prior to the spill, 1 kg sample of hydrate was removed for transient weight loss measurements as described in Section VI.

During the spill, zinc chloride solution in the store was spilled together with the hydrate. Two methods of spilling the hydrate were used in the test program: 1) Remote dumping using a cable and pulley arrangement so personnel could be upwind of the spill while dumping the hydrate; and 2) manual dumping by personnel wearing an air pack (Figure 7-2A, B).

7.2 INSTRUMENTATION

The chlorine vapor detection system for the tests included a multiplexing sampling system sampling from ten probe locations. A schematic diagram of the multiplexing system is shown in Figure 7-3. Use of an Eagle signal MT 11 timer and switch to activate three-way solenoid valves allowed all ten locations to be

FIGURE 7-1 PLAN OF FM TEST CENTER SHOWING FIELD TEST SITE

A. Cable-Pulley Spill Technique

B. Manual Spill Technique

FIGURE 7-2 OVERTURNED HYDRATE STORE DURING SPILL TESTS

FIGURE 7-3 MULTIPLEXING SAMPLING SYSTEM, SCHEMATIC DIAGRAM

alternately analyzed via an Interscan Corporation Model 1340 Sp (dual range 0-20/0-100 ppm) chlorine detector, while exhausting the remaining nine samples. The multiplexing scan time was varied during the test series, from 30 sec per sample in Test 1 to 2 min in Test 6.

To ensure proper placement of the chlorine sample probes, chemical smoke candles were lit on the spill pad prior to each test. The probes were placed along and at 10-20° angles to the centerline of the resulting downwind smoke cloud at distances of 7.6-30.4 m from the spill pad. All but one of the probes were 1.9 m above the ground; the other probe was 1 m above the ground. The probe locations for all six tests are shown in Appendix D.

In addition to the multiplexing system, a second chlorine analyzer was dedicated to one sample probe in Tests 4, 5 and 6 in order to obtain a complete concentration history at that location throughout the test. The second analyzer was a MSA Model 90 electrochemical chlorine analyzer also with a high range of 0-100 ppm of chlorine. Both analyzers were calibrated with a syringe injection unit before each test to verify their accuracy. The electrical output from the MSA analyzer was recorded on the potentiometric analog chart recorder and on a Hewlett-Packard FM analog tape recorder.

Visualization of the chlorine vapor cloud in Tests 5 and 6 was accomplished by placing cotton soaked in ammonia downwind of the spill pad. As the chlorine vapor blew over the ammonia-saturated cotton (strung on a cord between two posts), it reacted with the ammonia to produce a white ammonium chloride particulate cloud which was visible on site as well as on photographs and videotape. Slides were taken of each test and Tests 1, 5 and 6 were videotaped showing the shrinking size of the decomposing hydrate during the test and the bubbling of chlorine up through the hydrate.

Wind speeds were monitored using a Datametrics 700-5 hot wire anemometer for Tests 1, 2, and 3. The anemometer filament broke repeatedly, and a vane type anemometer had to be employed for Tests 4, 5 and 6. Consequently, only average wind speeds were recorded in Tests 4, 5 and 6, while root mean turbulent fluctuations were recorded as well as average velocity in Tests 1, 2, and 3.

7.3 TEST OBSERVATIONS AND RESULTS

7.3.1 Test 1

Test 1 was run on a cloudy day (75% cloud cover) with ambient temperature at the start of testing of 27.5 C (see test conditions, Table 7-1). The hydrate was a thick slurry (Figure 7-4) containing approximately 20 kg of chlorine, i.e., representative of an electric vehicle battery at 50% state of charge. Chlorine concentrations were initially monitored using the multiplexing system. However, at 25 min into the test, the analyzer was disconnected from the multiplexing system and hand carried downwind of the spill to directly measure the concentrations. Multiplexing data were lower than the data read directly on location possibly because the scanning rate was too fast for the detector to adequately respond. Chlorine concentrations (Table 7-2), measured in both multiplexing and direct sampling modes, fluctuated widely at any location due to the gusty wind that day. Typical peak fluctuating concentrations were 100 ppm at 15.2 m and 35 ppm at 30.4 m. No measurable concentrations were observed outside of the 30° pie-shaped region in which the probes were situated (Figure D-1).

7.3.2 Test 2

Test 2 was run on a day with 35% cloud cover, 65% relative humidity and an ambient temperature of 28°C. The hydrate contained ~7.7 kg of chlorine making it equivalent to ~19% fully charged EV battery store. The spilled hydrate was very loose and most of it ran off the pad and was absorbed by the ground. The wind ranged from 1.5-3.0 m/sec along the centerline of the probe array. Measurable chlorine vapor concentrations were recorded at only two data points, both at probe B, 8.2 m downwind. Peak concentrations at that location reached 50 ppm intermittently.

7.3.3 Test 3

For Test 3 the spill pad was diked on three sides to prevent spilled hydrate from running off. The fourth side was not diked to allow water to run off as the hydrate decomposed. The hydrate contained 9 kg of chlorine equivalent to a battery in a ~23% state of charge.

This was the first test run with sample lines shortened to reduce the delay time and with the multiplexing unit and analyzer out in the outdoor test

FIGURE 7-4 CHLORINE HYDRATE SPILLED DURING FIELD TEST 1

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TABLE 7-1

CHLORINE HYDRATE FIELD SPILL TEST CONDITIONS

Test No.	Ambient Temp. (°C)	Wind Velocity (M/S)	Slab Temp. (°C)	Initial Zn Cl Conc. (%)	Chlorine Weight (kg)	State of Charge (%)
1	27.5	4.1	(SSW)	33	20	(50)
2	28	1.5-3	(SSW)	34	15	(19)
3	33	.9-2	(S)	38	5.1	(23)
4	28	2	(NW)	34	4.6	(34)
5	25	2-4	(SW)	32	6	(26)
6	28	.7-.9	(SW)	33	5	20

TABLE 7-2
CHLORINE CONCENTRATIONS MEASURED IN TEST 1

Probe	Time (min)	X (meters)	Y (meters)	Z (meters)	C _{max} ^{**} (ppm)
A	8	15.2	0	1.8	>100
A	12	15.2	0	1.8	30
A	18	15.2	0	1.8	>100
J *	25	25.9	6.7	1.8	.6
between * J & I	25	22.1	5.7	1.8	>20
crosswind of pad *	32	0	7.6	1.8	.6
F *	33	18.3	4.7	1.8	.7
E *	34	25.9	6.7	1.8	.5
C *	35	22.8	0	1.8	12
H *	36	38.0	0	1.8	.8
between * C & H	38	30.4	0	1.8	35
C	40	22.8	0	1.8	.4
C	50	22.8	0	1.8	1.4
A	54	15.2	0	1.8	4
B	55	7.6	0	.9	7

* Analyzer hand carried into cloud

** Peak fluctuating concentration as read from the chart recorder or directly from the analyzer meter

area. The probes were placed all around the pad to accommodate changes in wind direction during the test. Due to exposure to heat and intense sunlight the analyzer output drifted and no reliable quantitative data were recorded.

7.3.4 Test 4

Test 4 was a spill of hydrate containing ~13.6 kg of chlorine relating to a ~35% state of charge on an EV battery. This test was the first in which two chlorine analyzers were used. The Interscan analyzer sampled in a multiplexing mode for the first 14 min before it was moved to a single location ~11 m from the spill to be used as a dedicated unit. The MSA detector was used throughout the test in a dedicated mode 8.2 m from the spill where concentrations exceeded 100 ppm (Figure 7-5) continuously for the first 2 1/2 min and intermittently for the next 20 min following the spill. According to Figure 3-1, the concentration exposure at that location was in the dangerous category. The wind direction was generally directed toward the instrumentation trailer located ~30 m from the spill pad (Figure 7-1) and the chlorine concentrations in the trailer were high enough to force personnel to leave. All personnel at the site during the spill felt some discomfort due to chlorine. Test Center personnel not involved in the spill tests reported a chlorine odor on the road leading to the test site ~65 m away and about 500 m away on a public road.

7.3.5 Test 5

Test 5 involved hydrate containing ~10 kg of chlorine or the equivalent of an electric vehicle battery at 26% state of charge. Photographs of the spill and the decomposed hydrate during this test are included here as Figure 7-6. The hydrate was entirely decomposed after about 30 min.

The sampling system again utilized the MSA and Interscan analyzers. Initially both analyzers were in a dedicated mode. After 5 min the Interscan was used in a multiplexing mode for 15 min and then again used as a stationary monitor until the end of the test. Peak concentrations measured on the Interscan at probe E, 22.8 m downwind ranged up to 99 ppm (Table 7-3, Figure 7-7) 20 min after the spill. Concentrations averaged over 2-min intervals at this location ranged from 1-21 ppm as indicated in Table 7-3. Concentrations on the MSA sampling at probe I, 15.2 m downwind measured over 100 ppm (Figure 7-8) intermittently during the first 24 min after the spill.

FIGURE 7-5 CHLORINE CONCENTRATION HISTORY DURING TEST 4 AT PROBE C ;
x = 0m, y = 7.6m, z = 1.8m

A. Spill

B. x=1 min

C. x=20 min

FIGURE 7-6 CHLORINE HYDRATE IN SPILL TEST 5

FIGURE 7-7 CHLORINE CONCENTRATIONS AT PROBE E (x = 22.8m; y = 0m) DURING TEST 5

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TABLE 7-3
CHLORINE CONCENTRATIONS RECORDED AT PROBE E - 22.8 METERS
DOWNWIND OF THE SPILL PAN DURING TEST 5

$\bar{C}^*$ (ppm)	$C_{\max}^{**}$ (ppm)	Time (min)
17	80	18-19
10	26	19-20
21	99	20-21
3.3	20	21-22
0	0	22-23
4.2	36	23-24
1.6	11	24-25
2.2	10	25-26
3.9	18	26-27
6.6	40	27-28

* 2-min average

** Peak fluctuation in 2-min interval

FIGURE 7-8 CHLORINE CONCENTRATION HISTORY DURING TEST 5 AT PROBE I;
 x = 15.2m, y = 0m, z = 1.8m

Test 5 was the first test in which cotton was soaked in ammonia and placed downwind of the spill to aid in visualization and videotaping of the chlorine-affected area. The resulting white ammonium chloride cloud (see Figure 7-9) fluctuated with the ambient wind gusts, but intermittently extended over the full 30° downwind wedge in which the cotton was placed. These visual observations, combined with the chlorine concentration data cited above, indicate that the downwind danger zone, i.e., the distress zone, is a sector with an angle of about 30° and a radius of at least 23 m.

7.3.6 Test 6

Test 6 was run with a hydrate store containing approximately 20 kg of chlorine or the equivalent of a 50% fully charged electric vehicle battery store.

The chlorine concentrations were monitored using the MSA in a dedicated mode 25 m downwind from the spill and the Interscan in a multiplexing mode. The number of probes used in the multiplexing system was reduced to six and the scan time increased to 2 min per channel. Cotton soaked in ammonia was again used as in Test 5 as well as in several other locations around the spill pad.

During the test there was a noticeable odor of chlorine in the trailer ~30 m crosswind from the spill. Peak chlorine concentrations at probe E, 25 m downwind, intermittently exceeded 100 ppm for the entire 56-min duration of the test (Figure 7-10). However, as Figure 7-10 indicates, these high concentration spikes were generally reduced in both amplitude and frequency after the first 15 min. Concentrations averaged over 2-min intervals for the multiplexed probes (Figures 7-11a,b,c,d and Table 7-4) ranged from 0 to 37 ppm. The 2-min averaged concentrations in Figure 7-11 would fall into the irritating-distressing categories of Figure 3-1. The peak concentration-exposure relationship in Figure 7-11 indicates the dangerous-fatal categories.

7.4 COMPARISON OF CONCENTRATION DATA WITH THEORETICAL CALCULATIONS

The quasi-steady area-source dispersion model previously described in Section 4.3 was utilized to calculate concentrations expected at the probe locations in Test 6. The calculations were based on empirical estimates of the chlorine release rates during Test 6 and Test 5 as obtained from photographs of the decomposing hydrate on the spill pad. Thus, the fraction of chlorine vaporized as a function of time is assumed to be equal to the fraction of

FIGURE 7-9 AMMONIUM CHLORIDE CLOUD FORMED DURING SPILL TEST 5

CHLORINE VAP. FIELD TEST #6

7-20

METEOROLOGY: 80% HUM

WIND SPEED : ~ 0.9 M/SEC

MATERIALS : 5 % $ZnCl$
20 KG Cl_2

STATE CHARGE : 50 %

CHARGING TIME : 5 HR

OBSERVED : THICK
STRUCTURE : SOLID

TEMP (MAT'L) : 6 °C

TEMP (AMBIENT) : 27.6 °C

TEMP (SURF'E) : 30 °C

TEMP (SLAB) : 33.3 °C

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FIGURE 7-10 CHLORINE CONCENTRATION HISTORY DURING TEST 6 AT PROBE E;
x = 22.8m, y = Cm, z = 1.8m

A. At probe I ($x = 15.2\text{m}$; $y = 0\text{m}$)

B. At probe A ($x = 7.6\text{m}$; $y = 2.0\text{m}$)

FIGURE 7-11 CHLORINE CONCENTRATION HISTORY DURING HYDRATE FIELD TEST 6

C. At probe J ($x = 22.8m$; $y = 6.0m$)

D. At probe H ($x = 15.2m$; $y = 4.0m$)

FIGURE 7-11 CHLORINE CONCENTRATION HISTORY DURING HYDRATE FIELD TEST 6 (Continued)

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TABLE 7-4

CHLORINE CONCENTRATIONS RECORDED AT VARIOUS PROBE LOCATIONS DURING TEST 6

Probe	Distance	Time (min)	$\bar{C}$ * (ppm)	C_{max} ** (ppm)
	Downwind (m) x, y			
I	15.2, 0.	2-4	31.0	100+
J	22.8, 6.0	4-6	9.2	32
C	7.6, 0	6-8	0	3
E	22.8, 0	8-10	11.0	29
A	7.6, 2.0	10-12	36.6	100+
H	15.2, 4.6	12-14	9.8	45
I		14-16	19.2	84
J		16-18	4.2	18
C		18-20	0	0
E		20-22	0	0
A		22-24	17.2	50
H		24-26	11.5	236
I		26-28	4.3	12
J		28-30	5.4	33
C		30-32	0	0
E		32-34	0	2
A		34-36	16.4	86
H		36-38	3.4	7
I		38-40	4.0	16
J		40-42	0	0
C		42-44	0	0
E		44-46	3.4	7
A		46-48	13.4	60
H		48-50	7.5	19
I		50-52	6.4	20
J		52-54	4.4	16
C		54-56	0	0
E		56-58	2.2	11
A		58-60	3.2	9

* Average over 2-min interval

** Peak fluctuation during 2-min interval

hydrate mass decomposed ($\Delta M/M_0$) at time, t . The latter fraction was found to fit the following two curve fits:

$$\text{in Test 5,} \quad \Delta M/M_0 = 0.039 t^{0.86} \quad (7-1a)$$

$$\text{in Test 6,} \quad \Delta M/M_0 = 0.024 t^{0.84} \quad (7-1b)$$

Differentiating eqs (7-1) and converting M_0 to the volume equivalents of chlorine vapor, we obtain:

$$\text{for Test 5,} \quad \dot{Q} = 0.0040 t^{-0.14} \text{ m}^3/\text{sec} ; \quad (7-2a)$$

$$\text{for Test 6,} \quad \dot{Q} = 0.0050 t^{-0.16} \text{ m}^3/\text{sec} \quad (7-2b)$$

where $\dot{Q}$ is the volumetric release required for the dispersion calculation (eq (4-7)).

Calculated concentration-versus-time relationships for the probe locations in Test 6 are shown as the dashed lines in Figure 7-11a,b,c,d. The calculated concentrations fall between the 2-min-averaged concentration data and the peak concentration data in Figures 7-11a,c, and d. In Figure 7-11b (Probe A), the calculated concentration history is lower than the 2-min-averaged data. The relatively low calculated concentrations at Probe A may be due to a slight error in estimating the wind direction. A small error in wind direction determination is more important for off-axis locations (such as Probe A) close to the spill where the crosswind standard deviation, σ_y , is small, than for locations further downwind (Probes H, I, and J) where the crosswind concentration distribution is broader.

The agreement between calculated and measured concentrations in Figure 7-11 is encouraging. In fact, the agreement in Figure 7-11 (within a factor of 5 at worst) is as good as, or better than, the agreement obtained with various steady-state chlorine dispersion models for constant release rates (Ref 15). It should be noted, however, that a more general prescription for the chlorine release rate, $\dot{Q}$, is needed if the quasi-steady dispersion model is to be used to predict chlorine concentrations downwind from hydrate spills for which no data are available. A more general formulation for $\dot{Q}$ is hypothesized and exercised for the casualty calculations described in Section 9.

VIII

INSURANCE IMPLICATIONS OF CHLORINE HAZARD

Before zinc-chlorine battery-powered vehicles are commercialized, insurance underwriting arrangements have to be made for manufacturers and for motorists. Since the chlorine hazard is a key issue in these underwriting arrangements, it is important to assess the insurance implications of the information presented in this report. In order to conduct a preliminary assessment, casualty and automobile insurance industry representatives were contacted during the latter stages of this study. These representatives were briefed on the zinc-chlorine battery design and operation, on physiological response to chlorine exposure, and on the theoretical and experimental results delineating the chlorine hazard. The comments of representatives from two insurance companies are described here.

Representatives of the Casualty Department of the Allendale Mutual Insurance Company met on September 4, 1979 to discuss this issue. Mr. Carlton Stidsen of Allendale led the discussion and raised questions to a group of six underwriters who had 3 to 27 years of automobile underwriting experience. The general consensus of the underwriters was that more information is needed in order to reach any decisions about the insurability of a zinc-chlorine electric vehicle battery. Specifically, they would require more definitive information on battery interlocks, chlorine absorbent specifications, battery location in the vehicle, and reliability data. They also expressed a need to see crash and impact test data to supplement the "controlled spill test" data obtained in this study. Low-speed crash test data as well as high speed crash data would be crucial to their determination of the comprehensive coverage risk. All six Allendale underwriters indicated they would be interested in reviewing the data again when the requested information is available.

Dr. Nathaniel Pulling, Project Director for Automotive Safety at Liberty Mutual Insurance Company, also provided some useful comments about his impression of the insurability of a zinc-chlorine battery-powered vehicle. The downwind chlorine concentrations measured in our hydrate spill tests were higher than Dr. Pulling would have liked to see for personal injury insurance policy coverage. Since Dr. Pulling also felt that contemporary automobile

structural design probably would not preclude battery case fracture during moderate-speed collisions, hydrate spill counteractive safeguards may be required. Crash test data indicating the contrary would be needed to convince him of an "acceptably safe" vehicle configuration containing a zinc-chlorine battery.

Regulatory agency representatives, as well as insurance industry personnel, have expressed a need for crash tests to be conducted before reaching any conclusions about the establishment of zinc-chlorine battery vehicle safety regulations. Mr. Steven Pierce of the National Highway Traffic Safety Administration commented to this effect at the conclusion of a project briefing at DOE.

IX

CHLORINE CASUALTY PROJECTIONS

9.1 METHODOLOGY

9.1.1 Statistical Formulation

Experimental results reported in Section VII demonstrate that dangerous chlorine vapor concentrations can exist at least 10-23 m downwind of a large hydrate spill onto a warm road surface. If the spill resulted from a vehicle accident, incapacitated or trapped vehicle occupants in this danger zone would be potential chlorine casualties. Fatalities can be expected if the spill is sufficiently large and if local meteorological conditions cause the resulting chlorine vapor cloud to envelop trapped or disabled people in the spill vicinity. The following formulation provides a preliminary basis for estimating the expected number of such fatalities in a particular city or state from which meteorological statistics are available.

The elementary equation for the expected number of chlorine-induced fatalities due to accidents involving zinc-chlorine electric vehicle batteries is:

$$\begin{aligned} \text{No. of Fatalities} &= \text{No. of Trapped/Disabled Vehicle Occupants} \\ &\quad \times \text{Probability of Occupant Being Enveloped in} \\ &\quad \text{Chlorine Cloud} \end{aligned} \tag{9-1}$$

In order to evaluate the two factors on the right hand side of eq (9-1), we invoke the following assumptions:

- 1) Collisions involving zinc-chlorine vehicles result in entrapped and disabled vehicle occupants at the same rate as is currently experienced with conventional vehicles.
- 2) The probability of a large- or moderate-size hydrate spill is an assumed function of vehicle impact speed in the collision.
- 3) The probability of an immobile person being enveloped in fatal chlorine vapor concentrations can be calculated from the quasi-steady virtual point source (area source) chlorine dispersion model described in Sections 4.3 and 7.3.

Using these assumptions, we can expand eq (9-1) in terms of its component conditional probabilities. Thus:

$$F^{\ell} = \sum_{k=1}^5 F_k^{\ell} = \sum_{k=1}^5 n_k \sum_{i=1}^5 \sum_{m=1}^3 \sum_{j=1}^3 \sum_{q=1}^3 p_{im}^{\ell} p_j^{\ell} p_{qk}^{\ell} f_{ijmq} \quad (9-2)$$

where F^{ℓ} = expected number of chlorine-induced fatalities per Billion Vehicle Miles (BVM) in city ℓ ;

F_k^{ℓ} = expected chlorine fatality rate (fatalities per BVM) in city ℓ in collision category k ;

n_k = expected number of trapped or incapacitated (per BVM) vehicle occupants in collision category k ;

p_{im}^{ℓ} = joint probability of occurrence of wind speed/stability category i, m (i = wind speed, m = stability category) in city ℓ ;

p_j^{ℓ} = probability of occurrence of temperature category j , in city ℓ ;

p_{qk}^{ℓ} = joint probability of spill area category q , and collision category k ;

f_{ijmq} = conditional probability of a trapped/incapacitated vehicle occupant being within fatal chlorine cloud given (wind speed, temperature, wind stability, spill area) conditions i, j, m, q .

We have estimated values of n_k by extrapolating data from the National Crash Severity Study (NCSS)^(28,29) conducted by the National Highway Traffic Safety Administration. The National Crash Severity Study is an accident data collection and analysis program involving towed passenger cars in seven selected localities in the United States. The NCSS data bank is the most comprehensive source of vehicle accident data compiled as a function of crash velocity (estimated change in vehicle velocity in collision). In addition to published data on injuries⁽²⁸⁾, the National Center for Statistics and Analysis of the National Highway Traffic Safety Administration provided FMRC with a separate tabulation of the number of trapped vehicle occupants and accidents as a function of crash velocity. We extrapolated this raw data from seven localities to national estimates of the number of survivable entrapments and disabling injuries (requiring hospitalization) per Billion Vehicle Miles (BVM) by multiplying by the ratio of the annual number of vehicle fatalities in the U.S. (48,000) divided by the number

of fatalities in the NCSS data bank (228 for the injury tabulation and 440 for the entrapment tabulation) and then dividing by the total number of BVM driven annually in the U.S. (1490 BVM). The resulting values of n_k are listed in Table 9-1.

The relative probability of occurrence of the five collision categories has also been ascertained from National Crash Severity Study data by calculating the percentage of all accidents involving entrapments in each of the five crash velocity categories. The results which are shown in the last column in Table 9-1 were used in the calculation of p_{qk} (joint spill/collision category probability) as explained below.

In lieu of any crash test data for zinc-chlorine batteries, hydrate spill probabilities had to be assumed. Six different sets of the spill probability matrix, p_{qk} , were used to span the range from highly conservative to highly optimistic. Each set of spill probabilities was obtained by first prescribing values for the conditional probabilities of (negligible, small, and large) spills, given a collision in the various crash velocity categories. These conditional probabilities were then multiplied by the relative probability of each collision category (last column in Table 9-1) to obtain the joint probability, p_{qk} . The values of the conditional and joint spill probabilities for all six cases are listed in Table 9-2. Within a given collision category the probability for a large spill is greatest for Case 1 (most conservative) and least for Case 6 (most optimistic).

Wind speed and stability category probabilities, p_{im} , were calculated from statistical wind distribution data provided by the National Climatic Center of the National Oceanic and Atmospheric Administration. Data were obtained for three cities (Boston, Detroit, and Los Angeles) with differing meteorological climates. The joint probabilities, p_{im} , for these cities are shown in Tables 9-3, 9-4, and 9-5. Comparing the data in these tables, it is evident that the probability of high winds is greatest for Boston and least for Los Angeles. Los Angeles has the greatest incidence of calm, stable winds, which are the meteorological conditions that promote long-lived, concentrated chlorine vapor clouds.

The air temperature category probabilities, p_j^{ℓ} , for Boston, Detroit, and Los Angeles, were calculated from monthly mean temperatures published in the

TABLE 9-1
TRAPPED AND DISABLED VEHICLE OCCUPANT DATA

Collision Category k	Crash Velocity (mph)	NCSS ¹ Data		Extrapolated Data ⁴		n _k (Entrapments + Disablements per BVM)	Relative Probability of Crash ⁵
		Hospitalization Injuries ²	Entrapments ³	Disabling Injuries	Entrapments		
1	0- 9	205	15	43,050	1,630	30.2	.044
2	10-19	776	69	162,960	7,520	115.5	.200
3	20-29	494	137	103,740	14,930	81.6	.396
4	30-39	267	62	56,100	6,760	43.2	.180
5	Over 39	140	62	29,400	6,760	25.1	.180
	Total	1,882	345	395,250	37,600	295.6	1.0

¹National Crash Severity Study

²From Figure 2 for Ref 28

³From computer tabulation for NCSS pre-April 1979 weighted data

⁴Extrapolated to annual national estimates by multiplying the hospitalization injury by 210 and the entrapment data by 109 as explained on pp 86-87.

⁵From NCSS Data on the relative number of accidents (involving disabling injuries or entrapments) in the various crash velocity categories.

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TABLE 9-2
ASSUMED HYDRATE SPILL PROBABILITIES

Collision Category	Crash Velocity (mph)	Conditional Spill Probability (Joint Probability, p_{qk}) [*]		
		Negligible Spill (A = 0)	Small Spill (A = 0.5m ²)	Large Spill (A = 2.3m ²)
Case 1 (Conservative)				
1	0- 9	.80 (.035)	.15 (.0066)	.05 (.0022)
2	10-19	.60 (.12)	.25 (.050)	.15 (.03)
3	20-29	.15 (.024)	.60 (.238)	.25 (.099)
4	30-39	.05 (.009)	.30 (.054)	.65 (.117)
5	Over 39	.01 (.002)	.09 (.016)	.90 (.162)
	Total	(.19)	(.37)	(.41)
Case 2				
1	0- 9	.90 (.040)	.09 (.0040)	.01 (.0004)
2	10-19	.75 (.150)	.24 (.048)	.01 (.002)
3	20-29	.25 (.099)	.60 (.238)	.15 (.060)
4	30-39	.10 (.018)	.50 (.090)	.40 (.072)
5	Over 39	0 (0)	.35 (.063)	.65 (.117)
	Total	(.307)	(.445)	(.251)
Case 3				
1	0- 9	.95 (.042)	.04 (.002)	.01 (.0004)
2	10-19	.80 (.16)	.19 (.038)	.01 (.002)
3	20-29	.50 (.198)	.40 (.158)	.10 (.0396)
4	30-39	.35 (.063)	.45 (.081)	.20 (.036)
5	Over 39	.20 (.036)	.50 (.090)	.30 (.054)
	Total	(.50)	(.37)	(.130)

^{*}The joint probability is the assumed spill probability within a given collision category multiplied by the relative probability of occurrence of that collision category.

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TABLE 9-2 (Continued)

Collision Category	Crash Velocity (mph)	Conditional Spill Probability (Joint Probability, p_{qk}) [*]		
		Negligible Spill (A = 0)	Small Spill (A = 0.5m ²)	Large Spill (A = 2.3m ²)
Case 4				
1	0- 9	.955 (.042)	.040 (.00176)	.005 (.00022)
2	10-19	.92 (.184)	.074 (.0148)	.006 (.0012)
3	20-29	.65 (.257)	.31 (.123)	.040 (.01584)
4	30-39	.55 (.099)	.37 (.0666)	.080 (.0144)
5	Over 39	.23 (.0414)	.59 (.1062)	0.18 (.0324)
	Total	(.623)	(.310)	(.0638)
Case 5				
1	0- 9	.997 (.0443)	.002 (.000089)	.001 (.0000448)
2	10-19	.99 (.198)	.008 (.0016)	.002 (.0004)
3	20-29	.89 (.353)	.10 (.0397)	.01 (.00397)
4	30-39	.75 (.135)	.23 (.0414)	.02 (.0036)
5	Over 39	.25 (.045)	.60 (.108)	.15 (.027)
	Total	(.770)	(.194)	(.035)
Case 6 (Highly Optimistic)				
1	0- 9	.998 (.044)	.001 (.00004)	.001 (.00004)
2	10-19	.998 (.199)	.003 (.0006)	.002 (.0004)
3	20-29	.95 (.376)	.045 (.018)	.005 (.0020)
4	30-39	.80 (.144)	.185 (.033)	.015 (.0027)
5	Over 39	.30 (.054)	.60 (.108)	.10 (.108)
	Total	(.817)	(.169)	(.027)

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TABLE 9-3

JOINT PROBABILITY DISTRIBUTION OF WIND SPEED
AND STABILITY CATEGORY FOR BOSTON ($\ell = 1$)

Reference: Annual Wind Distribution by Pasquill Stability Classes
STAR PROGRAM (1966-1970)
U.S. Dept. of Commerce National Oceanic and Atmospheric Administration
Environmental Data Service

Wind Speed (m/sec) (knots)		Stability Category			Wind Speed Category Subtotal
		Unstable A+B+C	Neutral D	Stable E+F	
0.77	0- 3	0.003561	0.001233	0.015	0.0198
2.57	4- 6	0.015616	0.017877	0.076507	0.1100
4.37	7-10	0.054315	0.067466	0.203151	0.3249
6.94	11-16	0.018151	0.168287	0.226986	0.4134
10.29	>17	<u>0.002397</u>	<u>0.064109</u>	<u>0.065343</u>	<u>0.1318</u>
Subtotal		0.09404	0.318972	0.586987	1.0

TABLE 9-4

JOINT PROBABILITY DISTRIBUTION OF WIND SPEED
AND STABILITY CATEGORY FOR DETROIT ($\ell = 2$)

Reference: Annual Wind Distribution by Pasquill Stability Classes (5)
STAR PROGRAM (1974)
U.S. Dept. of Commerce National Oceanic and Atmospheric Administration
Environmental Data Service

Wind Speed (knots)	Unstable A+B+C	Neutral D	Stable E	Wind Speed Category Subtotal
0- 3	0.003767	0.003082	0.012329	0.0192
4- 6	0.02945	0.044178	0.093493	0.1670
7-10	0.04589	0.218835	0.096575	0.3613
11-16	0.014726	0.325685	0.00	0.3404
>17	<u>0.002054</u>	<u>0.109932</u>	<u>0.00</u>	<u>0.1120</u>
Subtotal	0.095887	0.701712	0.202397	1.0

TABLE 9-5

JOINT PROBABILITY DISTRIBUTION OF WIND SPEED
AND STABILITY CATEGORY FOR LOS ANGELES ($\ell = 3$)

Reference: Annual Wind Distribution by Pasquill Stability Classes (6)
STAR PROGRAM (1/73 - 12/74)
U.S. Dept. of Commerce National Oceanic and Atmospheric Administration
Environmental Data Service

Wind Speed (knots)	Unstable A+B+C	Neutral D	Stable E+F+G	Wind Speed Category Subtotal
0- 3	0.026883	0.016781	0.171232	0.2160
4- 6	0.04726	0.065753	0.253596	0.3666
7-10	0.099829	0.079623	0.11798	0.2974
11-16	0.027055	0.054623	0.026712	0.1084
>17	<u>0.000514</u>	<u>0.008048</u>	<u>0.00411</u>	<u>0.0173</u>
Stability Category Subtotal	0.201541	0.224828	0.57363	1.0

Climatic Atlas.⁽³⁰⁾ Three temperature ranges were defined as listed in Table 9-6 to represent negligible, small, and large temperature differences between the spilled hydrate and the air. (The road surface was assumed to be equal to the air temperature for purposes of the hydrate vaporization calculations.) The probabilities shown in Table 9-6 represent the number of months in which the mean temperature was in a given range, divided by 12 months per year.

TABLE 9-6
TEMPERATURE CATEGORY PROBABILITIES

Category	Temperature (°C)	Probability, p_j^l		
		Boston	Detroit	Los Angeles
j=1	Under 10	.500	.500	0
2	10-20	.333	.250	.667
3	Over 20	.167	.250	.333

The technique for incorporating these temperature and wind speed/stability categories into the calculation of the chlorine vapor cloud probability denoted by f_{ijmq} in eq (9-2), is presented in the following discussion.

9.1.2 Dispersion Calculations

Our objective here is to calculate the probability of a trapped or injured person in the hydrate spill vicinity being located within the lethal chlorine vapor cloud. Our approach to this calculation is illustrated in Figure 9-1. The sketch in Figure 9-1 shows two vehicles involved in a collision in which there is a hydrate spill. The footprint of the 50-ppm chlorine isopleth is shown enveloping one of the vehicles. Conceptually, the probability of someone being within the 50-ppm isopleth, is proportional to the angle θ subtended by the isopleth. In fact, if we further assume the trapped/injured person is sufficiently close to the spill, the angle θ determines the probability without any influence of the absolute downwind/crosswind distances of the isopleth.

The angle θ depends on hydrate spill size, wind speed, wind stability category, and ambient temperature. These variables are represented by the indices q , i , m , and j in eq (9-2). As a first approximation, we can calculate

FIGURE 9-1 POTENTIALLY LETHAL ISOPLETH IN A COLLISION SPILL SCENARIO

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the probability f_{ijmq} from:

$$f_{ijmq} = \theta_{ijmq}/2\pi \quad (9-3)$$

where θ_{ijmq} is in units of radians. As a second approximation we can modify eq (9-3) to incorporate the effects of the height of the isopleth, z , in comparison to a characteristic vehicle height, H , representing the head height of trapped or injured occupants. One such modification would be:

$$f_{ijmq} = (\theta_{ijmq}/2\pi) \exp \left(- H/z_{ijmq} \right) \quad (9-4)$$

Equation (9-4) has been adopted with the value of H set equal to 0.4 m.

Accurate calculation of θ_{ijmq} and z_{ijmq} requires knowledge of the flow field and dispersion pattern around the vehicle. Since there is apparently no available general analytical description of this flow/dispersion field (for an arbitrarily directed wind flow), we must resort to an approximate model that ignores the vehicle/wind flow interaction. This is a fundamental limitation of these preliminary casualty projections.

To compute approximate values of θ_{ijmq} and z_{ijmq} , we have used the quasi-steady area source dispersion model described in Section 4.3. The time decaying chlorine vapor release rate, $\dot{Q}$, needed for the dispersion model has been estimated by extrapolating the empirical relationships for $\dot{Q}$ determined for the hydrate spill tests. We note that eq (7-2a) and (7-2b) (corresponding to spill tests 5 and 6, respectively) have approximately the same exponent for time decay, but different coefficients reflecting the different hydrate spill areas, hydrate composition, and slab temperatures. As a generalization of eq (7-2), we hypothesize:

$$\dot{Q}_{jk} = (T_j - 9.6^\circ\text{C}) A_k b t^{-0.14} \quad (9-5)$$

where T_j is a representative ambient temperature in category, j ; and A_k is the spill area for spill size category, k . The value of the constant b has been evaluated by substituting the values of T_j (28°C) and A_k (2.3 m^2) for Spill Test 6 into eq (9-5) and equating it to eq (7-2a). The result is:

$$\dot{Q}_{jk} = 1.2 \times 10^{-4} (T_j - 9.6^\circ\text{C}) A_k t^{-0.14} \text{ m}^3/\text{sec} \quad (9-6)$$

For temperature category $j=1$, we set $\dot{Q}_{jk} = 0$. For the other two temperature categories, we employ $T_2 = 15^\circ\text{C}$ and $T_3 = 25^\circ\text{C}$. The values of A_k , as shown in Table 9-2 are $A_1 = 0$, $A_2 = 0.5 \text{ m}^2$, and $A_3 = 2.3 \text{ m}^2$.

Employing eq (9-6) as a source term, chlorine vapor concentrations can be calculated as a function of time using eqs (4-7) through (4-12). Similarly, eqs (4-3) and (4-4) can be used to calculate chlorine isopleth boundaries. In particular, we can calculate the 50-ppm isopleth boundary at 30 min after the spill. According to Figure 3-1, this concentration-exposure combination lies on the fatality threshold.

As illustrated in Figure 9-1, the isopleth half-angle is given by:

$$\theta/2 = \arctan (y_{\max}/x_m) \quad (9-7)$$

where $y_{\max}$ and x_m are the coordinates of the maximum crosswind extent of the isopleth. (The indicial subscripts for θ have been omitted for simplicity in eq (9-7).) The following equations for $y_{\max}$, x_m , and z_m can be derived by differentiating eq (4-3). The result is:

$$x_m = [\dot{Q}(t=30 \text{ min}) / (2\pi \cdot 50 \times 10^{-6} a_y a_z \bar{U})] \frac{1}{b_y + b_z} \quad (9-8a)$$

$$y_m = a_y \sqrt{1 + b_z/b_y} X_m^y / \sqrt{\exp(b_y)} \quad (9-8b)$$

$$z_m = a_z \sqrt{1 + b_y/b_z} X_m^z / \sqrt{\exp(b_z)} \quad (9-8c)$$

where a_y , a_z , b_y , b_z are the dispersion coefficients defined in eq (4-11). Substituting eqs (9-8a,b,c) into eqs (9-7) and (9-4) we can calculate the values of f_{ijmq} for the various categories.

Computed probabilities f_{ijmq} for the non-zero $\dot{Q}$ combinations of categories are shown in Table 9-7. It is evident from Table 9-7 that the largest probabilities of being enveloped in the fatal chlorine cloud correspond to large spill areas, low wind speeds, and high ambient temperatures. The maximum probability in Table 9-7 is .0306.

TABLE 9-7

CASUALTY PROBABILITY

BASIS : TIME = 30 MIN.
CONC.(ISO) = 50 PPM

AMBIENT TEMP.(°C)	15°C										25°C									
SOURCE AREA (M ²)	0.5 M ²					2.32 M ²					0.5 M ²					2.32 M ²				
WIND VEL. ATM. (M/S) CATAG.	0.77	2.57	4.37	6.94	10.3	0.77	2.57	4.37	6.94	10.3	0.77	2.57	4.37	6.94	10.3	0.77	2.57	4.37	6.94	10.3
UNSTABLE $\sigma_z = .078X^{1.02}$ $\sigma_y = 0.2X^{0.91}$	.01222	.00374	.00164	.00064	.00023	.02466	.01503	.01055	.00702	.00453	.02104	.01091	.00685	.00402	.00227	.03056	.02354	.01941	.01550	.01213
NEUTRAL $\sigma_z = .12X^{0.81}$ $\sigma_y = .13X^{0.91}$	.01356	.00711	.00460	.00283	.00169	.02017	.01523	.01250	.00999	.00788	.01842	.01273	.00986	.00739	.00545	.02275	.01964	.01760	.01549	.01351
STABLE $\sigma_z = .018X^{0.96}$ $\sigma_y = .077X^{0.91}$	.00436	.00103	.00038	.00013	.00004	.01050	.00563	.00364	.00221	.00130	.00858	.00379	.00215	.00113	.00057	.01390	.00990	.00775	.00585	.00432

9.2 CALCULATED CHLORINE-INDUCED FATALITIES

Calculated results for the expected chlorine fatality rates in each collision category (F_k^l) and the totals in each of the three cities (F^l) are shown in Table 9-8 for all six sets of spill probability estimates. The expected chlorine fatality rates for Boston are considerably lower than those for Detroit which, in turn, are significantly lower than those for Los Angeles. The colder and windier climate in Boston causes the expected chlorine fatality rate to be only about 13% of that expected in Los Angeles. Detroit has an expected fatality rate between those of Los Angeles and Boston because Detroit is colder than Los Angeles (implying lower hydrate vaporization rates), but has lower wind speeds than Boston.

The calculated chlorine fatality rates for all three cities have been plotted in Figure 9-2. The abscissa in Figure 9-2 is the value of spill probability p_{43} (probability of a large spill during a 30-39 mph collision, which is used to represent the entire matrix p_{qk} for each of the six cases in Table 9-2. The 30-39 mph collision range (median speed 35 mph) spill probability has been selected for presenting the data in Figure 9-2 because 1) the calculated fatality projections are quite sensitive to assumed values of p_{43} in the range .015-.65, and 2) the approximate value of p_{43} for a particular battery case and vehicle design can readily be ascertained from a future series of crash tests or simulated crash tests. In fact, 35-mph crash test to determine battery case integrity would be directly analogous to the 30-mph crash test currently prescribed in Federal Motor Vehicle Safety Standard 301 to ascertain fuel system integrity and fire hazards in petroleum-fueled vehicles, and to ascertain electric vehicle compliance (with regard to battery materials remaining outside the passenger compartment) with one of the first phase safety standards for vehicles purchased under the Electric and Hybrid Vehicle Research, Development, and Demonstration Act of 1976.

The projected chlorine fatality rates shown in Table 9-9 and Figure 9-2 are small in comparison with the current vehicle rate of 32.7 fatalities (from all causes) per BVM. It is also interesting to compare the calculated chlorine fatality projections with the current fatality levels directly attributable to internal combustion engine vehicle propulsion systems. Internal combustion engines are responsible for fire fatalities and for carbon monoxide asphyxiation fatalities. According to National Fire Protection Association (NFPA) survey

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TABLE 9-8
CHLORINE FATALITY PROJECTIONS

Collision Category	Crash Velocity	Expected Fatalities per BVM in		
		Boston	Detroit	Los Angeles
	Case 1 (Conservative Spill Probabilities)			
1	0- 9	.001	.006	.010
2	10-19	.051	.228	.392
3	20-29	.169	.749	.130
4	30-39	.131	.589	.101
5	<u>Over 39</u>	<u>.103</u>	<u>.471</u>	<u>.798</u>
	Total	.456	2.04	3.51
	Case 2			
1	0- 9	.001	.002	.004
2	10-19	.027	.112	.202
3	20-29	.132	.571	1.005
4	30-39	.106	.465	.810
5	<u>Over 39</u>	<u>.087</u>	<u>.386</u>	<u>.665</u>
	Total	.353	1.54	2.69
	Case 3			
1	0- 9	.0003	.001	.003
2	10-19	.021	.091	.162
3	20-29	.090	.391	.687
4	30-39	.072	.316	.552
5	<u>Over 39</u>	<u>.060</u>	<u>.264</u>	<u>.460</u>
	Total	.244	1.06	1.86
	Case 4			
1	0- 9	.0003	.001	.002
2	10-19	.009	.039	.069
3	20-29	.057	.245	.435
4	30-39	.046	.200	.353
5	<u>Over 39</u>	<u>.043</u>	<u>.188</u>	<u>.331</u>
	Total	.156	.673	1.19

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TABLE 9-8 (Continued)

Collision Category	Crash Velocity	Expected Fatalities per BVM in		
		Boston	Detroit	Los Angeles
		<u>Case 5</u>		
1	0- 9	.000	.000	.000
2	10-19	.001	.005	.009
3	20-29	.017	.071	.126
4	30-39	.017	.074	.132
5	Over 39	.026	.112	.197
	Totals	.061	.262	.464
		<u>Case 6 (Optimistic Spill Probabilities)</u>		
1	0- 9	.000	.000	.000
2	10-19	.001	.003	.005
3	20-29	.008	.033	.059
4	30-39	.011	.046	.083
5	Over 39	.021	.089	.157
	Total	.040	.171	.303

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FIGURE 9-2 PROJECTED CHLORINE FATALITY RATES VERSUS LARGE HYDRATE SPILL PROBABILITY

statistics,⁽³²⁾ there were 722 motor vehicle fire deaths in 1977, corresponding to a rate of 0.48 fire fatalities per BVM. This value is represented by the bottom of the hatched band in Figure 9-2. According to National Safety Council statistics, there are about 900 annual carbon monoxide asphyxiations, but it is not possible to determine how many of those asphyxiations are due to motor vehicle incidents. Thus, the total annual number of motor vehicle fire and carbon monoxide fatalities is 722-1622 or 0.48-1.08 fatalities per BVM. This range is represented by the horizontal band in Figure 9-2.

The fatality rate comparison shown in Figure 9-2 might serve as a preliminary design target for the development of crashworthy zinc-chlorine-battery powered vehicles. Thus, if the battery and vehicle are sufficiently strong so that the probability of a large hydrate spill during a 35-mph crash is less than 2-7%, projected chlorine fatality rates will be less than current fatality rates due to petroleum-fueled vehicles. Furthermore, if zinc-chlorine-battery powered vehicles are operated predominantly in cold, windy climates, such as in Boston, significantly higher spill probabilities (as high as 60% for a 35-mph crash) might be tolerated.

The preceding preliminary comparison of fatality rates provides only one measure of the relative hazard of zinc-chlorine electric vehicle batteries. It is also important to realize that accidental releases of chlorine will occasionally cause temporary respiratory injuries and complaints from vehicle occupants and possibly from nearby bystanders. Although it does not appear to be feasible at this point to calculate the number of potential injuries and complaints from the myriad possible release scenarios, some related data are available from reports of accidents involving spills of liquid chlorine. The tabulation published by Simmons et al⁽¹⁸⁾ and newspaper accounts of more recent accidents include reports of over 100 people "gassed" (presumably seeking medical assistance) in several incidents where there was, at most, one fatality. Even though individual chlorine hydrate spills should not cause nearly as many injuries as liquid chlorine spills, the accident data indicate that chlorine-induced distress and injuries are an important potential problem to be considered together with the chlorine fatality projections presented here.

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CONCLUSIONS AND RECOMMENDATIONS

10.1 CONCLUSIONS

Theoretical and experimental results obtained in this hazard assessment of the zinc-chlorine electric vehicle battery lead to the following conclusions:

1. The major chlorine hazard associated with future widespread uses of these electric vehicle batteries is the potential for large chlorine hydrate spills during collisions. The extent of the downwind danger zone in this scenario depends upon battery state of charge, road and air temperatures, wind speed and turbulence level, local topography, and the size of the spill. Field tests under New England summer conditions at a rural site with the hydrate equivalent of a partially charged 50-KWh battery indicate that the zone in which chlorine concentrations are dangerously high extends at least 23 m downwind, with a subtended angle of about 30° around the mean wind direction.

2. The transient chlorine distribution downwind of a hydrate spill in an open area can be predicted (within a factor of five at worst and in many cases much closer) using a quasi-steady area source dispersion model with an empirical estimate of the chlorine release rate. In view of the uncertainty in predicting physiological responses to the rapidly fluctuating measured chlorine concentrations, this level of accuracy should suffice for future assessments of mishaps on open roadways.

3. Preliminary projections of expected chlorine-induced fatalities have been performed using the quasi-steady area-source chlorine dispersion model together with statistics on the number of vehicle occupants trapped and seriously injured (and presumably immobilized) in collisions of conventional motor vehicles. The projected chlorine fatality rates for three cities with different meteorological conditions are all significantly lower than the current vehicle fatality rate for all causes (33 fatalities per Billion Vehicle Miles). Projections for the Los Angeles area indicate that large hydrate spill probabilities of 2-7% for a 35-mph collision (and correspondingly lower probabilities at lower crash velocities) produce chlorine-induced fatality rates that are comparable to the current vehicle fatality rate due to fires and asphyxiations (0.5-1.1 fatalities per BVM). Results for the Boston climate (colder and windier than Los Angeles) indicate that 35-mph spill probabilities can exceed 60% before the equivalent fatality rate is reached.

4. Other outdoor accidental chlorine release scenarios, such as hydrogen-chlorine explosions and direct chlorine vapor discharge from a partially breached battery case may result in some distress and discomfort to nearby bystanders. However, these mishaps should not cause any serious injuries, providing bystanders are mobile and not suffering from severe respiratory ailments.

5. Accidental chlorine releases in road tunnels should not result in dangerous cross-section averaged chlorine concentrations provided ventilation velocities are about 6 m/sec. Lower ventilation velocities appear feasible in conjunction with chlorine detectors to actuate increased ventilation rates during accidents.

10.2 RECOMMENDATIONS

Regulatory agency authorities and insurance underwriters will require additional data before passing judgment on the acceptability of zinc-chlorine electric vehicle batteries. To supply these data, we recommend:

1. A detailed Failure Modes and Effects Analysis should be conducted for the zinc-chlorine electric vehicle battery and auxiliary (e.g., charging) systems.

2. Crash tests should be conducted with prototype electric vehicles powered by zinc-chlorine batteries. These crash tests and simulated crash tests with the battery alone should be designed to determine the expected sizes and probabilities of hydrate spills at different impact velocities. The crash results can then be used to refine the predictions presented here of expected chlorine fatality rates.

3. Fire tests should be conducted with prototype zinc-chlorine electric vehicle batteries. The fire tests should be designed to assess the influence of the chlorine content of the battery on its flammability (and the interaction of the chlorine with the initiating exposure fire) as well as the chlorine dispersion hazard during a fire.

4. More definitive design studies should be conducted for battery safety components such as rupture discs, chlorine absorbent foams, interlocks, and emergency shutdown conditions. Feasibility studies should also be conducted of emergency response techniques to be employed by people responding to accidents outdoors and in tunnels and garages.

5. The ventilation system of prototype electric vehicle passenger compartments should be reviewed to determine whether there is a significant potential of chlorine accumulating in the vehicle as a result of minor leaks from the battery.

6. As the zinc-chlorine battery design (in particular, the hydrate store) evolves into a significantly different configuration from that considered here, tests and analyses described here should be repeated with the new configuration.

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APPENDIX A

SMALL-SCALE HYDRATE SPILL TEST DATA

Chlorine hydrate mass loss and slab temperature data for the 13 small-scale laboratory and field spill tests are presented in this Appendix. For each test, curves of hydrate mass and slab surface temperature are reproduced directly from data recordings. In addition, curves for mass loss, M , instantaneous rate of mass loss, $\frac{dM}{dt}$, and cumulative mass loss rate, M/t , are presented as obtained by numerical differencing of the mass loss data.

TABLE A-1

GHORINE HYDRATE VAPORIZATION DATA SUMMARY

Test No.	Hydrate Mass (g)	Ambient Temp (°C)	Surface Temp (°C)	Mass Vaporized in 15 min		Final Mass (%)	Final Time (min)	Heater (Lab Tests)	ZnCl ₂ Conc (%)	Filtered
				(g)	(%)					
1	243	22	20	4	1.7	3.3	62	off	2	no
2	434	23	50	15	3.5	6.9	105	on	2	no
3	600	34	45	32	5.3	10.0	120	on	2	yes
4	323	32	40	47	14.6	34.4	74	off	2	part
5	504	28	36	48	9.6	17.2	75	off	2	part
6	562	24	40	26	4.6	10.7	118	off	12	yes
7	384	21	40	28	7.3	15.1	35	off	12	yes
8*	1,034	28	45	93	9.0	11.4		<u>Charge Time</u> 5 hr	20	<u>Structure</u> Thick
9*	1,105	28	43	71	6.4	7.5	39	2 hr	15	Loose
10*	683	33	52	36	5.3	6.8	35	2.3 hr	5	Thick
11*	1,057	28	45	77	7.3	8.7	37	3.4 hr	4.6	Thin
12*	822	25	27	40	4.9	5.0	34	2.6 hr	6	Thin
13*	730	28	30	48	6.5	10.1	36	5 hr	5	Thick

* Samples obtained from hydrate in field tests.

LABORATORY HYDRATE SPILL TEST 1

RKT

VAP LAB DATA

1	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
	1.	0.5	0.5	0.5	0.21
	2.	1.	0.5	0.5	0.41
	3.	1.3	0.43	0.3	0.53
	4.	1.6	0.4	0.3	0.66
	5.	2.	0.4	0.4	0.82
	6.	2.2	0.37	0.2	0.91
	7.	2.4	0.34	0.2	0.99
	8.	2.6	0.33	0.2	1.07
	9.	2.8	0.31	0.2	1.15
	10.	3.	0.3	0.2	1.23
	11.	3.2	0.29	0.2	1.32
	12.	3.4	0.28	0.2	1.4
	13.	3.6	0.28	0.2	1.48
	14.	3.8	0.27	0.2	1.56
	15.	4.	0.27	0.2	1.65
	30.	6.	0.2	0.13	2.47
	45.	7.	0.16	0.07	2.88
	60.	8.	0.13	0.07	3.29
	62.	8.	0.13	0.	3.29

Laboratory Hydrate Spill Test #1

LABORATORY HYDRATE SPILL TEST 2

RKT

VAP LAB DATA

2	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
	1.	4.	4.	4.	0.92
	2.	7.	3.5	3.	1.61
	3.	8.5	2.83	1.5	1.96
	4.	10.	2.5	1.5	2.3
	5.	12.	2.4	2.	2.76
	6.	12.3	2.05	0.3	2.83
	7.	12.5	1.79	0.2	2.88
	8.	13.	1.63	0.5	3.
	9.	13.5	1.5	0.5	3.11
	10.	14.	1.4	0.5	3.23
	11.	14.2	1.29	0.2	3.27
	12.	14.4	1.2	0.2	3.32
	13.	14.6	1.12	0.2	3.36
	14.	14.8	1.06	0.2	3.41
	15.	15.	1.	0.2	3.46
	30.	16.	0.53	0.07	3.69
	45.	19.	0.42	0.2	4.38
	60.	23.	0.38	0.27	5.3
	75.	24.	0.32	0.07	5.53
	90.	28.	0.31	0.27	6.45
	105.	30.	0.29	0.13	6.91

Laboratory Hydrate Spill Test # 2

LABORATORY HYDRATE SPILL TEST 3

VAP LAB DATA					RKT
3	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
	1.	3.	3.	3.	0.5
	2.	8.	4.	5.	1.33
	3.	12.	4.	4.	2.
	4.	16.	4.	4.	2.67
	5.	20.	4.	4.	3.33
	6.	21.	3.5	1.	3.5
	7.	23.5	3.36	2.5	3.92
	8.	25.	3.13	1.5	4.17
	9.	27.	3.	2.	4.5
	10.	29.	2.9	2.	4.83
	11.	30.	2.73	1.	5.
	12.	30.5	2.54	0.5	5.08
	13.	30.9	2.38	0.4	5.15
	14.	31.5	2.25	0.6	5.25
	15.	32.	2.13	0.5	5.33
	20.	37.	1.23	0.33	6.17
	45.	41.	0.91	0.27	6.83
	60.	43.	0.72	0.13	7.17
	75.	51.	0.68	0.53	8.5
	90.	54.	0.6	0.2	9.
	105.	58.	0.55	0.23	9.67
	120.	60.	0.5	0.13	10.

LABORATORY HYDRATE SPILL TEST 4

RKT

VAP LAB DATA

4	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
	1.	6.	6.	6.	1.86
	2.	11.	5.5	5.	3.41
	3.	13.	4.33	2.	4.02
	4.	15.	3.75	2.	4.64
	5.	18.	3.6	3.	5.57
	6.	19.	3.17	1.	5.88
	7.	22.	3.14	3.	6.81
	8.	24.	3.	2.	7.43
	9.	24.5	2.72	0.5	7.59
	10.	25.	2.5	0.5	7.74
	11.	28.	2.55	3.	8.67
	12.	29.	2.42	1.	8.98
	13.	30.	2.31	1.	9.29
	14.	32.	2.29	2.	9.91
	15.	47.	3.13	15.	14.55
	30.	81.	2.7	2.27	25.08
	45.	106.	2.36	1.67	32.82
	60.	111.	1.85	0.33	34.37
	74.	111.	1.5	0.	34.37

Laboratory Hydrate Spill Test #4

LABORATORY HYDRATE SPILL TEST 5

VAP LAB DATA					RKT
5	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
	1.	10.19	10.19	10.19	2.02
	2.	14.44	7.22	4.25	2.86
	3.	21.24	7.08	6.8	4.21
	4.	23.94	5.74	1.7	4.55
	5.	25.49	5.1	2.55	5.05
	6.	28.89	4.82	3.4	5.73
	7.	31.59	4.37	1.7	6.07
	8.	33.14	4.14	2.55	6.57
	9.	34.84	3.87	1.7	6.91
	10.	37.39	3.74	2.55	7.41
	11.	39.09	3.55	1.7	7.75
	12.	42.49	3.54	3.4	8.42
	13.	43.35	3.33	0.86	8.6
	14.	45.99	3.28	2.54	9.1
	15.	48.44	3.23	2.55	9.6
	30.	71.39	2.38	1.53	14.16
	45.	84.14	1.87	0.85	16.68
	60.	85.84	1.43	0.11	17.02
	75.	86.69	1.16	0.06	17.19

LABORATORY HYDRATE SPILL TEST 6

RKT

VAP LAB DATA

6	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
123	1.	2.	2.	2.	0.36
	2.	10.	5.	8.	1.78
	3.	12.	4.	2.	2.14
	4.	14.	3.5	2.	2.49
	5.	15.5	3.1	1.5	2.76
	6.	17.	2.93	1.5	3.02
	7.	19.	2.71	2.	3.38
	8.	21.	2.63	2.	3.74
	9.	21.5	2.39	0.5	3.83
	10.	22.	2.2	0.5	3.91
	11.	22.5	2.05	0.5	4.
	12.	23.	1.92	0.5	4.09
	13.	23.5	1.81	0.5	4.18
	14.	24.	1.71	0.5	4.27
	15.	26.	1.73	2.	4.63
	30.	32.3	1.08	0.42	5.75
	45.	37.	0.82	0.31	6.58
	60.	45.	0.75	0.53	8.01
	75.	51.	0.68	0.4	9.07
	90.	53.	0.59	0.13	9.43
105.	59.	0.56	0.4	10.5	
118.	60.	0.51	0.08	10.68

LABORATORY HYDRATE SPILL TEST ?

VAP LAB DATA					RKT
7	TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
	1.	5.02	5.02	5.02	1.31
	2.	8.03	4.02	3.01	2.09
	3.	10.04	3.35	2.01	2.61
	4.	12.05	3.01	2.01	3.14
	5.	15.07	3.01	3.02	3.92
	6.	16.07	2.68	1.	4.18
	7.	17.07	2.44	1.	4.44
	8.	18.08	2.26	1.01	4.71
	9.	19.08	2.12	1.	4.97
	10.	20.09	2.01	1.01	5.23
	11.	23.1	2.1	3.01	6.01
	12.	25.11	2.09	2.01	6.54
	13.	26.11	2.01	1.	6.8
	14.	27.12	1.94	1.01	7.06
	15.	28.12	1.87	1.	7.32
	30.	53.23	1.77	1.67	13.86
	45.	74.83	1.66	1.44	19.48
	60.	87.38	1.46	0.84	22.75
	75.	104.46	1.39	1.14	27.2
	90.	114.5	1.27	0.67	29.81
	105.	126.05	1.2	0.77	32.82

Laboratory Hydrate Spill Test # 7

CHLORINE VAR. FIELD TEST # 1

CHLORINE VAP. FIELD TEST # 1

RKT

TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
1.	12.64	12.64	12.64	1.22
2.	26.44	13.22	13.8	2.56
3.	36.79	12.26	10.35	3.56
4.	45.99	11.5	9.2	4.45
5.	50.58	10.12	4.59	4.89
6.	56.63	9.39	5.75	5.45
7.	59.63	8.38	3.3	5.67
8.	65.53	8.19	6.9	6.34
9.	70.13	7.79	4.6	6.78
10.	74.73	7.47	4.6	7.23
11.	79.33	7.21	4.6	7.67
12.	82.78	6.9	3.45	8.01
13.	89.67	6.9	6.39	8.67
14.	91.97	6.57	2.3	8.9
15.	93.12	6.31	1.15	9.01
16.	98.67	6.18	5.75	9.57
17.	103.47	6.09	4.6	10.01
18.	114.05	6.34	10.53	11.03
19.	114.51	6.03	0.46	11.08
20.	114.95	5.74	0.34	11.11
21.	114.97	5.47	0.12	11.12
22.	114.97	5.36	0.	11.12
23.	116.12	6.67	1.15	11.23
24.	117.27	3.78	1.15	11.35

CHLORINE VAP. FIELD TEST # 2

RKT

TIME (MIN) Σ MASS LOSS (GM) Σ LOSS RATE (GM/MIN) LOSS RATE (GM/MIN) CUM LOSS % (%)

1.	3.43	3.43	3.43	0.31
2.	10.39	5.15	6.66	0.93
3.	25.14	8.28	14.65	2.28
4.	53.7	13.43	28.56	4.86
5.	69.61	13.96	16.11	6.02
6.	69.92	11.65	0.11	6.33
7.	69.92	9.99	0.	6.33
8.	70.04	6.76	0.12	6.34
9.	70.04	7.78	0.	6.34
10.	70.37	7.03	0.22	6.36
11.	70.37	6.33	0.	6.36
12.	70.38	5.87	0.11	6.37
13.	70.38	5.03	0.	6.37
14.	70.5	4.7	0.12	6.38
15.	70.61	4.41	0.11	6.39
16.	70.72	4.16	0.11	6.4
17.	70.84	3.94	0.12	6.41
18.	70.84	3.37	0.	6.41
19.	71.38	3.37	1.14	6.52
20.	72.12	3.18	1.14	6.62
21.	74.27	3.09	1.15	6.72
22.	75.41	3.02	1.14	6.83
23.	76.55	2.94	1.14	6.93
24.	77.69	2.88	1.14	7.03
25.	78.84	2.82	1.15	7.14
26.	79.98	2.76	1.14	7.24
27.	81.12	2.7	1.14	7.34
28.	81.12	2.62	0.	7.34
29.	82.26	2.57	1.14	7.45
30.	82.26	2.11	0.	7.45

CUMULATIVE MASS LOSS (GM)

CUMULATIVE LOSS % (%)

TIME/MIN 1100 SS07 SS04

VOLUME (1000 cc)/min

CHLORINE VAP. FIELD TEST #3

RKT

TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
---------------	----------------------------	--------------------------------	-----------------------	-------------------

1.	10.1	10.1	10.1	1.48
2.	21.5	10.8	11.4	3.15
3.	37.2	9.1	5.7	3.98
4.	41.3	8.	4.6	4.66
5.	47.2	7.	3.4	5.16
6.	48.3	6.1	1.1	5.32
16.	48.3	2.3	0.	5.32
17.	47.4	3.2	1.1	5.48
20.	47.4	1.9	0.	5.48
21.	48.6	1.8	1.2	5.65
22.	48.6	1.8	0.	5.65
23.	48.7	1.7	1.1	5.81
24.	40.9	1.7	1.2	5.99
30.	40.9	1.4	0.	5.99
31.	43.1	1.4	2.2	6.31
32.	44.3	1.4	1.2	6.49
33.	45.4	1.4	1.1	6.65
34.	46.6	1.4	1.2	6.82
35.	46.6	1.4	0.	6.82

CHLORINE VAP. FIELD TEST # 4

RKT

	MASS LOSS	LOSS RATE	LOSS RATE	CUM LOSS %
(GMS)	(GM)	(GM/MIN)	(GM/MIN)	(%)
1.	12.6	12.6	12.6	1.17
2.	24.1	12.05	11.5	2.18
3.	34.4	11.47	10.1	3.25
4.	39.9	9.73	4.5	3.68
5.	45.3	9.16	6.9	4.33
6.	48.1	8.02	2.3	4.55
7.	52.7	7.53	4.6	4.98
8.	57.2	7.16	4.6	5.42
9.	59.4	6.49	1.1	5.52
10.	61.9	6.19	3.5	5.96
11.	66.4	6.04	4.5	6.28
12.	69.9	5.83	3.5	6.61
13.	71.	5.46	1.1	6.72
14.	73.2	5.24	2.3	6.93
15.	76.8	5.12	3.5	7.26
16.	79.	4.94	2.2	7.47
17.	80.2	4.72	1.2	7.59
18.	90.8	4.49	0.6	7.64
19.	91.3	4.38	0.5	7.69
20.	91.3	4.07	0.	7.69
21.	91.9	3.9	0.6	7.75
22.	91.9	3.72	0.	7.75
23.	92.5	3.59	0.6	7.8
24.	92.5	3.44	0.	7.8
25.	93.1	3.32	0.6	7.86
26.	93.1	3.2	0.	7.86
27.	93.6	3.1	0.5	7.91
28.	94.2	3.01	0.6	7.96
29.	94.8	2.92	0.6	8.02
30.	95.9	2.86	1.1	8.13
31.	97.1	2.91	1.2	8.24
32.	97.1	2.72	0.	8.24
33.	98.2	2.67	1.1	8.34
34.	99.4	2.63	1.2	8.46
35.	90.5	2.59	1.1	8.56
36.	91.6	2.54	1.1	8.66
37.	91.6	2.48	0.	8.66

CHLORINE VAP. FIELD TEST #5

CHLORINE VAP. FIELD TEST # 5

RKT

TIME (MIN)	Σ MASS LOSS (GM)	Σ LOSS RATE (GM/MIN)	LOSS RATE (GM/MIN)	CUM LOSS % (%)
1.	7.1	7.1	7.1	0.36
2.	10.6	5.3	3.5	1.39
3.	14.1	4.7	3.5	1.72
4.	20.	5.	5.9	2.43
5.	31.2	4.24	1.2	2.58
6.	35.9	4.32	4.7	3.15
7.	39.2	4.03	2.3	3.43
8.	39.5	3.81	2.3	3.71
9.	31.7	3.52	1.2	3.86
10.	32.9	3.29	1.2	4.
11.	34.1	3.1	1.2	4.15
12.	35.2	2.93	1.1	4.28
13.	37.6	2.69	2.4	4.58
14.	38.8	2.77	1.2	4.72
15.	39.9	2.66	1.1	4.86
16.	41.1	2.57	1.2	5.
17.	41.1	2.42	0.	5.
33.5	41.1	1.23	0.	5.

CHLORINE VAR. FIELD TEST #6

CHLORINE VAP. FIELD TEST #6

RKT

TIME (MIN) Σ MASS LOSS (GM) Σ LOSS RATE (GM/MIN) LOSS RATE (GM/MIN) CUM LOSS % (%)

1.	3.1	9.1	9.1	1.25
2.	17.	8.5	7.9	2.34
3.	22.7	7.6	5.7	3.12
4.	24.9	6.2	2.2	3.42
5.	27.8	5.6	2.9	3.82
6.	28.9	4.8	1.1	3.97
7.	29.5	4.2	0.6	4.06
8.	34.	4.7	4.5	4.67
9.	38.5	4.3	4.5	5.29
10.	40.8	4.1	2.3	5.61
11.	45.3	4.1	4.5	6.23
12.	47.6	4.	2.3	6.54
16.	47.6	3.	0.	6.54
17.	51.	3.	3.4	7.01
19.	51.	2.7	0.	7.01
20.	54.4	2.7	3.4	7.48
21.	55.5	2.6	1.1	7.63
22.	56.6	2.6	1.1	7.78
23.	59.9	2.6	2.3	8.1
24.	61.1	2.5	2.2	8.4
25.	62.3	2.5	1.2	8.56
29.	62.3	2.1	0.	8.56
30.	66.8	2.2	4.5	9.18
31.	70.2	2.3	3.4	9.65
32.	72.5	2.3	5.7	9.97
33.	73.6	2.2	1.1	10.12
36.	73.6	2.	0.	10.12

LOAD-CELL TRANSDUCER DRIFTING EVALUATION

BASIS : 700 GM MASS AS INITIAL WT.

TIME	DIVI- SION READ- ING	DRIFT- ING WT.	CUMULA- TIVE Δ WT.	INSTAN- TANEOUS Δ WT.
(MIN)	(DIV.)	(GM.)	(GM) (%)	(GM)
0.	59.00	699.6	0.0 0.00	0.0
1.	59.50	705.5	5.9 0.84	5.9
2.	59.70	707.9	8.3 1.19	2.4
3.	59.80	709.1	9.5 1.36	1.2
4.	59.90	710.3	10.7 1.53	1.2
5.	59.93	710.6	11.0 1.57	0.3
6.	59.95	710.9	11.3 1.62	0.3
7.	60.00	711.4	11.8 1.69	0.5
8.	60.00	711.4	11.8 1.69	0.0
9.	60.00	711.4	11.8 1.69	0.0
10.	60.00	711.4	11.8 1.69	0.0
11.	60.00	711.4	11.8 1.69	0.0
12.	60.05	712.0	12.4 1.77	0.6
13.	60.05	712.0	12.4 1.77	0.0
14.	60.05	712.0	12.4 1.77	0.0
15.	60.05	712.0	12.4 1.77	0.0
16.	60.10	712.6	13.0 1.86	0.6
17.	60.10	712.6	13.0 1.86	0.0
18.	60.15	713.2	13.6 1.94	0.6
19.	60.20	713.8	14.2 2.03	0.6
20.	60.25	714.4	14.8 2.12	0.6
21.	60.25	714.4	14.8 2.12	0.0
22.	60.25	714.4	14.8 2.12	0.0
23.	60.25	714.4	14.8 2.12	0.0
24.	60.20	713.8	14.2 2.03	-0.6
25.	60.15	713.2	13.6 1.94	-0.6
26.	60.10	712.6	13.0 1.86	-0.6
27.	60.10	712.6	13.0 1.86	0.0
28.	60.10	712.6	13.0 1.86	0.0
29.	60.05	712.0	12.4 1.77	-0.6
30.	60.00	711.4	11.8 1.69	-0.6
31.	60.00	711.4	11.8 1.69	0.0
32.	60.00	711.4	11.8 1.69	0.0
33.	59.90	710.3	10.7 1.53	-1.1
34.	59.90	710.3	10.7 1.53	0.0
35.	59.80	709.1	9.5 1.36	1.2
36.	59.80	709.1	9.5 1.36	0.0
37.	59.75	708.5	8.9 1.27	-0.6
38.	59.75	708.5	8.9 1.27	0.0
39.	59.75	708.5	8.9 1.27	0.0
40.	59.75	708.5	8.9 1.27	0.0
41.	59.70	707.9	8.3 1.19	-0.6
42.	59.70	707.9	8.3 1.19	0.0
43.	59.70	707.9	8.3 1.19	0.0
44.	59.75	708.5	8.9 1.27	0.6
45.	59.75	708.5	8.9 1.27	0.0
46.	59.75	708.5	8.9 1.27	0.0
47.	59.80	709.1	9.5 1.36	0.6
48.	59.85	709.7	10.1 1.44	0.6
49.	59.90	710.3	10.7 1.53	0.6
50.	59.95	710.9	11.3 1.62	0.6
51.	60.00	711.4	11.8 1.69	0.5
52.	60.00	711.4	11.8 1.69	0.0

FACTORY MUTUAL RESEARCH CORPORATION

OC1N8.RK

APPENDIX B

COMPUTER REGRESSION RESULTS FOR HYDRATE TEST DATA
DESCRIBED IN SECTION 4.4

***** STEPWISE REGRESSION *****

8 VARIABLES; VARIABLE: MV15 IS DEPENDENT

STANDARD ERROR OF Y = 26.01908

STEP NO. 1

ENTERING VARIABLE: M0

F-LEVEL 40.66412 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 12.12378

COEFFICIENT OF DETERMINATION = 0.8026216

COEFFICIENT OF MULTIPLE REGRESSION = 0.8958915

INCREASE IN COEFFICIENT OF DETERMINATION = 0.8026216

CONSTANT -13.273

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
M0	0.8342892E-01	0.1308311E-01

STEP NO. 2

ENTERING VARIABLE: F

F-LEVEL 3.220537 WITH PROB. 0.1002

STANDARD ERROR OF ESTIMATE 10.96713

COEFFICIENT OF DETERMINATION = 0.8546377

COEFFICIENT OF MULTIPLE REGRESSION = 0.9244662

INCREASE IN COEFFICIENT OF DETERMINATION = 0.5201607E-01

CONSTANT -22.718

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
M0	0.8729611E-01	0.1202952E-01
F	11.71375	6.527275

STEP NO. 3

ENTERING VARIABLE: LNMO

F-LEVEL 3.359280 WITH PROB. 0.0967

STANDARD ERROR OF ESTIMATE 9.761998

COEFFICIENT OF DETERMINATION = 0.8976257

COEFFICIENT OF MULTIPLE REGRESSION = 0.9474311

INCREASE IN COEFFICIENT OF DETERMINATION = 0.4298799E-01

CONSTANT 316.06

VARIABLE	COEFF.	STD. ERR. OF COEFF.	STANDARDIZED COEFFICIENT	T-VALUE	PROB.
M0	0.1916	0.5793E-01	2.057980	3.308	0.011
LNMO	-64.37	35.12	-1.122760	-1.833	0.104
F	19.47	7.186	0.3852337	2.709	0.027

LIST THE INDEPENDENT VARIABLES?

MO, LNMO, ZNCL, LNZNCL, TO, LNT0, F

WHICH IS THE DEPENDENT VARIABLE? LNMV15

***** STEPWISE REGRESSION *****

8 VARIABLES? VARIABLE: LNMV15 IS DEPENDENT

STANDARD ERROR OF Y = 0.8447110

STEP NO. 1

ENTERING VARIABLE: LNMO

F-LEVEL 40.20200 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 0.3954067

COEFFICIENT OF DETERMINATION = 0.8008048

COEFFICIENT OF MULTIPLE REGRESSION = 0.8948769

INCREASE IN COEFFICIENT OF DETERMINATION = 0.8008048

CONSTANT -7.1835

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
LNMO	1.665677	0.2627042

STEP NO. 2

ENTERING VARIABLE: F

F-LEVEL 7.206609 WITH PROB. 0.0212

STANDARD ERROR OF ESTIMATE 0.3105975

COEFFICIENT OF DETERMINATION = 0.8893811

COEFFICIENT OF MULTIPLE REGRESSION = 0.9430700

INCREASE IN COEFFICIENT OF DETERMINATION = 0.8857635E-01

CONSTANT -7.6188

VARIABLE	COEFF.	STD. ERR. OF COEFF.	STANDARDIZED COEFFICIENT	T-VALUE	PROB.
LNMO	1.689	0.2065	0.9074313	8.178	0.000
F	0.4887	0.1820	0.2978825	2.685	0.025

***** STEPWISE REGRESSION *****

7 VARIABLES; VARIABLE: LNMV IS DEPENDENT

STANDARD ERROR OF Y = 1.258318

STEP NO. 1

ENTERING VARIABLE: M(T)

F-LEVEL 41.81361 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 1.140587

COEFFICIENT OF DETERMINATION = 0.1827409

COEFFICIENT OF MULTIPLE REGRESSION = 0.4274821

INCREASE IN COEFFICIENT OF DETERMINATION = 0.1827409

CONSTANT -6.7232

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
M(T)	1.195008	0.1848043

STEP NO. 2

ENTERING VARIABLE: LNDT

F-LEVEL 64.73440 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 0.9850140

COEFFICIENT OF DETERMINATION = 0.3937402

COEFFICIENT OF MULTIPLE REGRESSION = 0.6274872

INCREASE IN COEFFICIENT OF DETERMINATION = 0.2109993

CONSTANT -8.9612

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
M(T)	1.519241	0.1646066
LNDT	0.6845001	0.8507578E-01

STEP NO. 3

ENTERING VARIABLE: FMED

F-LEVEL 43.26955 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 0.8891497

COEFFICIENT OF DETERMINATION = 0.5086595

COEFFICIENT OF MULTIPLE REGRESSION = 0.7132037

INCREASE IN COEFFICIENT OF DETERMINATION = 0.1149193

CONSTANT -11.292

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
M(T)	1.857401	0.1572284
LNDT	0.7273710	0.7707202E-01
FMED	1.172041	0.1781771

MODEL 3 (cont.)

STEP NO. 4

ENTERING VARIABLE: T

F-LEVEL 22.46797 WITH PROB. 0.0000
 STANDARD ERROR OF ESTIMATE 0.8416556
 COEFFICIENT OF DETERMINATION = 0.5621275
 COEFFICIENT OF MULTIPLE REGRESSION = 0.7497516
 INCREASE IN COEFFICIENT OF DETERMINATION = 0.5346797E-01
 CONSTANT -10.714

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
M(T)	1.805673	0.1492296
T	-0.3042707E-01	0.6419160E-02
LNDT	1.157641	0.1164572
FMED	1.111993	0.1691348

STEP NO. 5

ENTERING VARIABLE: FTHIN

F-LEVEL 21.77376 WITH PROB. 0.0000
 STANDARD ERROR OF ESTIMATE 0.7978223
 COEFFICIENT OF DETERMINATION = 0.6086868
 COEFFICIENT OF MULTIPLE REGRESSION = 0.7801839
 INCREASE IN COEFFICIENT OF DETERMINATION = 0.4655933E-01
 CONSTANT -9.6106

VARIABLE	COEFF.	STD.ERR. OF COEFF.	STANDARDIZED COEFFICIENT	T-VALUE	PROB.
M(T)	1.673	0.1443	0.5983814	11.59	0.000
T	-0.3059E-01	0.6085E-02	-0.3832380	-5.027	0.000
LNDT	1.097	0.1111	0.7595132	9.873	0.000
FMED	0.8176	0.1723	0.2502296	4.745	0.000
FTHIN	-0.6327	0.1356	-0.2346799	-4.666	0.000

Enclosure 4: MODEL 4

***** STEPWISE REGRESSION *****

5 VARIABLES; VARIABLE: LNMV IS DEPENDENT

STANDARD ERROR OF Y = 1.258318

STEP NO. 1

ENTERING VARIABLE: LNM(T)

F-LEVEL 41.81361 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 1.140587

COEFFICIENT OF DETERMINATION = 0.1827409

COEFFICIENT OF MULTIPLE REGRESSION = 0.4274821

INCREASE IN COEFFICIENT OF DETERMINATION = 0.1827409

CONSTANT -6.7232

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
LNM(T)	1.195008	0.1848043

STEP NO. 2

ENTERING VARIABLE: LNDT

F-LEVEL 44.73440 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 0.9850140

COEFFICIENT OF DETERMINATION = 0.3937402

COEFFICIENT OF MULTIPLE REGRESSION = 0.6274872

INCREASE IN COEFFICIENT OF DETERMINATION = 0.2109993

CONSTANT -8.9612

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
LNM(T)	1.519241	0.1646066
LNDT	0.6845001	0.8507578E-01

STEP NO. 3

ENTERING VARIABLE: T

F-LEVEL 22.41679 WITH PROB. 0.0000

STANDARD ERROR OF ESTIMATE 0.9327751

COEFFICIENT OF DETERMINATION = 0.4592624

COEFFICIENT OF MULTIPLE REGRESSION = 0.6776890

INCREASE IN COEFFICIENT OF DETERMINATION = 0.76552216E-01

CONSTANT -8.4545

VARIABLE	COEFFICIENT	STD ERROR OF COEFF.
LNM(T)	1.481264	0.1560831
T	-0.3358813E-01	0.7094129E-02
LNDT	1.161895	0.1290631

- Model 4 (continued) -

STEP NO. 4

ENTERING VARIABLE: LNT0

F-LEVEL 11.68398 WITH PROB. 0.0008

STANDARD ERROR OF ESTIMATE 0.9069538

COEFFICIENT OF DETERMINATION = 0.4915489

COEFFICIENT OF MULTIPLE REGRESSION = 0.7011055

INCREASE IN COEFFICIENT OF DETERMINATION = 0.3228659E-01

CONSTANT -8.9389

VARIABLE	COEFF.	STD.ERR. OF COEFF.	STANDARDIZED COEFFICIENT	T-VALUE	PROB.
LNMT	1.209	0.1714	0.4324632	7.053	0.000
T	-0.3341E-01	0.6898E-02	-0.4186176	-4.844	0.000
LNMT	1.138	0.1257	0.7876630	9.055	0.000
LNT0	0.6600	0.1931	0.2032370	3.418	0.001

MODELS 3 & 4

Statistics

THERE ARE 7 VARIABLES AND 189 OBSERVATIONS

VAR.	MEANS	STD.DEV.	VARIANCE
LN MV	0.7209044	1.258318	1.583365
LN MCT)	6.229320	0.4501296	0.2026167
LN TO	3.312338	0.3874607	0.1501258
T	12.57672	15.76492	248.5326
LN DT	0.3188902	0.8709210	0.7585033
FMED	0.1798942	0.3851195	0.1483170
FTIN	0.3174603	0.4667246	0.2170318

***** CORRELATION MATRIX *****

VAR.							
LN MV	1.0000						
LN MCT)	0.4275	1.0000					
LN TO	0.3904	0.4619	1.0000				
T	0.0980	-0.2245	-0.0539	1.0000			
LN DT	0.3407	-0.2448	-0.0446	0.7931	1.0000		
FMED	0.1480	-0.3170	0.0383	-0.0329	-0.0002	1.0000	
FTIN	-0.4033	-0.0354	-0.3862	-0.0915	-0.1350	-0.3194	1.0000

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APPENDIX C

CHLORINE HYDRATE SYNTHESIS APPARATUS FOR FIELD TESTS

The chlorine hydrate synthesis loop used in the spill tests is designed to produce as much as 128 liters of pressure filtered hydrate synthesized from chlorine vapor and cold zinc chloride aqueous solution. The major components of the synthesis plant (Figure C-1) include: heat exchanger HX-3, the hydrate forming coil, coolant supply, 0.13-m^3 capacity hydrate store, zinc chloride reservoir, chlorine separator, and chlorine supply.

The first step in the synthesis operation was to prepare the zinc chloride (electrolyte) solution (the zinc chloride concentration used depends on the simulated state of charge). The electrolyte, flowing through the system, is cooled and saturated with chlorine before hydrate formation can begin.

To form hydrate the electrolyte flow was maintained at 5 l/min, the chlorine flow at 20 l/min, and the coolant flow and temperature maintained such that the electrolyte temperature is maintained at $3\text{-}5^\circ\text{C}$. The electrolyte is pumped from the Cl_2 separator and through the heat exchanger. When the electrolyte leaves HX-3 (Figure C-1) chlorine gas is introduced into the flow. As the gas passes through the hydrate-forming coil some of the water and chlorine combine to form hydrate. The hydrate remains in the store and the unreacted chlorine/zinc chloride solution passes through the store filters and returns to the chlorine separator, where the process is repeated with some changes. When the chlorine and electrolyte return to the chlorine separator most of the chlorine will separate from the electrolyte and be contained in the top of the separator. By adjusting pump P2 and valve V_1 (Figure 2) this chlorine will be recycled into the system. A problem can develop if the chlorine remaining in solution with the electrolyte joins with water to form hydrate in the heat exchanger. To prevent this, the electrolyte is circulated through the reservoir and heated to slightly above formation temperatures. After being cooled in HX-3, hydrate will form in the forming coil. If the temperatures and flows have been kept constant there will be a minimum amount of chlorine passing through the system and the amount of hydrate formed can be calculated using the known chlorine flow rates and volume of chlorine in hydrate form.

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APPENDIX D

CHLORINE SAMPLE PROBE ARRANGEMENTS FOR FIELD TESTS

Sample probes for the field tests were placed downwind of the spill pad fanning out at 15° on both sides of the wind centerline. The probe positions relative to the wind and the spill pad are shown in Figures D-1 through D-5 for Tests 1-6. With one exception, the probes were 1.8 m (6 ft) high; the exception was .9 m (3 ft) high. The sample lines were 0.6 cm polyethylene tubing, 30.5 m long (Tests 4, 5 and 6) and 60.0 m long (Tests 1, 2 and 3). The travel time in the tubing was over 1 min in Tests 1, 2 and 3 and reduced to 20-30 sec in Tests 4, 5 and 6.

FIGURE D-1
Chlorine Sample Probe Array
For
Test 1 and Test 2

FIGURE D-2
Chlorine Sample Probe Array
For Test 3

- Key
- ▼ Interscan multiplexing up to 14 minutes, stationary after
 - MSA Stationary Interscan multiplexing up to 14 minutes
 - Interscan mutiplexing till 14 minutes

FIGURE D_3

Chlorine Sample Probe Array for Test 4

Key

- Interscan multiplexing chlorine sample probe.
- Interscan multiplexing and M.S.A. probe
- ▲ Interscan stationary first 5 minutes, multiplexing after 5-20 minutes
- ▼ Interscan multiplexing 5-20 minutes, stationary after 20 minutes
- Cotton soaked in ammonia.

FIGURE D-4

Chlorine Sample Probe Array for Test 5

Key

- Chlorine sample probe for interscan detector
- MSA detector
- Cotton soaked with ammonia

FIGURE D-5

Chlorine Sample Probe Array for Test 6