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SAFETY AND ENVIRONMENTAL ASPECTS OF ZINC-
CHLORINE HYDRATE BATTERIES FOR
ELECTRIC-VEHICLE APPLICATIONS

By
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March 1978

Work Performed Under Contract No. EY-76-C-02-2966

Energy Development Associates
Madison Heights, Michigan

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

MASTER

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FOR ELECTRIC-VEHICLE APPLICATIONS

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Foreword

This safety and environmental aspects study and this report which describes the work were part of a combined study of zinc-chlorine battery safety for utility and vehicular applications. There are significant differences between the batteries for the two applications, but the many similarities allow many parts of a safety and environmental aspects study to be done only once. Funding for this safety study on zinc-chlorine batteries was provided jointly by EDA and DoE, while a parallel study on zinc-chlorine batteries for peak-shaving was funded by EPRI as part of a joint EDA-EPRI program. The parallel effort on peak-shaving batteries allowed a more comprehensive analysis of portions of the vehicular battery study.

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EXECUTIVE SUMMARY

Energy Development Associates

The zinc-chlorine battery, with the chlorine stored as chlorine hydrate, has been shown in previous reports to meet the cost and performance requirements necessary for a successful battery in the electric vehicle market. The third and final requirement that has to be satisfied before a battery can be used on the public highways is that of safety and this preliminary report examines this issue for the zinc-chlorine battery.

Analysis of the potential safety hazards of the zinc-chlorine hydrate battery shows chlorine to be the only major safety concern. The use of chlorine hydrate for chlorine storage allows safe battery operation at near ambient temperature and pressure. This is not possible with liquid chlorine. This report examines the safety and environmental impact in the event that chlorine is released from the battery and examines the battery safeguards necessary to prevent any chlorine release at all from component failure or minor accident situations.

Chlorine is a major industrial chemical with in excess of 12 million tons produced annually. This chlorine has many diverse applications, from the chlorination of swimming pool water to the manufacture of industrial plastics and, as a result, is widely handled and transported on the nation's highways. Despite this widespread usage and extensive transportation of chlorine, with the attendant accidental chlorine release, injury to health and property damage due to acute exposure to chlorine has been very limited. However, when large quantities of gas are released rapidly, dangerous situations can result as was the most recent chlorine release from a derailed tank car containing some 180,000 lbs of liquid chlorine in Florida on February 26, 1978.

With respect to the zinc-chlorine battery, containing at most 90 lbs of chlorine tied up as solid chlorine hydrate, the safety and environmental problems fall at the other end of the spectrum to the transportation of large tank car quantities of high pressure liquid chlorine. As an example of this, the following isopleths show the 50 ppm chlorine concentration boundary for a most improbable accident scenario, where the bottom of both the vehicle and battery are split open and a full charge of chlorine hydrate is deposited on the highway. A chlorine concentration in the air of 50 ppm is the level dangerous in 30 minutes to one hour. Furthermore, the meteorological conditions selected were the worst dispersion conditions proposed by Pasquill to describe the diffusion characteristics of the lower atmosphere. These conditions of hot (100°F) and stable air at a low wind speed (4 knots)

serve to maximize the area affected by high concentrations of chlorine.

As can be seen from the isopleths, the 50 ppm concentration is limited to a zone 49 ft long (less than three car lengths) by 4 ft wide and only 1-1/2 feet above the ground. This is a very small zone, considering that both a very severe accident is needed to deposit hydrate on the road and the most unfavorable atmospheric conditions need to be prevailing to obtain this worst case result. In fact, contrary to what might be expected, these isopleths are not for a hot sunny day when conduction from the road, convection from the air and solar radiation (300 Btu/hr/ft^2) act to decompose hydrate, but for a hot evening when obviously the solar radiation is missing. The reason is that, although the wind speeds were chosen at the same low level for both cases, significant local turbulence exists during the day because of solar radiation and even though the chlorine evolution rate is higher this turbulence disperses the chlorine much more rapidly than in the evening. All other accident scenarios examined gave a more rapid dispersal of released chlorine and much smaller 50 ppm isopleths than the one above.

The reason for the very limited area affected by chlorine from a worst case zinc-chlorine powered vehicle accident is primarily due to the nature of chlorine hydrate. When compared to liquid chlorine, chlorine hydrate is:

- An immobile solid with a small heat transfer area, not a volatile spreadable liquid with a large heat transfer area.
- A material needing four times the heat input, for decomposition, that liquid chlorine requires for vaporization, based on equal amounts of chlorine.

- More stable due to its decomposition temperature of 9.6°C , being much closer to ambient temperature than the -34°C for liquid chlorine.

These factors combine together to engender a considerable measure of safety from acute exposure to chlorine following a very severe accident when chlorine hydrate is used as the chlorine storage means.

A more probable serious-accident scenario is one where the battery case is ruptured or punctured but the hydrate remains within the battery. In this situation the rate of chlorine escape, because of insulation, is much lower than the hydrate spill scenario and the area subjected to a high chlorine concentration is localized to within a few feet of the car. Iso-pleths presented in this report show the chlorine dispersal for the punctured case for Los Angeles and Detroit on a hot day with the most probable wind conditions. For all other accidents and failure modes of the battery, chlorine will not escape into the environment. To accomplish this, three major safety features are incorporated into the first commercial zinc-chlorine hydrate battery design:

- The battery will be completely sealed both for safety reasons and because all the chlorine must be retained within the battery from material balance considerations.
- Under all operating conditions the battery case will be under a negative pressure. If at any time the case pressure approaches atmospheric pressure, due to component failure or puncture, the battery will self-discharge to remove all the chlorine. This applies on charge, discharge, and stand.
- The battery will be encapsulated in an insulating foam. This foam will contain sufficient absorbent to react with all the chlorine in the battery.

A review of the literature regarding the physiological and environmental effects of chlorine, that potentially could be released from zinc-chlorine hydrate batteries, shows very little cause for concern. The level of chlorine, even in the immediate vicinity of the vehicle, is low enough such that complete recovery would be expected; in fact, chlorine at the 5 ppm level has been used as a therapeutic agent for respiratory complaints. Even acute exposure does not cause any permanent clinicophysiological damage to the person exposed, and complete recovery is the rule not the exception. The limited rate and quantity of chlorine released from the battery will cause no regional environmental effect because of the high reactivity of chlorine with most of the substances in the ambient and, therefore, rapid removal. For the same reasons released chlorine will have an extremely limited economic impact on local property and plant life.

Clean-up operations from a hydrate spill will require very little in the way of specialized equipment. The spill could be foamed with conventional fire-department foaming equipment to cut down heat transfer to the hydrate and then be removed from the accident site in an insulated box for disposal. Chlorine is also soluble in water and scrubbing with a water spray is an alternative clean-up technique.

The Department of Transportation (DOT) presently regulates the transportation of chlorine (as to the type of packing, placarding, etc., required). The requirements change with the quantity of chlorine involved. No regulations regarding the transportation of chlorine as chlorine hydrate presently exist and regulations will, therefore, have to be formulated.

It must be emphasized that this report is the initial attempt to identify and analyze potential safety and environmental problems associated with zinc-chlorine hydrate vehicle batteries and that a much more extensive analysis, together with experimental verification, will be required to fully satisfy the safety question. However, the overall results from this preliminary safety and environmental study strongly suggest that electric vehicles powered by zinc-chlorine hydrate batteries will pose minimal health and environmental hazards on our nation's highways and streets.

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ABSTRACT

Public acceptance of high-performance cost-effective zinc-chlorine hydrate batteries for the random-use electric-vehicle application will require meeting stringent safety and environmental requirements. These requirements revolve mainly around the question of accidental release and spread of toxic amounts of chlorine gas, the only potential hazard in this battery system. Available information in the areas of physiological effects, environmental impact, and governmental regulation of chlorine have been reviewed. The design, operation, and safety features of a first-commercial electric-vehicle battery have been conceived and analyzed from the chlorine release aspect. Two types of accident scenarios have been analyzed in terms of chlorine release rates, atmospheric dispersion, health hazard, and possible clean-up operations. The worst-case scenario, a quite improbable accident, involves the spillage of chlorine hydrate onto the ground, while the other scenario, a more probable accident, involves the release of chlorine gas from a ruptured battery case. Heat-transfer and chlorine-dispersion models, developed to analyze these scenarios, establish a firm basis for a comprehensive and factual position statement on this topic. The results of this preliminary study suggest that electric vehicles powered by appropriately designed zinc-chlorine hydrate batteries will pose negligible health or environmental hazards on our nation's streets and highways.

Section 1

INTRODUCTION

Depletion of our nation's domestic oil reserves and increased dependence on foreign suppliers has created the need for alternative energy sources for a variety of applications. One of these applications is the random-use vehicle market. Development of vehicles powered by energy sources other than combustion engines would reduce our nation's increasing dependence on gasoline fuel to meet passenger and route type transportation needs. One of the promising alternatives is battery-powered electric vehicles.

In this application batteries must meet established criteria in the areas of performance, life, cost, and safety. These criteria can be summarized as follows:

- Delivered energy density of 45 Wh/lb
- Sustained specific power of 35 W/lb
- Peak specific power of 45 W/lb
- Overall energy efficiency of >50%
- Battery life equivalent of 100,000 vehicle miles
- Selling price - excluding charging equipment of \$35/kWh
- Meet all DOT safety requirements

Commercial acceptance of advanced battery systems for this application will depend on meeting the requirements in these areas.

Zinc-chlorine hydrate batteries are potentially well-suited for this application despite the rigorous requirements. The potential to meet these requirements can be summarized as follows:

- The system uses inexpensive and readily available active materials.
- The system is well-behaved and allows the use of potentially inexpensive electrodes with high voltaic efficiency.
- At constant current, the voltage time profile for zinc-chlorine hydrate batteries is virtually flat during both charge and discharge.

- The system can be made to operate close to ambient temperature.
- The coulombic efficiency of the system can be maximized by suitable arrangements to control the dissolved chlorine concentration in charge and discharge. This obviates the need for expensive and potentially life-limiting separators.
- Battery operating conditions can be chosen under which life expectancy of electrodes is acceptable and performance degradation is slow.

The use of chlorine hydrate as the chlorine-storage medium offers some advantages over other halogen storage methods (1).

- The system can be operated very close to ambient pressure thus conferring greater safety on the system.
- Chlorine hydrate appears to offer cost advantages since the complex uses water at virtually zero cost.
- The enthalpy of formation of chlorine hydrate is sufficiently large so as to provide significant battery cooling in discharge.
- It is unnecessary to dry the chlorine before hydrate formation which leads to capital cost, operating cost, operational reliability and safety advantages.
- Since chlorine hydrate is a solid, having a large heat of formation, tank rupture does not lead to massive chlorine gas leakage.
- Storing the halogen external to the electrochemical cell prevents activated stand losses by direct reaction of chlorine with zinc.

A recent cost and design study discusses the potential of first commercial zinc-chlorine hydrate batteries in meeting the established performance and cost criteria (2). This study is the first to be performed on the safety and environmental aspects of zinc-chlorine hydrate electric vehicle batteries. It addresses the principal safety question of: Will toxic amounts of airborne chlorine escape from these batteries? This question is addressed by reviewing, analyzing, and summarizing available information in the following areas:

- The known environmental and physiological effects of chlorine
- Governmental regulations regarding chlorine
- The design, operation, and safety features of commercial zinc-chlorine hydrate batteries
- Accidental release and spread of airborne chlorine
- The most probable effects on the environment and human health as a result of such accidents

Section 2

ENVIRONMENTAL EFFECTS OF CHLORINE

INTRODUCTION

Chlorine is a very reactive element that chemically reacts with most of the substances in the ambient. For this reason it is rarely found in the atmosphere in a free state except in the immediate vicinity of industrial producers or consumers of chlorine, where it might accidentally leak. Because it is rarely found in the free state it has not been considered as a common pollutant like SO_2 , oxides of carbon and nitrogen, etc. However, from the observations of chlorine accidents and from laboratory experiments it is noticed that chlorine, if present in the atmosphere, can create some local environmental problems.

EFFECT OF CHLORINE ON PLANT LIFE

Chlorine is a phytotoxic agent and is known to cause from minor damage to death to plants depending on its concentration in the atmospheric air, duration of exposure, water stress (low ground moisture) and meteorological conditions. Different species of plants have different degrees of resistance to chlorine exposure and there is no single threshold concentration that causes damage to all plants. Observations of plant reaction to chlorine exposure include both the accidental exposures to unknown concentrations and to known concentrations under controlled laboratory conditions. These observations are limited to some of the most common weeds and commercial plants and the reaction of many other varieties of plants to chlorine exposure is still unknown.

Some of the accidental exposures occurred near water and sewage treatment plants. Stout (3) reported one such case where lettuce and native grasses were exposed to unknown levels of chlorine. Outer leaves of the lettuce turned brown and other leaves became dry and brittle on exposure to chlorine. Another (4) incident resulted in the defoliation of peach, apple and quince trees from chlorine exposure. In another accident (5) involving leakage of 30 tons of chlorine in a rural area severe damage occurred to the plants in the surrounding area. All the native grasses and clover burned and became brittle. In the neighboring fields onions were killed, evergreens and azalea were defoliated and exhibited arrested growth. Many shrubs shed leaves in an abnormal manner. Some of the pasture lands in this rural area were burnt and useless. State and local agricultural agencies were of the opinion that this damage was local and

temporary in nature.

There are several studies under controlled conditions to determine the effect of chlorine on different plants and seeds. Barton (6) exposed moist and dry seeds to chlorine and several other gases. Delay and reduction in germination percentage was the main observation in moist seeds. In some cases all the moist seeds were killed by this fumigation. In general SO₂ proved to be more toxic than Cl₂. In the case of dry seeds, long exposure resulted in reduction in germination percentile.

A group of common weeds were exposed to air containing 0.5 to 2.5 ppm of chlorine for 4 hours (7). Mustard and chickweed were found to be the most sensitive and Kentucky bluegrass and pigweed were the most insensitive to chlorine. Weeds grown under high soil moisture condition were more vulnerable than the same weeds grown under low soil moisture conditions. This observation was also made by others.

Zimmerman (8) exposed 19 different plant species to chlorine at different concentrations. The range of concentration varied between 0.46 to 4.67 ppm. Sixteen of these plants were susceptible to injury at this level. Chinese holly, egg plant and tobacco were the three plants unaffected. Threshold concentrations for injury were recorded as 0.46 ppm for 1 hour for buckwheat, 0.56 ppm for 2 hours for bramble, 1.3 ppm for 0.5 hours for bean and radish, and 1.5 ppm for 0.5 hours for rose. Spotting of the leaves was the most characteristic response. These spots first appeared as cooked, then turned straw white or brown depending on the species involved.

Brennan (9) et al conducted similar experiments on several plants. The range of chlorine concentration in the air varied from 0.1 to 0.5 ppm and the duration of exposure was up to 4 hours. Necrosis was the most common symptom. In some plants like alfalfa, necrosis of the leaves was marginal in position and in some other plants such as tomato, tobacco, etc. necrosis was scattered all over the leaves. The necrotic area in most cases was between veins. Bleaching of leaves resulted from low level exposure and the pattern of bleaching was similar to that caused by ozone. On squash, the younger leaves started "cupping" besides necrosis. From their experiments, the threshold chlorine concentration causing damage to different plants was determined (Table I).

Table I

CHLORINE THRESHOLD CONCENTRATIONS

0.1 ppm <u>2 hours</u>	0.1 to 0.25 ppm <u>4 hours</u>	0.5 ppm <u>4 hours</u>	0.8 ppm <u>4 hours</u>	1.0 ppm <u>4 hours</u>
Radish	Tobacco	Tomato	Petunia	Chenopodium
Alfalfa	Zinnia	Cucumber	Pinto Bean	Polygonum
	Gomphrena	Dahlia	Scotia Bean	Oxalis
	Onion	Nasturtium	Squash	Begonia
	Corn	Dandelion	--	Pepper
	Mustard	--	Cowpea	--
	Sunflower	--	Geranium	--
	--	--	Azalea	--

Low soil moisture resulted in reduced damage and plants kept in shade after exposure, in general, suffered less damage than those kept in sunlight.

Measurement (10) of pH value on exposure to chlorine indicated a significant reduction in the leaves and very little change in the stem. Change in pH value was also considerably smaller if the plant was not exposed to sunlight. Visible damage to the plant correlated well with the reduction in pH value. Defoliation was reported (11) to have occurred without any symptoms in some cases.

From the above and other studies it can be seen that necrosis and chlorosis are the common symptoms of exposure to chlorine. Severe cases of necrosis are normally followed by defoliation and death of the plant. In general, plants under shade or in the absence of sunlight seem to have suffered less damage from chlorine. Low soil moisture also has a similar effect.

Damage to plants from chlorine is restricted to the immediate vicinity of the accidental chlorine release and does not cause a regional problem like SO₂, etc. For this reason, chlorine is not an economically significant air pollutant.

EFFECT OF CHLORINE ON PROPERTY

Chlorine is not considered as a common pollutant causing property damage, mainly because of its absence in measurable quantities in air. There is no data available correlating property damage to the presence of chlorine in the air.

It is a very reactive element and reacts with most elements and compounds under specific conditions. Most of the common industrial metals like iron, steel, copper, lead, nickel and other metals like silver and platinum are resistant to dry chlorine at room temperature. At elevated temperatures chlorine may react with these metals rapidly. Carbon steel ignites in chlorine at 251°C.

Aluminum is one of the most common engineering materials that rapidly reacts with dry chlorine. Arsenic, gold, mercury, selenium, tellurium, tin and titanium also react with dry chlorine.

Chlorine in the presence of water forms dilute hydrochloric and hypochlorous acids and becomes very corrosive to most common metals. In the Louisiana (12) accident it was observed that corrosive damage to farm equipment was considerably more where the metal was covered with dew drops. Any property damage due to chlorine leaks will be confined to the immediate vicinity of the accident and the extent of damage depends on the local meteorological conditions. High humidity and temperature may result in significantly more damage by chlorine than dry cool wind. Strong wind has the tendency to dilute chlorine to low enough concentrations so as not to cause any visible damage.

Section 3

PHYSIOLOGICAL EFFECTS OF CHLORINE

INTRODUCTION

Chlorine is one of the most widely used industrial chemicals, both in small quantities for chlorination of swimming pools and in large quantities for the manufacture of plastics. Its yearly consumption in the U.S. alone was about 12 million short tons in 1975 and is expected to reach about 18 million tons by 1980 (13). Manufacture, shipment and use of such large quantities involves handling by many people. Despite this, the number of accidents involving chlorine, acute exposure of humans to chlorine and the resultant loss in human lives and property is very limited.

Chlorine is a non-flammable, nonexplosive but toxic gas. Its recognition as such led to its use as a war gas during the initial stages of gas warfare in World War I, even though it was replaced by other gases during the later stages of the war (14). No accurate records were maintained to identify the chlorine victims during the war from those exposed to other gases and hence its effectiveness as a war gas is not known (15). Studies on some of these war victims will be discussed later. During this period it was also observed that workers in the chlorine plant at Edgewood Arsenal suffered no influenza attacks when a major influenza epidemic struck the community where they were living (16). This led to its discovery and use as a therapeutic agent for respiratory diseases and the results of this use will also be discussed later.

Most of the reported acute chlorine exposures were caused either during the war or by accidents during its shipment, storage and use. Due to this nature of exposure, there is no information as to the level of exposure and not enough information on the immediate reaction of victims on exposure to high concentrations of airborne chlorine. Once these people were admitted to the hospital, their response to the treatment and its long term effect on their health or lack of it was very well recorded by medical personnel. Some of these cases will be briefly discussed in the subsequent pages of this section.

EFFECTS OF HUMAN EXPOSURE TO CHLORINE

Chlorine is primarily a respiratory irritant and Gay (17) summarizes the reaction of humans on exposure to it at different levels and suggests

treatment as follows:

- "1. Mild. - Minimal sensation of burning of mucous membranes of nose, mouth, throat, and perhaps of the eyes is present. There may be a slight cough. No treatment is necessary and the symptoms will clear within a few minutes to an hour.
2. Moderate. - Immediate, severe irritation of the mucous membranes of the nose, throat, and eyes is accompanied by a distressing, sometimes paroxysmal [a fit, attack], cough. Anxiety is usually present. Except for a few rales, physical examination is otherwise normal. X-ray of the lungs is negative. Treatment consists of having the patient lie down with his head and shoulders elevated. Oxygen should be administered in periods of a few minutes at a time until the cough and anxiety are relieved. A sedative cough syrup is useful. Often a bronchodilator administered by nebulizer will abort the paroxysmal cough. Most of these patients can be up within a few hours and many return to full activity the following day.
3. Severe. - Severe, productive cough, difficulty in breathing and frequently cyanosis [a bluish or purplish discoloration due to deficient oxygenation of blood], are present. Vomiting may be severe. Restlessness and apprehensiveness are often marked. Rales [an abnormal sound that accompanies normal respiratory sounds] may be heard throughout the lungs. X-ray of the lungs is negative, but the expirogram may show considerable expiratory reduction. Treatment consists of rest with the head and shoulders elevated, warmth, and reassurance. Inhalation of oxygen for periods of 15 minutes or longer is effective in alleviating the symptoms and should be repeated as necessary. Sedative cough syrups are indicated. Productive cough, bronchial rales, and an abnormal expirogram may persist for a day or two. Residual pulmonary damage does not occur and recovery is complete. Most of these patients are able to return to full duty on the following day.

If a person has been trapped in an area of high concentration of chlorine gas, the physician is

confronted with a medical emergency. Shock, coma, and respiratory arrest may be present. Treatment is supportive and the physician must rely upon his clinical judgment to meet the conditions at hand. Resuscitation measures, including inhalation of 100% oxygen and methods to combat shock, may be required. Corticosteroids may be helpful for pulmonary edema. Complications such as pneumonia, either of infectious or aspiration origin, should be anticipated."

Gay's summary also does not give any quantitative levels of exposure. Fieldner (18) et al prepared a list of industrial gases and their toxic doses for the Bureau of Mines under the title "Gas Masks for Gases Met in Fighting Fires". Table II is an extract for chlorine from this list.

Table II
PHYSIOLOGICAL RESPONSE TO VARIOUS
CONCENTRATIONS OF CHLORINE GAS

<u>Effect</u>	<u>Parts of Chlorine Gas per Million Parts of Air, by Volume (ppm)</u>
Least amount required to produce slight symptoms after several hours exposure	1
Least detectable odor	3.5
Maximum amount that can be inhaled for one hour without serious disturbances	4
Noxiousness, impossible to breathe several minutes	5
Least amount required to cause irritation to throat	15.1
Least amount required to cause coughing	30.2
Amount dangerous in 30 minutes to one hour	40-60
Kills most animals in very short time	1000

MILD EXPOSURE

Chlorine is moderately soluble in water (2.26 g/l). When inhaled along with air it tends to affect the entire respiratory system unlike SO₂

which attacks upper respiratory passages because of its high solubility in water and phosgene which primarily attacks lungs because of its low solubility in water (19, 20). The toxicological property of chlorine along with its solubility in water is used to effectively kill the bacteria in the drinking and waste water and to prevent slime formation on the heat transfer surfaces in heat exchangers. It was reported (21, 22) that people chronically exposed to low concentrations of chlorine are immune or less prone to attacks of influenza, common colds, and other respiratory diseases.

Vedder et al exposed 15 different strains of cultured bacteria to continuous flow of air with about 4 ppm of chlorine. All the bacteria were killed within 135 minutes of continuous exposure. For treatment of respiratory problems (coryza, laryngitis, bronchitis, etc.) they exposed 931 humans with respiratory diseases to air containing about 5 ppm of chlorine, in sessions lasting for about an hour each. 71.4% of them were completely cured, 23.4% indicated some improvement and the remaining 5.2% noticed no change in their condition. Very few of them required treatment beyond one session. This suggests that chlorine in the air may attack and kill the bacteria in the respiratory passages relieving the patient of the disease. At this level of concentration the effect of chlorine on mucous membrane may be insignificant to cause any symptoms. However, as the concentration increases to slightly higher levels, it may attack the tissue and cause incipient inflammation of mucous membranes resulting in discomfort and cough. At these concentrations it can also cause eye and skin irritation (23). Beyond this level there is no known experimental correlation between the concentration of airborne chlorine and the reaction of humans on exposure to it.

ACUTE EXPOSURE

The cases of massive accidental exposures to high airborne concentrations of chlorine are very well studied and documented. But in all these incidents the level of concentration, duration of exposure and the immediate reaction of humans to the exposure are not known. Quantities of chlorine involved and in some cases even the duration of chlorine leakage (or spill) are known, but this does not help to establish the quantitative degree of exposure of any one of the victims involved to enable us to draw any meaningful relationship between the level and duration of exposure and the resultant symptoms that can be anticipated. Different people apparently exposed to the same extent reacted differently. Even at the odor threshold levels this variation is apparent. The recorded range reported by different people (24) for odor threshold varies from a low of 0.02 ppm to a high of 3.5 ppm. The following are some of the case histories of acute chlorine exposures by the attending physicians.

Beach (25) et al reported their investigation of seven chemical workers who were accidentally exposed to high concentrations of chlorine in different accidents. The usual symptoms as reported were cough, dyspnea (labored respiration) and chest pains. The symptoms started within 10 minutes of exposure and lasted from 2 to 8 days. Radiographs of chest exhibited congestion, consolidation and nodules. Pulmonary edema was present in severe cases. Clearing of these symptoms took about a week and in severe cases lasted for up to 10 days. On treatment all these patients recovered completely.

On June 1, 1944, about 100 lbs. of liquid chlorine leaked from a container on the street in the vicinity (18" away) of a grate covering a subway ventilation shaft in Brooklyn, New York. Due to the high density of chlorine and the suction effect created by departing trains, most of the chlorine was believed to have entered the subway station (26). No visible cloud was seen on the street. At 2:46 p.m. a train pulled into the station and the concentration of chlorine was high enough to force some of the occupants to leave the train and go to the street. The next train arrived at 2:47:30 p.m. and the concentration of chlorine in the subway was so high that everybody (including the crew) left the train and ran to the street. By 2:53 p.m. the employees of the subway were able to walk the platform without any serious irritation.

A total of 418 victims of this accident were examined at different hospitals and 208 of them were admitted. Thirty-three of these patients were observed periodically for 16 months after the accident. All of them were hospitalized for one to two weeks and they all had tracheo-bronchitis. Pulmonary edema was detected in 23 out of 30 cases and 14 of the victims developed pneumonia. Sixteen of these patients had anxiety reactions throughout the period of this study. The report concludes that at the end of this period none of the victims had evidence of residual lung damage. From the medical records it was noticed that only 2 of these 418 victims were exposed to chlorine outside the subway and no deaths occurred due to this accident.

Another accident involving a tank car derailment and subsequent rupture and leakage of 30 tons of liquid chlorine through a 4 ft. sq. opening occurred at 8:15 a.m. on January 31, 1961. A factual report following the accident was prepared by Segaloff (27) et al and one medical report by Joyner (28) et al dealt with immediate effects of exposure and another report published by Weill (29) et al discussed the long term effects of chlorine exposure. Four hours after the accident, concentrations of chlorine as high as 400 ppm were recorded at a location 225 ft. away from the site of accident. About 100 persons were treated for various degrees of chlorine exposure at different medical facilities. An eleven month old boy, from a home about 150 ft. away from the spill was the only fatality resulting from this massive chlorine leak. On exposure to chlorine the boy started choking and the father took him outside the home expecting some relief and perhaps that is where the boy got the critical dose. A two month old baby who remained in the same home survived the exposure. All people exposed to high

concentrations exhibited dyspnea, coughing and vomiting. The cough produced frothy, white, thin sputum. On the second day one of the patients had blood tinged sputum. Some suffered first degree burns on the face due to chlorine vapor exposure. By the sixteenth day all hospitalized patients were released. Twelve of those subjected were selected for long term study to determine the effects of chlorine. Eleven of the twelve were from among the sixteen who were hospitalized. Pulmonary edema was commonly detected in this group. They were examined three and seven years after the accident. The chest films showed normal lungs in all subjects. Other tests to determine the function of the lungs were conducted and concluded that there was no permanent lung damage caused by this exposure.

Kowitz (30) et al reported the results of their study of chlorine exposure victims in an accident in Baltimore Harbor, involving about 150 long-shoremen. There were no deaths as a result of this accident. Several of the victims were hospitalized, 37 of them immediately following the accident and a few more during the ensuing 48 hours. Studies were conducted on 56 of the other patients between 18 and 20 months after the accident. Twelve of these cases were not included in the analysis because of pre-existing pulmonary conditions. The results of the study indicated a decrease in vital capacity, decrease in diffusing capacity and an increase in the elastic work of breathing.

Another chlorine accident in Cleveland resulted in two fatalities among thirty-seven who were seriously exposed. Kaufman (31) et al and Adelson (32) et al conducted studies on these cases. Post-mortem of the dead revealed pulmonary edema and lung congestion. The lungs were heavy and filled with large quantities of water and frothy fluid. The first death occurred in 25 hours and the second in 76 hours after the accident. In the second victim there was evidence of kidney and brain damage in addition to the above findings. Immediate and follow up studies were conducted on 18 patients from this accident including 5 who were employed at the chlorine plant and who had a history of exposures to chlorine at high enough concentrations to cause cough and dyspnea. These workers were also among the most severely exposed in this accident. Studies on all the patients continued up to 14 months after exposure. Workers exhibited comparatively low incidence of pulmonary edema. Initially obstructive air-way disease was evident among all the people under study, but within 30 to 90 days this defect cleared up among non-workers whereas the workers exhibited this even after one year. The authors attribute this abnormality to the chronic exposure to chlorine and conclude that even acute chlorine exposure does not leave any permanent clinicophysiological abnormalities in the victim.

During the first World War there were many casualties and fatalities caused by war gases. The exact number of each gas is not known since it was difficult to isolate these victims from the victims of other causes. Among U.S. soldiers about 1843 were recorded (33) to have been the victims of chlorine exposure. A few of them died and there is no universal agreement on the number of disabled.

Meakins (34) et al followed the cases of about 700 Canadian soldiers exposed to chlorine gas during the war. Their study was conducted 4 years after exposure and the entire data was extracted from medical records of these soldiers. Among them, 200 did not have any subsequent complaints and were assumed to be free from any residual effects, while 478 of them were received at the base medical hospital for further treatment. Of these, 146 were treated at the base medical hospital and from the records it was assumed that they have recovered completely. Six of the victims died and 332 were sent to U.K. for further treatment. Seventy-two of these returned to France for duty after about 9 weeks treatment (on the average) in the hospital followed by 10 months home service. Eight of them, after about 14 weeks hospitalization and 15 months home service were also returned to France for base duty. Forty-eight were retained in U.K. and the remaining 204 were sent to Canada. Of the 204, sixteen were not gas victims. On the average these soldiers required about seventeen weeks of hospital care followed by 5-1/2 months home service. From their medical records, Meakins prepared the following list (Table III) describing the condition of the victims after 4 years.

Table III

CASE HISTORY OF 188 SEVERE EXPOSURE VICTIMS OF THE
700 CHLORINE EXPOSURE CASES AMONG CANADIAN SOLDIERS

<u>Physical Condition</u>	<u>Number</u>
No appreciable disease	54
Irritable Heart	78
Neuroses	18
Bronchitis, etc.	18
Asthma	8
Unable to trace	14

DISCUSSION

All the above studies are aimed at determining the immediate and long term effects of acute chlorine exposure on humans. A close scrutiny of the results does not indicate an established pattern of symptoms, either immediate or residual. The review committee (35) to establish the occupational standard has also expressed the need to conduct more studies before any conclusions can be drawn. From the above studies it appears that there is no residual pulmonary damage in the majority of the cases after a single acute exposure to chlorine.

Since any leakage of chlorine from a zinc-chlorine battery is expected to be caused by an accident resulting in short-term exposure, discussion of chronic exposure cases is not included in this report.

Section 4

GOVERNMENTAL REGULATION OF CHLORINE

OCCUPATIONAL EXPOSURE

In order to protect the health and assure the safety of workers in the industry, the National Institute for Occupational Safety and Health has established (according to the Occupational Safety and Health Act of 1970) a maximum limit on the concentration of airborne chlorine in the work area to which employers are required to comply. The limit so established and still in effect is 1 ppm for an 8 hour work day and is based on the recommendation of American Conference of Governmental Industrial Hygienists (ACGIH) (36). A review committee in its report in May, 1976, recommended a reduction of the above limit to 0.5 ppm for a work day of 10 hours in a 40 hour work week (37). While making this recommendation, the committee expressed its belief that this new level is safe, can be measured with the available instruments for the purpose of implementation and can be attained by the industry with the existing technology. This committee also expressed that the presently available information is inadequate to establish a correlation between levels of chlorine exposure and acute and chronic effects. This is very well reflected by the wide range of concentration limits (0.35 to 5 ppm) for prolonged exposure recommended by different people at different times (38, 39, 40, 41, 42).

Most of the industrial nations have adopted standards for maximum allowable concentrations (MAC) of chlorine in the workplace. Table IV lists some of those countries and the corresponding MAC values (43).

Though 1 ppm is the MAC value in workplaces under normal circumstances, emergencies are bound to arise when the concentration will increase beyond 1 ppm in the manufacturing area and its neighborhoods, storage facilities and surrounding areas and during the transportation of chlorine. Zielhuis recommended maximum exposure times at various concentration levels of chlorine (Table V) in such emergencies (44).

Table IV
MAXIMUM ALLOWABLE CONCENTRATIONS OF
CHLORINE IN THE WORKPLACE

<u>Country</u>	<u>MAC in workplace mg/m³</u>
West Germany	2
East Germany	1
Great Britain	3
Hungary	1
Yugoslavia	3
Czechoslovakia	3 (mean) 6 (peak)
USSR	1

Table V
MAXIMUM EXPOSURE TIMES TO CHLORINE
AS A FUNCTION OF CONCENTRATION

<u>Time of Exposure minutes</u>	<u>Concentration of Chlorine ppm</u>
60	3
30	4
15	5
5	7

PUBLIC EXPOSURE

Long term public exposure guidelines established by Environmental Protection Agency do not cover the occasional circumstances when the concentrations may be higher for brief periods. They may occur in an industry involving batch processes where the chlorine release is intermittent, a rocket launching where the contamination is for a short duration after the launch, etc. These are the known sources of pollution and a committee on toxicology

appointed by the National Research Council recommended limits (Table VI) for the short term exposure of public to such sources of pollution (45). The committee believes that the limits recommended are below the level of irritation which cause any significant discomfort.

Table VI

SHORT TERM PUBLIC EXPOSURE LIMITS (STPL'S)

Time of Exposure	Concentration of Chlorine
<u>minutes</u>	<u>ppm</u>
10	1.0
30	0.5
60	0.5

During manufacture, transportation and use of chemicals, accidents are likely to occur resulting in their release to the atmosphere and exposure of the general public to them. The above committee also recommended limits (Table VII) for such exposure of the public to chlorine.

Table VII

PUBLIC EMERGENCY LIMITS

Time of Exposure	Concentration of Chlorine
<u>minutes</u>	<u>ppm</u>
10	3
30	2
60	2

These limits, Public Emergency Limits (PEL's) are higher than STPL's and may cause some temporary discomfort, but they are not supposed to have any residual effect on human health.

TRANSPORTATION

The Department of Transportation (DOT) regulates the transport of chlorine as to the type packing, placarding, etc., required. These requirements change with the quantity of chlorine involved. So far there are no known regulations on the transportation of chlorine hydrate as it is not

a commodity for interstate transportation yet. The equilibrium properties of hydrate are far different from those of liquid chlorine. Under atmospheric pressure chlorine evaporates at -29.3°F as against hydrate decomposition temperature of 49.3°F . Latent heat of hydrate is 18.6 kCal/mole of chlorine compared to 4.87 kCal/mole of liquid chlorine. For 100°F ambient temperature and under identical packing conditions the rate of chlorine release from a chlorine container will be about 10 times as large as from a hydrate container. At lower ambient temperatures this difference becomes even larger with the release from hydrate reaching zero at 49.3°F . In case of a tank rupture, chlorine being liquid readily flows and evaporates very fast, whereas the hydrate decomposition rates will be extremely slow.

Section 5

BATTERY DESCRIPTION

INTRODUCTION

An iteration performed on the first-commercial electric-vehicle battery design, presented in a recent cost and design study (46), indicated the need to repackage the components to provide increased safety. The design presented here differs from that design only in the arrangement of the battery components, while the components and operation of the two batteries are similar.

These first-commercial electric-vehicle (FCEV) batteries are designed to meet the requirements of the random use electric vehicle market, as it develops. The projected usable delivered power and energy capabilities of these FCEV batteries, as described below, will meet the performance criteria established for commercial electric vehicle batteries if the battery weight is held at 1100 lb or less. Table VIII compares the projected performance specifications for these batteries with the established performance criteria (46).

Table VIII

COMPARISON OF PROJECTED SPECIFICATIONS WITH PERFORMANCE CRITERIA

	<u>FCEV Specifications</u>	<u>Performance Criteria</u>
Delivered Energy Density (Wh/lb)	45.7	45.0
Sustained Specific Power (W/lb)	36.0	35.0
Peak Specific Power (W/lb)	45.0	45.0
Overall Energy Efficiency (%)	55.3	>50.0

In addition to these performance criteria FCEV batteries must meet established criteria in the areas of cost, life, and safety. The cost and battery life have been addressed elsewhere (46 and 47). The general review of the FCEV battery presented here will emphasize the safety and environmental aspects of the design and operation.

LEGEND

P-1 ELECTROLYTE PUMP	HX-1 CHARGE HEAT EXCHANGER — CHILLER
P-2 CHLORINE GAS PUMP	HX-2 SUMP HEAT EXCHANGER — FOR TEMP.
V-1 DISCHARGE VALVE — PRESSURE CONTROL WITH OVERRIDE	REGULATION — AIR COOLED
V-2 CHARGE VALVE — PRESSURE CONTROL	RD RUPTURE DISC
	PR PASSIVE REACTOR
	----- HYDRATE FILTER
	3 STREAM IDENTIFICATION

9898

Figure 1. Positional and operational schematic of the vehicle battery. Note self-contained design.

BATTERY DESIGN

A positional schematic of the FCEV battery is shown in Figure 1. The outside dimensions of the battery are approximately 53 in x 21 in x 21 in (length x width x height) to provide a 13.5 cu. ft. package. Six 8.4 kWh submodules in a tri-level dual-bank arrangement form the stack of the battery as shown at one end of the battery. Fully submersible electrolyte and gas pumps are located in the sump of the battery. The hydrate former (HX-1) and air cooled temperature regulator (HX-2) are also located in the sump of the battery. The store compartment is a separate sealed container inside the sealed battery case. At full charge the battery is projected to contain 40.9kg of chlorine stored in this compartment as 124.0kg of chlorine hydrate ($\text{Cl}_2 \cdot 8\text{H}_2\text{O}$) and 37.8kg of metallic zinc stored in the stack of the battery. Storage of the active components in separate compartments of the battery minimizes the self-discharge losses on standby.

The six 21.2 volt submodules are electrically connected in series to form a 127 volt battery. Under the nominal open highway cruising power demand of 12.6 kW the battery is projected to operate for four hours delivering a net usable energy of 50.4 kWh. The battery is also projected to deliver 39.6 kW sustained power for maintaining speed up a grade and ~50 kW peak power for acceleration purposes. The battery is also projected to operate at an overall roundtrip energy efficiency of 55% at the four-hour discharge rate.

This basic design concept of unitized construction eliminates exposed transfer lines inherent in designs where the hydrate store is packaged separately from the stack and the sump. This eliminates line rupture as a possible source of chlorine leakage to the environment - the only source is case rupture. Case rupture could result in either the release of gaseous chlorine from the battery or in the situation of a severe rupture, spillage of chlorine hydrate from the battery. Preliminary analyses of these scenarios will be discussed in Section 6. As will be shown later, chlorine stored in the form of chlorine hydrate significantly reduces the rate of chlorine release, relative to storage as liquid chlorine, in the event of an accident and dangerous levels of chlorine are apparently restricted to the immediate vicinity of the leak.

BATTERY OPERATION

Figure 1 can be used to describe the operation of the FCEV battery. The operation of the battery will be controlled by a single pressure sensor located in the stack. A back-up sensor will be located in the store. A four to five psi pressure differential is maintained between the stack and the store using a gas pump to transfer gas from the stack to the store via line (5). Electrolyte return and pressure relief of the store is accomplished via line (7). Absolute pressure control is accomplished during charge by controlling the rate of chlorine hydrate formation and during discharge by controlling the rate of chlorine hydrate decomposition. The hydrate formation rate on charge is controlled by the rate of heat

removal from the store, which is controlled by the flow of coolant through the hydrate formation heat exchanger (HX-1). The hydrate decomposition rate on discharge is controlled by the rate of transfer of electrolyte from stack to store via line (2).

During the charge mode, the main electrolyte pump (P-1) feeds dechlorinated electrolyte to the chlorine electrodes in the stack via line (1). Electrolyte overflows from the cells of the stack, collects in separate return lines, and returns by gravity to the sump. The chlorine gas generated during charge is pumped from the stack, via line (5), by the gas pump (P-2) where it is mixed with chilled electrolyte from line (3) to form chlorine hydrate. The electrolyte is chilled in HX-1 just prior to mixing with the chlorine gas. Electrolyte transfer from the stack to the store is accomplished via one leg of line (2). Valve V1 is locked closed during charge to prevent interchange of unchilled electrolyte. The store is held at -1 psig during charge by controlling the rate of hydrate formation as previously described. The gas pump (P-2) establishes the pressure differential between the store and the stack while electrolyte return and pressure relief of the store is accomplished via line (7). The $-5 \pm 1/2$ psig established on the stack accomplishes dechlorination of the electrolyte during charge. The temperature of the stack and sump are permitted to float during charge and a steady state is achieved near 9°C in the stack for a 0°C store temperature.

During the discharge mode the electrolyte pump (P-1) feeds chlorinated electrolyte to the chlorine electrodes in the stack via line (1). Again, electrolyte overflows the stack and returns by gravity to the sump through separate return lines. Chlorination of the electrolyte is accomplished by injecting gaseous chlorine at 2 psig into the electrolyte on the high pressure side of the main electrolyte pump (P-1) via line (7). Chlorine gas is formed in the store by decomposition of chlorine hydrate. Flow of 30°C electrolyte from the stack to the store via line (2) accomplishes decomposition of the hydrate. Control of the electrolyte interchange rate, via valve V1, controls the rate of chlorine gas formation and provides the absolute pressure control on discharge at $-2 \pm 1/2$ psig. The gas pump (P-2) is again used to establish the 4 psi pressure differential between the store and the stack. Return of electrolyte from the store to the stack is accomplished via line (7). Temperature control of the stack and sump is accomplished in HX-2, an air cooled heat exchanger.

The use of only one control valve in each mode of operation (V2 on charge to control coolant flow to HX-1 and V1 on discharge to control electrolyte interchange rate) significantly simplifies the operation and control of the battery system.

SAFETY FEATURES AND INTERLOCKS

The design and operational considerations relating to the safety and environmental aspects of the battery are discussed below. They can be summarized as follows:

- Unitized construction
- Sealed store compartment inside a sealed battery case
- Less than ambient pressure operation of the battery during charge and discharge
- Appropriate safety interlocks on the battery
- Battery foamed into the chassis of the vehicle
- Chlorine absorbent dispersed in the foam layer around the battery
- Controlled pressure relief device

The benefits of the unitized FCEV design in eliminating exposed transfer lines were mentioned previously. This concept also facilitates the double-walled hydrate store protection feature and the less than ambient pressure operation of the battery. The separate sealed store compartment permits maintenance of a 5 psi pressure differential between the stack and the store during charge and discharge. Since the store walls are not common to the ambient, the possibility of store wall rupture with subsequent release of chlorine from the store directly to the ambient is minimized. The design pressures for the stack during charge and discharge are -5 psig and -2 psig, respectively. Should a leak develop in the battery case ambient air will leak into the battery and signal a failure mode.

These features coupled with the following safety interlocks essentially negate the possibility of internal malfunctions causing chlorine to be released from these batteries. The safety interlocks currently being considered for the FCEV battery are:

- Back-up pressure control for deactivation of module
- Passive H_2/Cl_2 reactor
- Sail sensors for monitoring pump failures
- All internal failure modes will deactivate the battery module and self-discharge it at the ten-hour rate or slower

The normal operation of the battery will be controlled off a single pressure sensor in the stack compartment of the battery. A back-up pressure sensor in the store compartment will override the primary sensor and safely control the deactivation of the battery if the primary sensor fails.

A passive H_2/Cl_2 reactor will be developed to catalyze the recombination of hydrogen with chlorine. This passive reactor will replace the present fluorescent light reactor system which can fail by either loss of power or bulb failure.

The sail sensors on the high pressure side of the pumps will signal pump failures. Pump failures, as well as other internal failure modes will

cause deactivation of the battery from normal service and switch it into a self-discharge operation.

Foaming the battery into the chassis of the vehicle provides maximum protection from shocks, including those resulting from collisions. In addition to making the battery integral with the vehicle chassis, the foam provides thermal insulation for the battery and significantly reduces the rate of chlorine release from the hydrate in the situation where the hydrate remains inside the battery subsequent to case rupture.

Dispersion of a chlorine absorbent within the foam layer provides a means of reacting or absorbing most or all of the chlorine being released from a ruptured battery. The effectiveness of the absorbent will depend on the type and magnitude of the case rupture and whether or not the foam layer is also ruptured.

The final safety feature is a low pressure (5-10 psi) rupture disc which provides a means of releasing chlorine at low pressure to the absorbent if a positive chlorine pressure should develop in the battery. This failsafe device is a back-up to the safety interlock features and precludes battery-case rupture due to excessive pressure accumulations.

DISCUSSION

The FCEV battery design and operation have received appreciable attention from the safety and environmental viewpoints and will continue to do so. The unitized design concept operating at less than ambient pressure significantly reduces the possibility of accidental release of dangerous amounts of chlorine. The additional safety features and interlocks further minimize this possibility. Foaming the battery into the chassis of the vehicle appears to provide the maximum protection from battery case rupture as a result of a collision or other severe shock to the vehicle. It also provides additional thermal insulation to minimize chlorine release rates from a ruptured battery containing stored hydrate. Dispersion of a chlorine absorbent within this foam layer provides a means of absorbing or reacting most or all of the chlorine released from a ruptured battery. The low pressure mechanical relief device, to release chlorine to the absorbent in the case of an internal pressure accumulation, is a failsafe device to prevent internally caused explosions.

A thorough analysis of all internal failure modes, via a failure modes and effects analysis (FMEA) on this design, may suggest the need for additional or alternative safety features or devices. It is recommended that this analysis be the next step in our development of safety features and interlocks for FCEV batteries.

Section 6

ACCIDENTAL RELEASE OF CHLORINE

ACCIDENT SCENARIOS

Normal operation of the battery will be below atmospheric pressure. This mode of operation is chosen mainly because of the increased operating efficiency and incidentally offers safety from battery explosion from internal pressure buildup. Redundant pressure controls are provided to maintain the internal pressure within a narrow band. Vacuum operation of the battery eliminates the possibility of any undetected leaks from the battery. Small quantities of carbon dioxide are generated during the operation of this battery. This gas will be separated from the rest by chemical process and purged into the atmosphere periodically. But for this, there is no exchange of mass between this battery and the ambient after its installation in the vehicle. Energy (in the form of heat and electrical) is the only major exchange between this battery and the ambient, thus making the electric car operating with this battery among the least polluting vehicles yet. Hence, under normal operation its overall impact on the environment will be negligible.

However, like any other system, malfunction of the components and controls resulting in abnormal operating conditions and physical damage that can be caused by accidents cannot be discounted in considering the safety of this battery for electric vehicle. Any of these causes may expose the contents of the battery to the atmosphere and the resultant impact on the environment and safety of people from this contamination has to be analyzed carefully. The following is a list of the materials that form the battery.

1. Zinc
2. Graphite
3. Titanium
4. PVC and other plastics
5. Potassium chloride
6. Hydrochloric acid
7. Zinc-chloride
8. Chlorine Hydrate
9. Chlorine

From this list it can be seen that items 1 through 5 are very common engineering materials and hence may not need any further consideration from safety standpoint. Item 6, hydrochloric acid, is in a very dilute state (80 meq/liter). Zinc chloride (item 7) is present in the battery in the form of aqueous solution. Even if it is spilled due to an accident, its vapor pressure in the air will be too low to be of any concern.

Chlorine hydrate (item 8) is a pale yellow solid which decomposes into chlorine and water at 49.3°F. This process of decomposition is an endothermic reaction requiring about 18.6 kcal for each mole of chlorine released. Chlorine, as explained earlier in this report, is a toxic substance and its release to the ambient can cause health and environmental problems.

Item 9, chlorine, is present in the gas space of the battery. Its total volume does not exceed a few liters. The rate of release of this gas into the atmosphere depends on the type of damage suffered by the battery. Leakage through a crack in the battery case can hardly be noticeable. This is because of low pressure (vacuum) operation of the battery which leads to escape of chlorine by molecular diffusion, a very slow process. In case of a major accident (e.g., splitting the battery into pieces) this gas will be released rather fast. Concentrations of this chlorine in the air will not be high except in the close proximity of the battery. But the entire episode lasts such a short time and its effect on the environment will be so minimal that any further consideration of this gas is not included in this report.

From the above analysis it is apparent that item 8, the chlorine hydrate, is the only substance which needs detailed analysis as to its rate of decomposition and chlorine release into the atmosphere and its dispersion in the air. The rate of chlorine release depends on the rate of heat transfer to the hydrate. Heat transfer to the hydrate is a function of ambient conditions (such as temperature, wind and insolation) and the existing insulation around the block of hydrate. The battery case itself is provided with very good thermal insulation, primarily to minimize the standby losses which are caused by chlorine released from hydrate. Hence, a block of hydrate remaining in the store decomposes rather very slowly. On the other hand, a block of hydrate spilled onto the pavement is exposed to the wind, solar radiation and ground directly resulting in the highest possible heat transfer rates for any given ambient conditions. Hence, these two cases, one with the hydrate spilled on the pavement and the other with the hydrate remaining in the battery store area, will form two extreme cases from the point of view of chlorine release rates. The former, depicting a block of hydrate on the pavement will be identified as Scenario I and the latter as Scenario II, henceforth. These two cases by being the two extremes will encompass all the other accident scenarios possible with this battery. Results of their analysis should also represent the limits to the extent of the spread of chlorine in the vicinity of the accident. Table IX gives a comparison of the two scenarios from the heat transfer point of view.

Table IX

COMPARISON OF THE TWO ACCIDENT SCENARIOS

	Scenario I	Scenario II
1. Location of hydrate	on the pavement	in the store area of the battery
2. Solar radiation	directly exposed	protected by the cover
3. Heat from air	directly exposed	protected by insulation
4. Heat from pavement	directly exposed	no contact with the pavement

A fully charged battery has 40.9kg of chlorine in the form of hydrate. The volume of this hydrate is 4.46 cu. ft. It is formed into a cube, the shape of the hydrate store. As the heat transfer depends on the surface area and the surface area will be the maximum for the largest possible volume of hydrate, both these scenarios are analyzed for a fully charged battery - resulting in maximum possible chlorine release rates in each case. Heat transfer and chlorine release rate calculations for Scenario I are presented in Appendix A. Similar calculations for Scenario II are given in Appendix B.

The two scenarios selected for analysis are the result of a major accident, caused by either internal equipment malfunction or by external forces resulting from a major accident. The hydrate is stored in an internal box which is enclosed in the battery case. Even in a major accident it is very unlikely that the hydrate block will be knocked loose from the internal box and spilled on the pavement. The impact has to be strong enough to disintegrate the battery to cause this. A more likely result of a major accident is a ruptured battery case with hydrate decomposing in the store.

ATMOSPHERIC DISPERSION

Chlorine is a toxic gas and becomes a health hazard if its concentration in the air exceeds a certain limit. Accidental release of chlorine, as described in the above defined scenarios, results in the contamination of air in the vicinity of the source of release. For safety reasons it is necessary to know the concentration levels of chlorine in the air at different distances from the source. This helps in determining if there is any possibility of chlorine concentrations in the air reaching toxic levels and if so what is the area covered by such levels.

Turbulent dispersion of chlorine (or any other gas) depends primarily on the wind velocity and atmospheric stability conditions at the location.

These conditions vary over a wide range with the place and time. Sometimes these conditions aid in rapidly dispersing the pollutants thus keeping the pollution levels very low and sometimes they are stagnant resulting in local accumulation of pollutants and creating episodes like the ones experienced by London and Los Angeles. It is impossible to predict what the meteorological conditions are going to be at any location at any given time. Pasquill (48) has proposed six stability classes to describe the diffusion characteristics of the lower atmosphere. These are based on wind speed, solar radiation, cloud cover and time of the day, i.e., day or night. Pasquill's classes range from very unstable (class A) to moderately stable (class F) and are reproduced in Table X.

Table X

RELATION OF TURBULENCE TYPES
TO WEATHER CONDITIONS

A - Extremely unstable conditions	D - Neutral conditions*
B - Moderately unstable conditions	E - Slightly stable conditions
C - Slightly unstable conditions	F - Moderately stable conditions

Surface wind speed, m/sec	Daytime insolation			Nighttime Conditions	
	Strong	Moderate	Slight	Thin overcast or $\geq 4/8$ cloudiness†	$\leq 3/8$ cloudiness
<2	A	A	B	--	--
2	A-B	B	C	E	F
4	B	B-C	C	D	E
6	C	C-D	D	D	D
>6	C	D	D	D	D

*Applicable to heavy overcast, day or night.

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

The above table (Table X) establishes the relationship between the wind velocity, insolation and Pasquill's stability class. From the table, it is obvious that Pasquill F, with 2m/sec, is the worst condition from diffusion point of view. However, this occurs only in the night and hence the incident solar radiation is zero. For Scenario I defined earlier, the condition results in chlorine release rates lower than what they would be during daytime under bright sun. Heat transfer and chlorine release calculations for the above stability class and wind velocity are given in Case I in Appendix A. Chlorine concentrations in the air in the

vicinity of the accident under these conditions are calculated and isopleth for 50 ppm level is presented in Figure 2. The dispersion calculations are based on the plume model. Modified Sutton's equation (49) for such a model is:

$$\chi(x,y,z,H) = \frac{V}{2\pi\sigma_y\sigma_z U} \exp\left[-1/2\left(\frac{y}{\sigma_y}\right)^2\right] \left\{ \exp\left[-1/2\left(\frac{z-H}{\sigma_z}\right)^2\right] + \exp\left[-1/2\left(\frac{z+H}{\sigma_z}\right)^2\right] \right\}$$

where U = wind velocity

χ = concentration of chlorine in the air

x = coordinate of the point in the down wind direction from the leakage source

y = coordinate of the point in the cross wind direction from the leakage source

z = height of point above ground level

H = height of the plume center line (0 meters)

V = rate of chlorine release from the source

σ_y and σ_z are obtained from Pasquill-Gifford charts for the class of stability assumed.

For comparison, the above calculations are repeated for daytime under bright sun, which result in the highest chlorine release rates. From Table X, for low wind speeds (2m/sec) under strong sun the atmospheric stability is Pasquill's Class A. Heat transfer and chlorine release rates for this are given under Case II in Appendix A and isopleths for 50 ppm level are presented in Figure 3.

The rates of chlorine release for both the cases in Appendix A (Scenario I) are a function of time. The rates are the highest immediately following the accident and decrease gradually with time. This is primarily because of the gradual cooling of the pavement. In both the above dispersion calculations the corresponding initial rates are used. The dispersion equation is derived for a steady state release. Use of this equation in the present case with a gradually decreasing rate introduces some error. But this error is insignificant compared to the total and the result is conservative.

Fieldner's table (Table II) indicates 40-60 ppm level of chlorine concentration in the air to be dangerous to people in 30-60 minutes. We have selected an average of this range, 50 ppm level for isopleths, to describe the severity of this accident. As explained earlier, an accident resulting in Scenario I is an extremely unlikely event. Notwithstanding the probability of occurrence, this should represent the upper limit to the degree of danger present in operating this battery.

HOT AND RELATIVELY CALM EVENING DISPERSION OF CHLORINE

Figure 2. Maximum downwind dispersion of 50 ppm chlorine level for the worst-case accident under the worst-case meteorological conditions. Note this hazardous level is restricted to a narrow ground level band which extends a maximum distance of three car lengths from the spilled hydrate.

HOT AND RELATIVELY CALM DAY-TIME DISPERSION OF CHLORINE

Figure 3. Maximum downwind dispersion of 50 ppm chlorine level for the worst-case accident under meteorological conditions which promote highest chlorine release rates. Note this hazardous level is restricted to a ground level band which extends less than a car length from the spilled hydrate.

From the weather records for a given location it is possible to predict the atmospheric dispersion characteristics on a percentile basis. It is intended to analyze a more realistic accident (Scenario II) with the statistical data for five major U.S. metropolitan areas. Meteorological data for these areas was obtained from National Climatic Center and the most probable wind velocity and atmospheric stability class for each one of them is listed in Table XI. Fieldner's table (II) gives 3.5 ppm as

Table XI

MOST PROBABLE WIND VELOCITIES AND STABILITY CLASSES

City	Average Wind Velocity Knots	Atmospheric Stability Class
Chicago	11	D
Detroit	11	D
Houston	7	D
L. A.	4	D
New York	11	D

the least detectable odor level for chlorine. From Table XI the best and the worst conditions for atmospheric dispersion are selected and isopleths for 3.5 ppm level are calculated for chlorine release rates for Scenario II and the results are presented in Figures 4 and 5, respectively.

These isopleths indicate the extent to which the odor level extends from the accident for the best and worst of the most probable meteorological conditions for the five metropolitan areas chosen.

At this level, everyone readily recognizes the presence of chlorine by its pungent smell. Perception of chlorine at such a low concentration is perhaps one of the reasons for the low casualty rates from chlorine accidents. Even though this is the highest olfactory level reported, people can smell chlorine at levels far below this.

CLEAN-UP OPERATIONS

Scenarios I and II describe the decomposition of hydrate on the pavement and in the battery case, respectively. The decomposition rate is higher for Scenario I than for Scenario II. But even for Scenario I, the decomposition rate is so low that it will take several hours for the whole block of hydrate to completely decompose. Hence, it requires immediate measures to control the release of chlorine before the hydrate block is removed to a safe place. Several methods of controlling the chlorine release may be envisioned, but the most suitable one may be covering the hydrate with foam or even a piece of cloth or paper. This reduces

TYPICAL DISPERSION OF CHLORINE FOR AREAS EXPERIENCING 12-13 MPH WIND CONDITIONS

Figure 4. Maximum downwind dispersion of 3.5 and 50 ppm chlorine levels for battery case rupture accident under the most probable meteorological conditions for New York, Detroit, and Chicago. Note the zone between the two isopleths is where chlorine is detectable but not hazardous to human health within a 30-60 minute exposure duration.

TYPICAL DISPERSION OF CHLORINE FOR AREAS EXPERIENCING 4-5 MPH WIND CONDITIONS

Figure 5. Maximum downwind dispersion of 3.5 and 50 ppm chlorine levels for battery case rupture accident under the most probable meteorological conditions for Los Angeles. Note the lower wind speed extends the downwind dispersion over that presented in Figure 4.

the heat transfer to the hydrate and maintains high concentration of chlorine in the enclosed space. Both these tend to minimize the chlorine release rates. At 32°F or below, water that is released by decomposition will readily freeze and provide a very good cover thus stopping any further decomposition. Equilibrium temperature for hydrate under atmospheric pressure is 49.3°F. Between 32°F and 49.3°F the release rates will be very small. As the temperature increases above this level, chlorine release rates gradually increase and at 100°F, the rates are significant as shown in Appendix A. The above suggested interim methods (covering the hydrate with foam, cloth, etc.) of controlling chlorine release are necessary when the ambient temperature is high.

The hydrate block can be safely removed for proper disposal. This block is very similar to a block of ice, except that it melts at a higher temperature. It can easily be scooped from the pavement into an insulated box and transported to the place of disposal. It can also be covered with chlorine neutralizers (e.g., caustic soda) in case it is felt necessary.

In an accident described in Scenario II, the internal battery pressure will be equal to or slightly higher than that of the ambient. Since discharging the battery at normal rates under these pressures is considered to be unsafe, controls are provided to deactivate the battery. The electric vehicle becomes immobilized and has to be towed to a garage. In the meantime the chlorine release, if there is any, will be too small to cause any health or environmental problems.

Section 7

DISCUSSION

The preceding sections of this report have reviewed available information in the areas of:

- Known environmental and physiological effects of chlorine
- Governmental regulations regarding chlorine
- The design, operation, and safety features of commercial zinc-chlorine hydrate electric vehicle batteries
- Accidental release and spread of airborne chlorine from zinc-chlorine hydrate batteries

Since chlorine reacts readily with moisture and other materials in the atmosphere its impact on the environment and human health is restricted to the local area of an accidental chlorine spill, even for large spills. Apparently for this reason, the Environmental Protection Agency has not found it necessary to establish air quality standards, new stationary source standards, or hazardous air pollutant emission standards for airborne chlorine (50, 51). As such chlorine is not considered to be a major public health hazard or environmental air pollutant despite the fact that more than 12 million tons of chlorine are produced annually. The only governmental regulations regarding chlorine are in the areas of recommended exposure limits and transportation. The transportation regulations cover bulk quantities of liquid chlorine in excess of 1,000 lbs. For smaller quantities only approved containers with proper placarding are required.

The use of chlorine hydrate, instead of liquid chlorine, as the chlorine storage medium in the zinc-chlorine battery significantly reduces the potential health and environmental hazards in the immediate vicinity of an accidental spill. Table XII compares the pertinent properties of these two storage media. These properties affect the rate at which chlorine gas can be liberated from these media upon spillage.

In the form of a solid block, hydrate will not spread along the ground like liquid chlorine and thus exposes much less surface area to ambient heat transfer sources. Hydrate also has a 3.8 times greater latent heat for chlorine gas release than does liquid chlorine. This difference, as well as hydrate's higher gas formation temperature (smaller thermal driving force) significantly reduce the chlorine gas release rates under all ambient conditions. A simple first-approximation analysis of these properties

Table XII

COMPARISON OF SELECTED PROPERTIES WHICH ILLUSTRATE
THE RELATIVE DIFFICULTY IN FORMING GASEOUS
CHLORINE FROM CHLORINE HYDRATE AND LIQUID CHLORINE

	<u>Cl₂·8H₂O</u>	<u>Liquid Chlorine</u>
Physical form	solid	liquid
Latent heat to form gaseous chlorine (kCal/g·Mole)	18.6	4.88
Minimum temperature to form gaseous chlorine (°C)		
Decomposition temperature	9.6	---
Boiling point	---	-34.05

suggests two orders of magnitude, or greater, differences in the rates of chlorine gas release from these media. Therefore, the 50 ppm isopleths for Scenario I would be >5000 ppm isopleths if liquid chlorine were the storage medium which spilled from the battery.

The use of chlorine hydrate as the storage medium offers some advantages in the performance, efficiency, and cost areas as well as the safety area. These additional advantages can be summarized as follows:

- The system can be operated very close to ambient pressure thus conferring additional safety on the system.
- Hydrate appears to offer cost advantages since the complex uses water at virtually zero cost.
- Its large enthalpy of formation provides significant cooling of the battery during discharge.
- Drying of the chlorine gas is not necessary to store it as hydrate which is a cost and reliability advantage.
- Storage of chlorine as hydrate external to the electrochemical cell minimizes activated stand losses via direct reaction of chlorine with zinc.

In addition to these advantages, clean-up of accidentally spilled hydrate can be handled via a number of conventional methods. Something as simple as throwing a blanket or a coat over the spilled hydrate will reduce the rate of heat transfer from the ambient to the hydrate thereby reducing the chlorine release rates. Covering it with foam would be more effective and a water spray of the chlorine gas envelope will absorb gaseous chlorine and reduce the airborne chlorine concentration in the immediate vicinity of the spill. These temporary measures can be instituted until the remaining hydrate can be removed from the accident site and transported to an appropriate location for disposal.

The chlorine release and dispersion analyses of the two accident scenarios suggest that use of the chlorine hydrate storage medium will limit the spread of hazardous levels of airborne chlorine to the immediate vicinity of the leakage source, even in the worst case spill scenario. The design and operational safety features of the battery practically preclude this worst case spill scenario. Firstly, the hydrate is contained within a double-walled container (store container enclosed in the battery case). Secondly, the hydrate retains the form of a solid block throughout the discharge and can only spill from the battery if the bottom portions of both the battery case and store container are severed from the battery. Thirdly, the battery will be well protected by the chassis of the vehicle, being formed in place to make them integral with one another.

Analysis of both scenarios presented in this study involves the mathematical modeling of heat transfer to the hydrate (either contained in the battery or spilled on the ground) and the atmospheric dispersion of released chlorine gas. These models were developed on the basis of practical assumptions. They will be used in continuing studies of this type and will be updated and refined to correlate them with experimentally obtained data, as it becomes available. Through these efforts and a failure modes and effects analysis on the battery EDA plans to develop a comprehensive and factual position statement on the safety and environmental aspects of zinc-chlorine hydrate electric-vehicle batteries. This preliminary study has established a firm basis for this development.

Section 8

RESULTS, CONCLUSION, AND RECOMMENDATIONS

The results of this study can be summarized as follows:

- Despite the low chlorine threshold limits for plant life, chlorine does not appear to pose a regional pollution problem, even in the case of massive accidental release, due to its high chemical reactivity. Damage to vegetation is restricted to the immediate vicinity of the leakage source.
- Although toxic in large enough doses humans can completely recover from short-term acute exposure to airborne chlorine.
- No chlorine will be emitted from zinc-chlorine batteries during normal operations.
- Potential chlorine release rates are minimized due to the storage of chlorine as chlorine hydrate -- 18.6 kCal required to decompose each mole of chlorine hydrate.
- Accidental chlorine release probabilities from the batteries are minimized by the design and operational safety features, including the safety interlocks.
- Mathematical models have been developed for analyzing the release rates and dispersion of accidentally released chlorine.

The results obtained from the dispersion analyses indicate the following:

- Ground level dispersion of dangerous levels of airborne chlorine will be restricted to the immediate vicinity of the battery for most probable type accidents.
- For the worst case improbable type accident under the worst-case meteorological conditions the dispersion of dangerous levels of airborne chlorine is restricted to a narrow (3.5 ft wide) ground level band which extends a maximum of three car lengths from the spill.

Obviously, under more favorable meteorological conditions or for smaller hydrate spills the 50 ppm ground level concentration will extend a lesser distance from the spill. Conventional methods of thermally insulating the spilled hydrate will further reduce the chlorine release rates and downwind dispersion.

This study is the first of its type to be performed on zinc-chlorine FCEV batteries. As part of this preliminary study practical mathematical models were developed for analyzing the accidental release rates and dispersion of chlorine from zinc-chlorine batteries. The models need to be refined and updated to conform to experimentally obtained data, as it becomes available. Also a thorough analysis of potential failure modes and their effects needs to be performed. It is, therefore, recommended that work in the following areas be performed to support and validate the results of this preliminary study:

- Failure modes and effects analysis (FMEA) on the FCEV battery.
- Hydrate spill experiments to verify heat transfer and chlorine release rate models.
- Field tests using chlorine to verify the dispersion model.
- Computer modeling studies based on current and updated models to comprehensively evaluate the safety and environmental aspects of zinc-chlorine FCEV batteries.

Section 9

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Appendix A

RATE OF CHLORINE RELEASE FROM HYDRATE SPILL

CASE I: Stability Class "F" and 2m/sec wind speed

Figure 6 is a simple sketch of the hydrate block spilled from the battery store and resting on the pavement on one of its faces. The maximum volume of the block is 4.46 cu. ft. when the battery is fully charged, and consists of 40.9kg of chlorine. Decomposition is an endothermic reaction and its rate is proportional to the heat transfer rate to the hydrate block. As the figure (6) illustrates, heat transfer to the block occurs due to conduction from the ground, convection from the wind and radiation from the sun.

Figure 6. Hydrate spilled on the floor.

The following are the assumptions and boundary and initial conditions used in the calculation of heat transfer:

- The battery is fully charged with the hydrate formed as a cube.

- The pavement is at a uniform temperature T_a (100°F) and is made of asphalt.
- The atmospheric temperature is also T_a (100°F).
- There is no lateral conduction in the pavement.
- Decomposition of hydrate occurs at T_h (49.3°F).
- The latent heat of decomposition of hydrate is 18.6 kCal/gm-mole of chlorine.
- Because of the surface roughness of the pavement and hydrate block, there will be a layer of water and chlorine at the interface with an equivalent heat transfer coefficient of 'h'. For the present analysis a water layer thickness of $\frac{3}{32}$ in. and an equivalent gas layer thickness of $\frac{1}{32}$ in. are assumed.

The total rate of heat transfer to the hydrate is given by equation A-1.

$$Q_T = Q_R A_R + Q_{cv} A_{cv} + Q_{cd} A_{cd} \quad \text{A-1}$$

where

- Q_T = total rate of heat transfer to the hydrate
- Q_R = rate of heat transfer due to radiation per unit area of hydrate exposed to the radiation source
- A_R = area of hydrate exposed to the radiation source
- Q_{cv} = convective heat flux to the surface
- A_{cv} = convective heat transfer surface area
- Q_{cd} = conductive heat flux to the hydrate from the floor
- A_{cd} = area of contact between hydrate and floor

Calculation of $Q_R A_R$:

From the stability table (Table X) for the conditions used for dispersion calculations the insolation is zero, as these conditions can occur only during night.

Therefore $Q_R = 0$ and hence $Q_R A_R = 0 \quad \text{A-2}$

Calculation of $Q_{cv} A_{cv}$:

Convective heat transfer coefficient between the air and the hydrate block is a function of the boundary layer characteristics, properties of air and transpiration effect of chlorine released. There is turbulence present in the air, but under the stability conditions assumed it will be very low and hence a parallel flow of air is assumed. This tends to give a slightly lower heat transfer coefficient. Because of the complex

nature of the problem, the transpiration cooling effect of the chlorine released is ignored and this will perhaps more than offset the above introduced error. Nusselt number (Nu) for the top and two side surfaces parallel to the wind direction is given by Equation A-3 (52).

$$Nu = .664 Pr^{1/3} Re^{1/2} \quad A-3$$

where Pr and Re are the Prandtl and Reynolds numbers, respectively.

Evaluating the properties of air at film temperature and substituting in equation A-3

$$Nu = \frac{hD}{K} = 116.32 D^{1/2}$$

$$\text{or } h = 1.74 D^{-1/2}$$

A-4

where h = heat transfer coefficient (Btu/HrFt²O_F)

and D = length of the hydrate block (ft.)

For the leeward and windward sides of the block, the heat transfer coefficient is assumed to be same as on the other sides and hence the total heat transfer by convection is

$$\begin{aligned} Q_{cv} A_{cv} &= 5 \times D^2 \times 1.74 \times D^{-1/2} \times (T_a - T_h) \\ &= 441.1 D^{3/2} \end{aligned}$$

A-5

As decomposition occurs, the water released slides down the sides of the hydrate block and the thermal resistance of this water film can be proved to be negligible compared to the resistance between the surface and the air. Therefore, the existence of this film is ignored in the heat transfer calculations.

Calculation of $Q_{cd} A_{cd}$:

For the conditions assumed the heat flux (Q_{cd}) at the interface is given by Equation A-6 (53),

$$Q_{cd} = (T_a - T_h) h \exp \left[\frac{h^2}{K^2} \alpha t \right] \left[1 - \operatorname{erf} \frac{(h \sqrt{\alpha t})}{K} \right] \quad A-6$$

where h = interface heat transfer coefficient

K = thermal conductivity of the pavement

α = thermal diffusivity of the pavement

and t = time from the instant of hydrate spill

Area of contact $A_{cd} = D^2$

Heat transfer by conduction is given by Equation A-7,

$$\begin{aligned} Q_{cd} A_{cd} &= D^2 \times (T_a - T_h) h \exp \left[\frac{h^2}{K^2} \alpha t \right] \\ &\quad \left[1 - \operatorname{erf} \left(\frac{h}{K} \sqrt{\alpha t} \right) \right] \end{aligned} \quad A-7$$

The total heat transfer Q_T to the hydrate is obtained by substituting Equations A-2, A-5, and A-7 in Equation A-1.

If h_{fg} is the latent heat of decomposition of hydrate then the chlorine release rate is given by

$$V = \frac{Q_T}{h_{fg}} \quad \text{A-8}$$

Table XIII gives the chlorine release rates calculated by using the above procedure.

Table XIII

CHLORINE RELEASE RATES FROM HYDRATE

Time in minutes after the spill	Chlorine Release Rate in ml/sec
0	109
10	105
20	104
30	102

Case II: Stability class "A" and 2m/sec wind speed

For these conditions from Table X the insolation has to be very strong. A direct sunlight with an intensity of 300 Btu/HrFt² and absorptivity of 0.5 for the surface are assumed. This radiative term is included in Equation A-1 besides the convective and conductive terms as calculated in Case I above. The resulting chlorine release rates with time are presented in Table XIV.

Table XIV

CHLORINE RELEASE RATES FROM HYDRATE

Time in minutes after the spill	Chlorine Release Rates in ml/sec
0	147
10	143
20	142
30	140

Appendix B

RATE OF CHLORINE RELEASE FROM THE BATTERY

The calculations in this section give the chlorine release rates from the battery in case if there is a battery case rupture and all the chlorine generated by decomposition of the hydrate leaks from the battery. Figure 1 is a sketch of the battery showing hydrate store, stack and sump areas. Heat transfer to the store area occurs from outside through the walls on five sides and from the electrolyte in the sump and chlorine gas in the stack through the partition wall inside. The total rate of heat transfer Q_T to the store is given by equation B-1:

$$Q_T = Q_a + Q_s + Q_c \quad \text{B-1}$$

where Q_a = heat transfer from the ambient

Q_s = heat transfer from the sump

Q_c = heat transfer from the stack

Calculation of Q_a :

The cross-section of the wall separating the ambient from hydrate is shown in Figure 7.

Figure 7. Section of the wall between store and ambient.
Heat transfer from the ambient to the hydrate is given by equation B-2.

$$Q_a = UA_a(T_a - T_h) \quad \text{B-2}$$

where U = overall coefficient of heat transfer

A = area of the wall

T_a = ambient temperature (100°F)

T_h = decomposition temperature of the hydrate
($7^{\circ}\text{C} \approx 44.6^{\circ}\text{F}$)

For this case U is given by Equation B-3,

$$U = \frac{1}{\frac{1}{h_o} + \frac{\Delta x_1}{K_1} + \frac{\Delta x_2}{K_2} + \frac{\Delta x_3}{K_3} + \frac{1}{h_i}} \quad \text{B-3}$$

where h_o and h_i are the convective heat transfer coefficients and K_1 , K_2 and K_3 are the conductivities of various sections of the wall. Substituting appropriate values for these constants in the above equation

$$U = 0.11 \text{ Btu/hr} \cdot \text{ft}^2 \cdot ^{\circ}\text{F}$$

$$Q_a = 0.11 \times 13.89 \times 55.4 = 84.6 \text{ Btu/hr}$$

B-4

Calculation of Q_s :

Figure 8 gives the section of the partition wall between the sump and store.

Figure 8. Section of the wall between store and sump.

Overall heat transfer coefficient U_s , for this section is given by

$$U_s = \frac{1}{\frac{1}{h_s} + \frac{\Delta x_1}{K_1} + \frac{\Delta x_2}{K_2} + \frac{\Delta x_3}{K_3} + \frac{1}{h_i}} \quad \text{B-5}$$

substituting the appropriate values in Equation B-5

$$U_s = 0.284 \text{ Btu/hr. ft}^2 \text{ } ^\circ\text{F}$$

$$\text{and } Q_s = U_s A_s (T_s - T_a)$$

B-6

where T_s = temperature of the electrolyte in the sump
(30 $^\circ\text{C}$ = 86 $^\circ\text{F}$)

$$\text{and } A_s = \frac{5 \times 20}{144} = 0.694 \text{ sq. ft.}$$

$$Q_s = 7.24 \text{ Btu/hr}$$

B-7

Calculation of Q_c :

Overall coefficient of heat transfer between chlorine in the stack and hydrate is obtained by substituting h_c (heat transfer coefficient between Cl_2 and wall) for h_s in Equation B-5.

$$U_c = 0.255 \text{ Btu/hr ft}^2 \text{ } ^\circ\text{F}$$

$$\text{and } Q_c = 0.255 \times A_c \times (T_c - T_h)$$

$$A_c = 2.038 \text{ sq. ft.}$$

$$T_c = 86^\circ\text{F}$$

$$Q_c = 19.5 \text{ Btu/Hr.}$$

B-8

substituting the values for Q_a , Q_s and Q_c from equations B-4, B-7, and B-8 in equation B-1

$$Q_T = 84.6 + 7.24 + 19.5 = 111.34 \text{ Btu/Hr.}$$

If h_{fg} is the latent heat of hydrate decomposition, the rate of chlorine release V is given by

$$V = \frac{Q_T}{h_{fg}} = 10.5 \approx 11 \text{ cc/sec.}$$