CHARACTERISTICS OF CHLORINE AND AN APPLICATION TO LIFE-CYCLE MANAGEMENT

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I. CHARACTERISTICS

A. Background

Chlorine is one of the chemical elements which number slightly more than 100. Because it is a highly reactive material, it typically appears in nature as a chloride salt.

Chlorine was discovered in 1774 by a Swedish pharmacist, Carl Wilhelm Scheele. Until the early part of this century, its only recognized usefulness was as a fabric whitener.

In 1908, Jersey City, New Jersey began to use chlorine on a large scale to treat its drinking water. Its use rapidly spread as the public health benefits of chlorination became known. After chlorine's introduction into the public water supply, deaths from typhoid in the United States dropped dramatically from 25, 000 in 1900 to less than 20 in 1960 to virtually none today.

Today, 12.5 million tons of chlorine are manufactured in North America. About 1.5 million tons are produced and used in Canada. There are twelve chlor-alkali production facilities and seven chlorine repackaging facilities operating in Canada today.

Chlorine is used in a variety of products and is considered the key building block chemical in commerce today. The largest single use is PVC.

B. Physical and Chemical Properties

Chlorine is a gas at room temperature, greenish yellow in color, with a density about two and one-half times that of air. Liquid chlorine is amber in color with a density about 50% greater than water. At atmospheric pressure, it boils at about -34°C and freezes at -101°C. One volume of liquid chlorine, when vaporized, yields about 460 volumes of gas.

Dry chlorine (as supplied by the producer) is not corrosive to many metals. Chlorine is strongly corrosive when moisture is present. An exception is titanium. Dry chlorine will react with titanium metal while wet chlorine will not. At elevated temperatures, chlorine becomes increasingly corrosive to many metals. At about 250°C, chlorine will spontaneously react with steel.

C. Toxicity of Chlorine

Chlorine is an acutely toxic chemical that can cause adverse effects on the eyes, upper respiratory system, lungs, kidneys, liver, and the nervous system at high exposure levels and may be fatal at concentrations in excess of 60 ppm.

Toxic effects from short-term, high level exposures are usually transient in nature, with full recovery normally seen. Chronic exposures to low concentration (less than 1.0 ppm) do not reveal any long term-effects in occupational environments. There do not appear to be any additional risks of cancer, mutation, reproductive effects or developmental effects associated with chlorine exposure.

The American Industrial Hygiene Association has developed Emergency Response Planning Guidelines for several chemicals including chlorine. For chlorine, they are as follows:

ERPG-1: 1 PPM

Maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects.

ERPG-2: 3 PPM

The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects.

ERPG-3: 20 PPM

The maximum airborne concentration which it is believed nearly all individuals could be exposed for up to one hour without experiencing or developing life threatening health effects.

The American Conference of Governmental Industrial Hygienists has adopted a 0.5 ppm TWA and a 1 ppm STEL for chlorine. In the United States, OSHA's PELs are the same.

It is the recommendation of the Chlorine Institute, that when working with chlorine, a person should carry or have immediately available an approved, escape-type respirator.

D. Shipping Containers

Chlorine is shipped in bulk in railroad tank cars, tank motor vehicles, portable tanks, and barge tanks. It also may be transferred in bulk by pipeline.

Chlorine in shipped in lesser quantities in a variety of cylinder sizes between 0.45 and 68 kilogram. It is also shipped in short ton containers (907 kg).

II. APPLICATION TO LIFE-CYCLE MANAGEMENT

A. Background:

There are numerous opinions of what should and should not be included as part of life-cycle management of a chemical. For the purposes of this paper, the application of life-cycle management means the development and implementation of appropriate management techniques that will result in the safe manufacture, distribution, transportation, and use of that chemical, including effective mitigation, and emergency response.

Comprehensive Life-Cycle Management for any hazardous chemical should include the following components:

- Technology Transfer
- Community Dialogue
- Public Awareness

The Chlorine Institute believes that Life-Cycle Management for a hazardous chemical must include a total commitment to Responsible Care®. The Canadian Chemical Producer's Association began the world-wide initiatives on Responsible Care®. In the United States, the Chemical Manufacturers Association has established the Responsible Care® initiative for American chemical companies. The Chlorine Institute is a Partner Association in CMA's Responsible Care® initiative.

The remainder of this paper will discuss the application of chlorine to life cycle management and why this is a necessary commitment of all the sectors dealing with chlorine.

B. Area Affected by a Chlorine Release:

■ Failure of a 1" chlorine gas line (infinite supply).

Depending on atmospheric conditions, the chlorine cloud containing in excess of 25 ppm will travel between 1,000 and 4,000 feet.

■ One ton container - assume the liquid valve is struck and sheared off.

Depending on atmospheric conditions, the chlorine cloud containing in excess of 25 ppm will travel between 3,000 and 11,000 feet.

■ 90 ton chlorine tank car derailment and puncture.

Depending on atmospheric conditions, the chlorine cloud containing in excess of 25 ppm will travel between 6,000 and 18,000 feet.

C. How Manufacturers, Distributors, and Users of Chlorine Should Apply Life-Cycle Management Techniques:

- Document operating procedures.
- Document safety information.
- Insure that all personnel are appropriately trained.
- Insure the mechanical integrity of equipment handling chlorine.
- Implement management of changes procedures.
- Investigate all incidents that resulted in or could have resulted in a chlorine release.
- Establish an equipment quality assurance program for critical equipment.
- Conduct pre-start up safety reviews of new processes.
- Develop a formal emergency response plan.
- Conduct process hazard reviews.
- Involve employees.
- Involve the community.
- Involve CHLOREP when needed.
- Insure that your customers and shippers are handling and using chlorine appropriately.
- Conduct internal compliance audits.

If many of the above items sound to you like the U.S. Occupational Safety and Health Process Safety Code, you are right. The Institute formally recommended that chlorine manufacturers adopt all these process safety measures more than two years ago. Many of these measures have been formally recommended by the Institute in a variety of publications issued before there was an OSHA or an Environmental Protection Agency.

D. How Shippers of Chlorine Can Apply Life-Cycle Management Techniques:

Many of the items are the same as listed above. Transportation incidents have the potential for being very serious whether or not a hazardous chemical is involved. While some changes are required in the statement of the specific technique (e.g., conduct pre-start up safety reviews of new facilities (instead of processes)), the objectives are the same.

E. How the Community or the Public Can Apply Life-Cycle Management Techniques:

The Chlorine Institute believes that it is the responsibility of the chemical industry to initiate dialogue with the affected publics. However, we believe these publics have the right to ask what is being done to minimize the possibility of a chlorine incident from occurring and to ask what would be done to mitigate the consequences of a chlorine incident in the event something goes wrong.

The Chlorine Institute fully supports an open dialogue between the chlor-alkali industry and the affected publics. Such dialogue should discuss concerns of the publics, all of which should be appropriately addressed.

III. SUMMARY

The chlor-alkali industry stands tall in our past accomplishments in the safe handling, use, distribution, and shipment of chlorine. However, we believe we, not only can, but must foster the continuous evaluation and improvement of our safety performance.

The Chlorine Institute believes this conference will enhance the life-cycle management of chlorine through the exchange of technology, fostering of dialogue, and enhancing public awareness.

BACKGROUND

- CHLORINE DISCOVERED IN 1774 BY CARL WILHELM SCHEELE

- LITTLE COMMERCIAL USE UNTIL EARLY IN THE 20TH CENTURY

- 1908 - JERSEY CITY, NJ
  LARGE SCALE USE OF CHLORINE AS A DISINFECTANT

- 12.5 MILLION TONS PRODUCED IN NORTH AMERICA IN 1991

  (11.3 MILLION METRIC TONS)

- CHLOR-ALKALI INDUSTRY 3RD LARGEST (BASED ON TONNAGE)

- 67 CHLOR-ALKALI FACILITIES IN NORTH AMERICA

- 96 REPACKAGING FACILITIES

USES OF CHLORINE

EDC/VCM	27 %
PULP AND PAPER	14
POLYURETHANES	14
SOLVENTS	13
OTHER ORGANICS	12
INORGANICS	9
TITANIUM DIOXIDE	6
WATER TREATMENT	5

SOURCE: Chemical Marketing Reporter (June 1, 1992)

PHYSICAL AND CHEMICAL PROPERTIES

- GREENISH YELLOW GAS AT ROOM TEMPERATURE

- 2.5 TIMES THE DENSITY OF AIR

- LIQUID CHLORINE IS AMBER IN COLOR

- AT ATMOSPHERIC PRESSURE

  BOILING POINT = -34°C

  FREEZING POINT = -101°C

- ONE VOLUME LIQUID CHLORINE EQUALS 460 VOLUMES OF GAS

- DRY CHLORINE NOT CORROSIVE TO MOST METALS

  EXCEPTION IS TITANIUM

- AT ABOUT 250°C, CHLORINE REACTS SPONTANEOUSLY WITH STEEL

TOXICITY OF CHLORINE

- **CHLORINE IS ACUTELY TOXIC**
  - **EYES**
  - **UPPER RESPIRATORY SYSTEM**
  - **LUNGS**
  - **KIDNEYS**
  - **LIVER**
  - **NERVOUS SYSTEM**

- **OSHA PELs/ACGIH TLVs**

0.5 PPM	**T.W.A.**
1.0 PPM	**S.T.E.L.**

- **IDLH**

30 PPM

- **ERPGs**

NO.	**1**	**2**	**3**
PPM	**1**	**3**	**20**

FIRST AID - ACUTE CHLORINE EXPOSURE

- REMOVE FROM CONTAMINATED AREA
- REMOVE CONTAMINATED CLOTHING
- CALL A PHYSICIAN ASAP

IF BREATHING HAS CEASED:

- BEGIN CPR IMMEDIATELY
- ADMINISTER HUMIDIFIED OXYGEN ASAP

IF BREATHING HAS NOT CEASED:

- PLACE PATIENT IN A COMFORTABLE POSITION
- ENCOURAGE SLOW REGULAR BREATHING
- ADMINISTER HUMIDIFIED OXYGEN ASAP
- RENDER OTHER NECESSARY FIRST AID

APPLICATION TO LIFE CYCLE MANAGEMENT

THE DEVELOPMENT AND IMPLEMENTATION OF APPROPRIATE MANAGEMENT TECHNIQUES THAT WILL RESULT IN THE SAFE MANUFACTURE, DISTRIBUTION, TRANSPORTATION, AND USE OF CHLORINE INCLUDING EFFECTIVE MITIGATION AND EMERGENCY RESPONSE

NOTE: **All the chlorine release scenarios described on the following pages are taken from the Chlorine Institute Publication #74, Estimating the Area Affected by a Chlorine Release**

CHLORINE RELEASE SCENARIOS

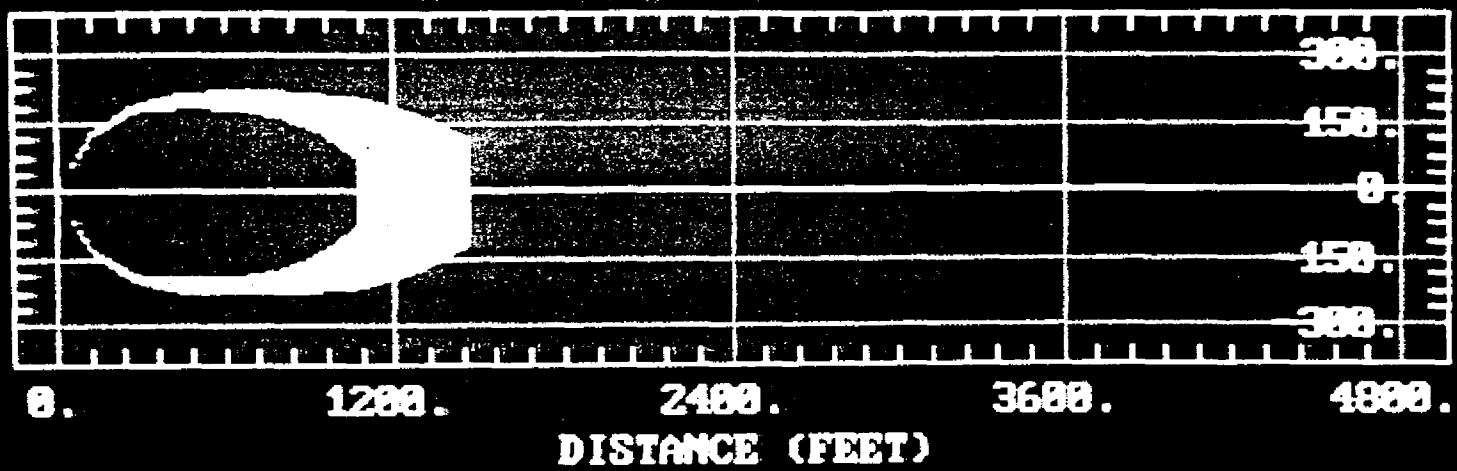
SCENARIO #1: 150 LB. CYLINDER

A. A 150 POUND CHLORINE CYLINDER FALLS OVER AND SHEARS OFF THE VALVE. (GAS AND LIQUID RELEASE)

B. THE CYLINDER IS FULL = 150 LBS. OF CHLORINE

C. THE VALVE BODY HAS A 3/8 INCH HOLE

D. THE CYLINDER IS ON A CONCRETE SLAB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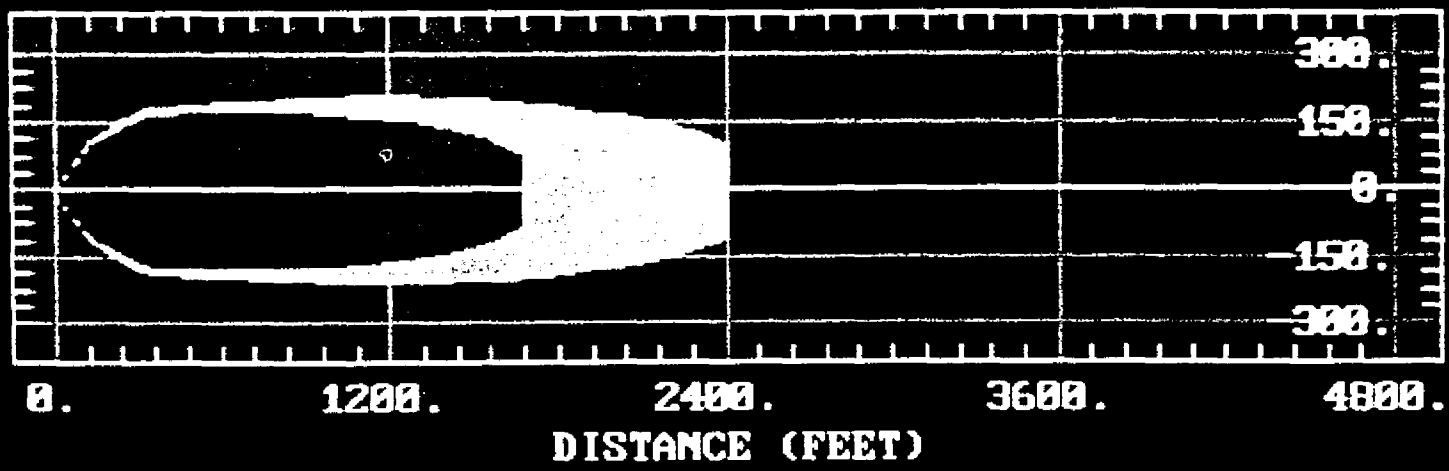
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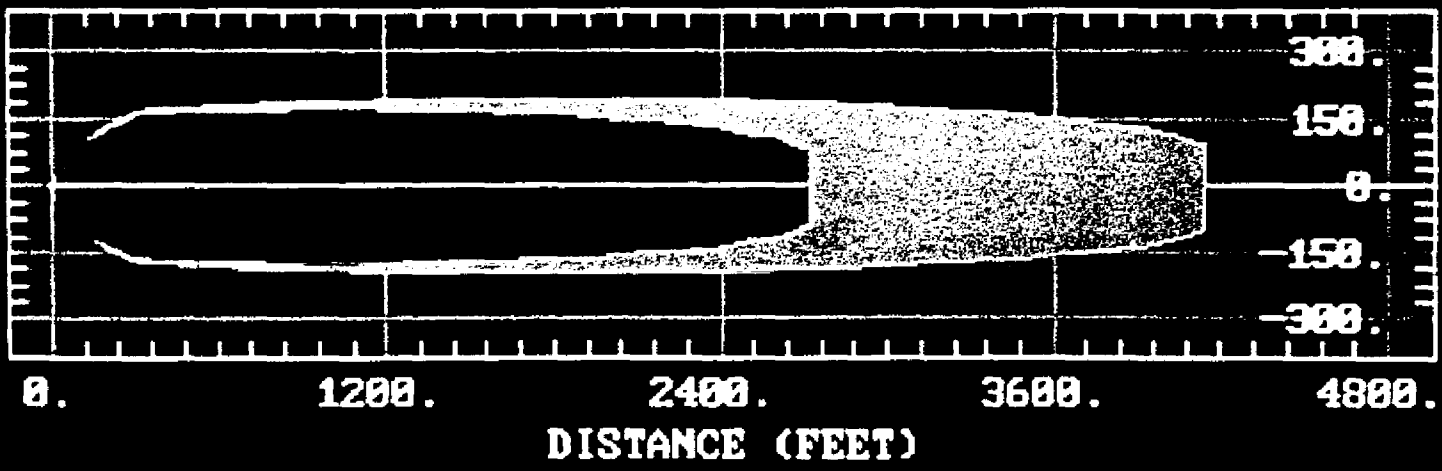
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ATMOSPHERIC STABILITY CLASSES

_B_ (Top Graphs)

MORNING - CLEAR, LOW WINDS

_D_ (Middle Graphs)

ALL OTHER CONDITIONS

_F_ (Bottom Graphs)

NIGHTTIME - MOSTLY CLEAR SKIES, LOW WINDS

CHLORINE RELEASE SCENARIOS

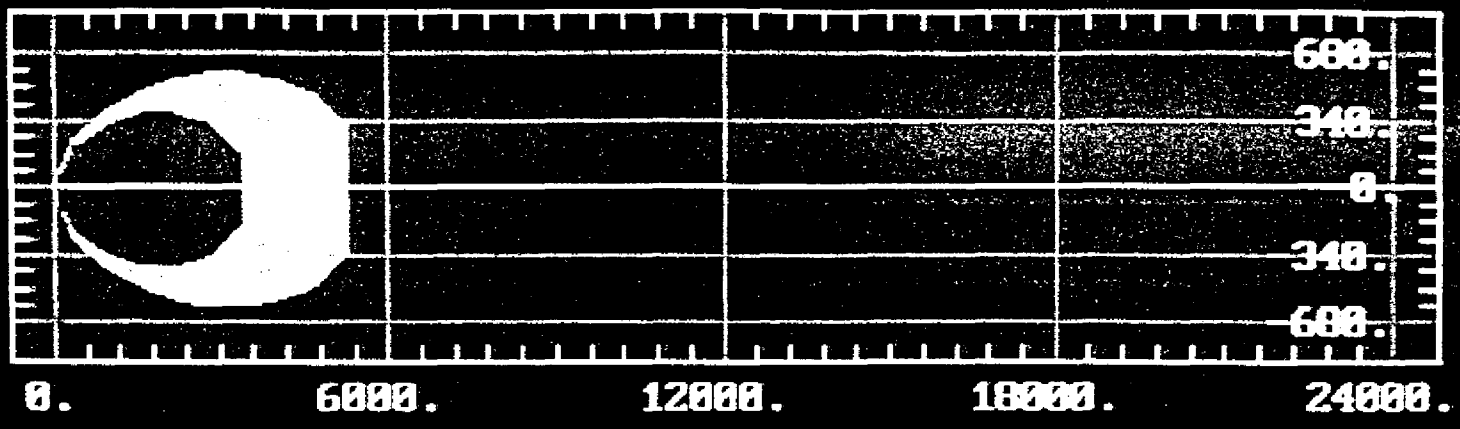
SCENARIO #2: 1 TON CONTAINER

A. A ONE-TON CONTAINER IS STRUCK AND THE LIQUID VALVE IS SHEARED OFF (LIQUID RELEASE)

B. THE CONTAINER IS FULL - 2,000 LBS OF CHLORINE

C. THE VALVE BODY HAS A 3/8 INCH HOLE

D. THE CONTAINER IS ON A CONCRETE SLAB



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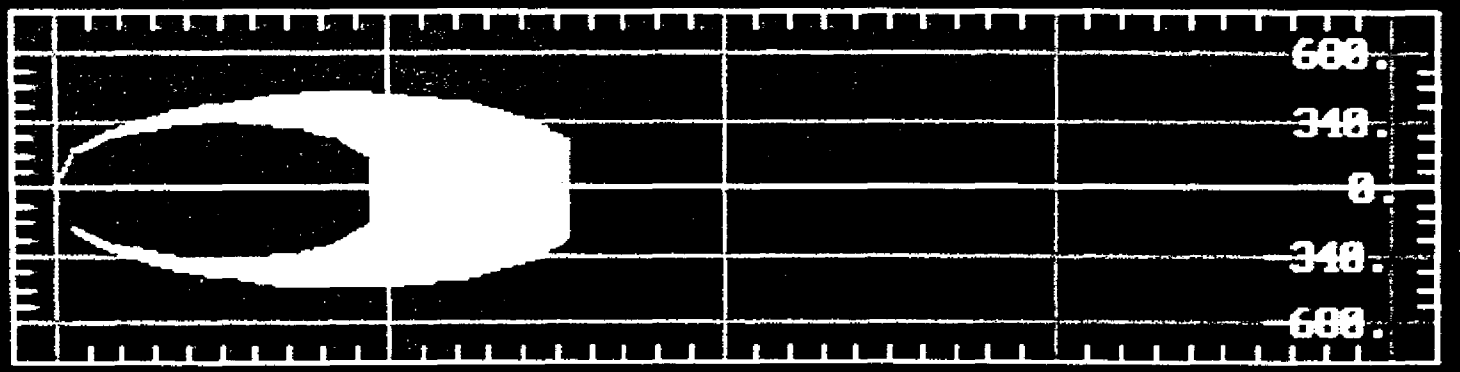

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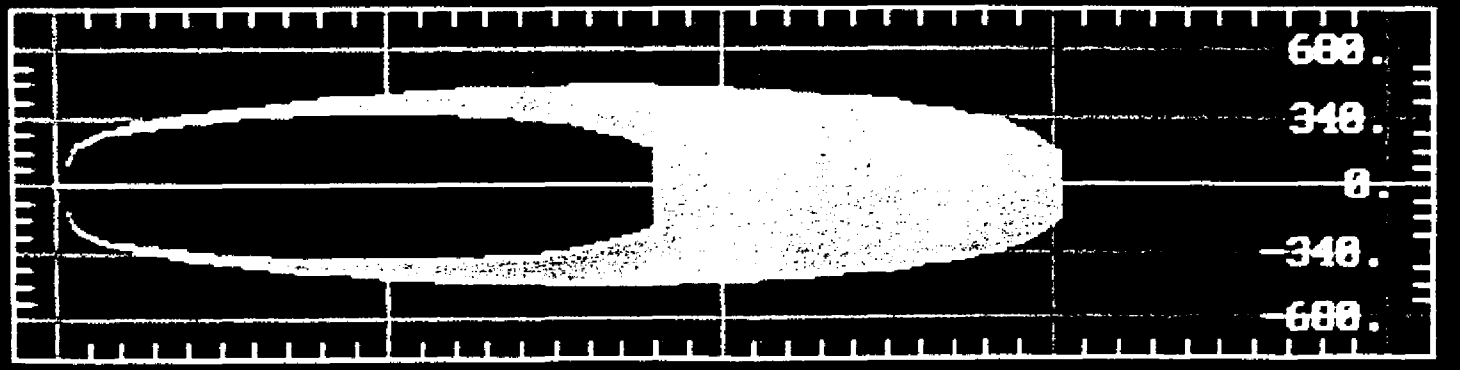

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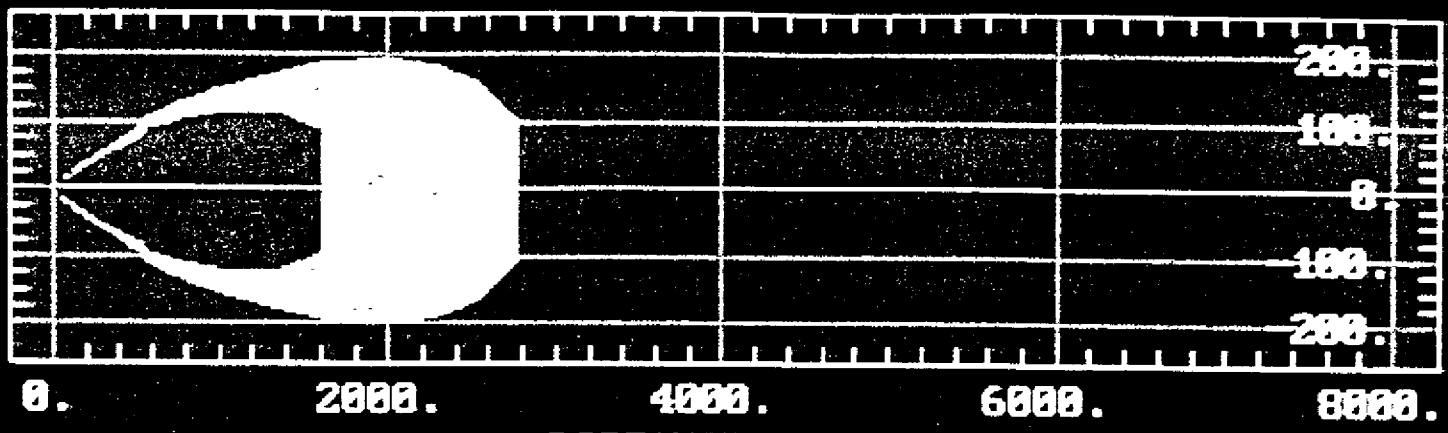
CHLORINE RELEASE SCENARIOS

SCENARIO #5: TANK CAR RELIEF VALVE

A. A PRESSURE RELIEF VALVE ON A 90-TON CAR OPENS AND STAYS OPEN FOR TEN MINUTES (CHLORINE GAS ONLY)

B. HEIGHT OF RELEASE = 13' - 6"



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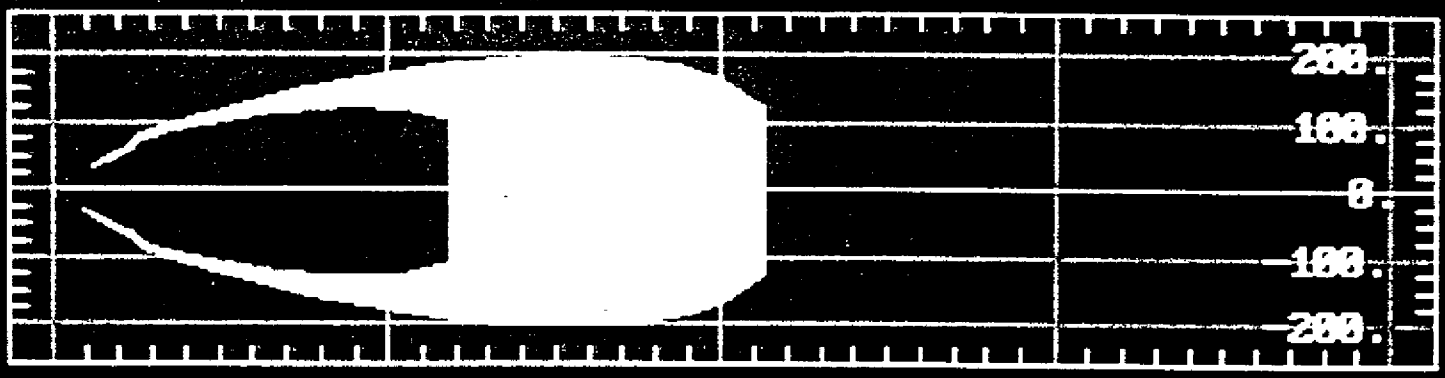

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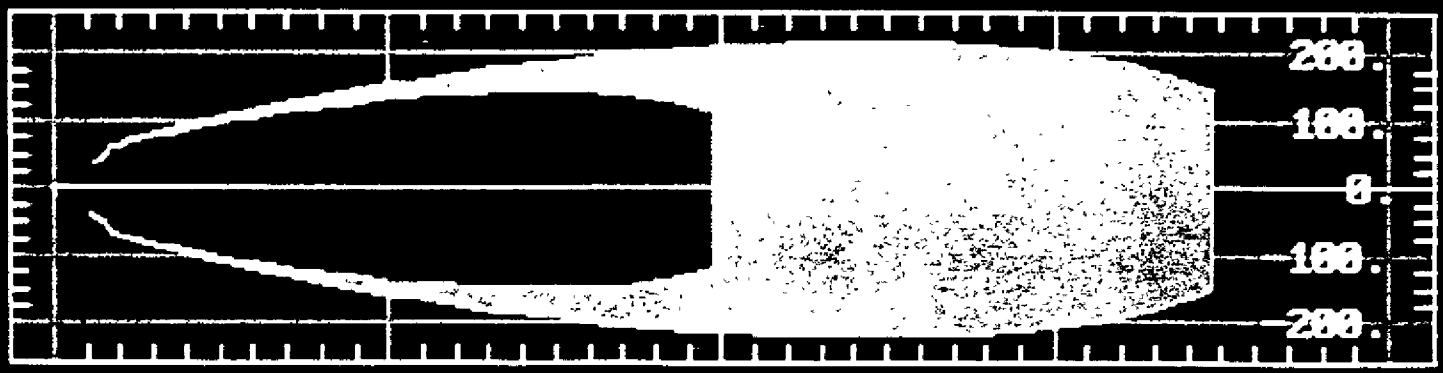

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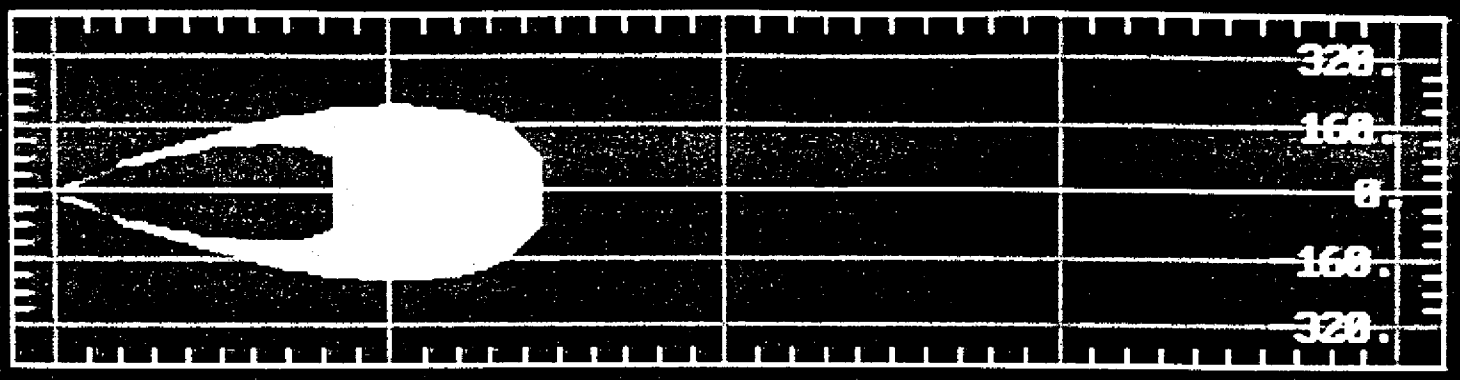
CHLORINE RELEASE SCENARIOS

SCENARIO #8: 1 INCH TUBING - GAS RELEASE

A. A 1-INCH SCHEDULE 80 PIPE IS SHEARED OFF. (CHLORINE GAS ONLY - INFINITE SUPPLY)

B. HEIGHT OF RELEASE = 3 FEET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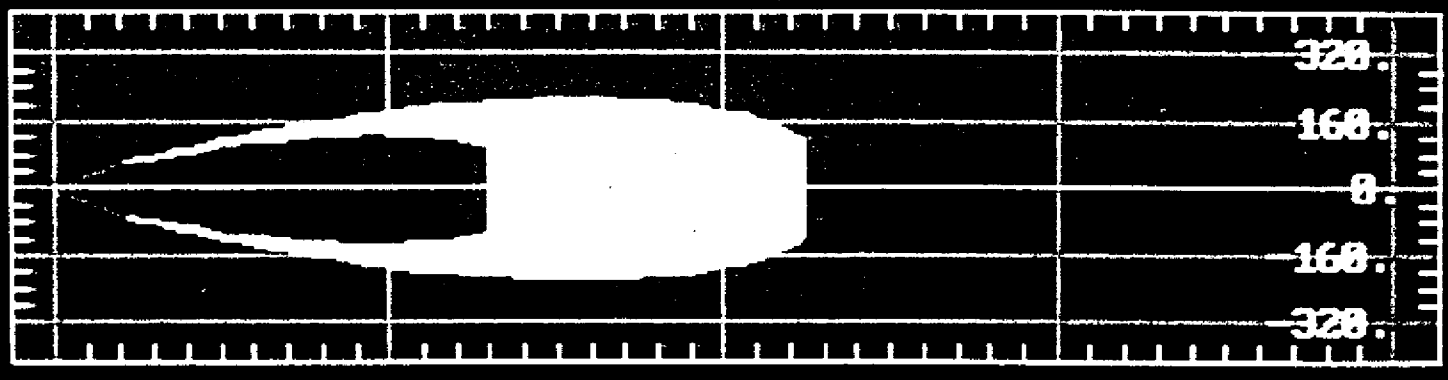
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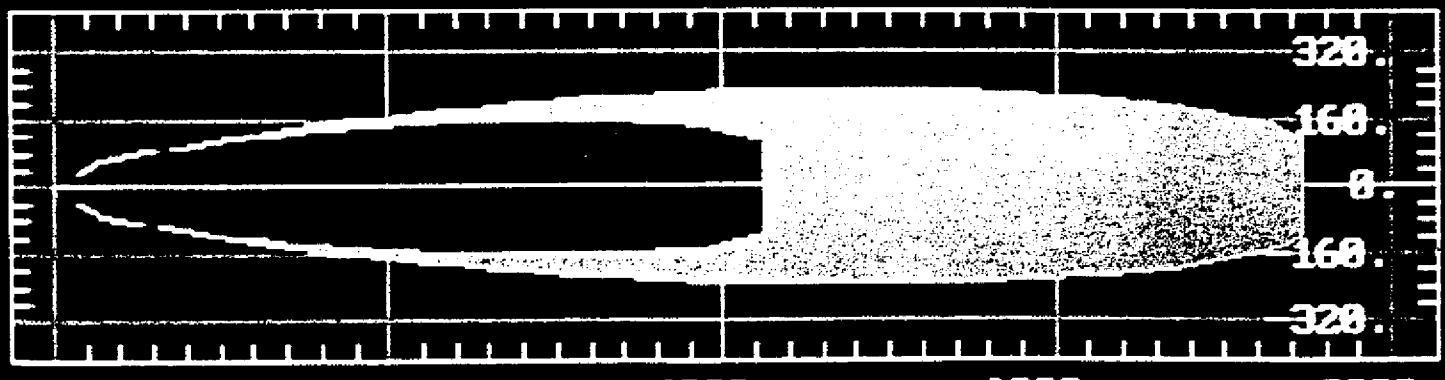
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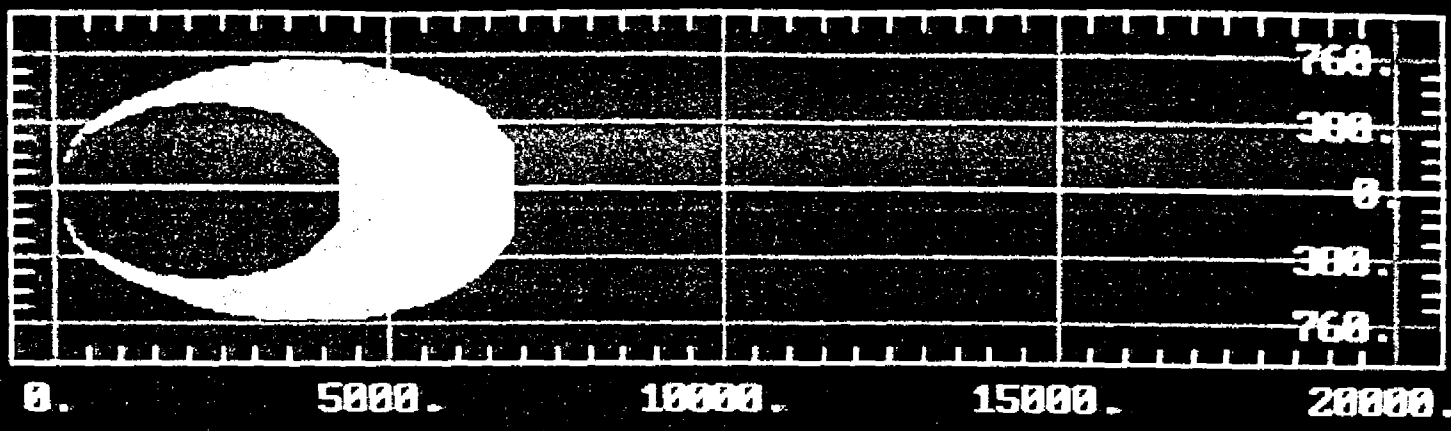
CHLORINE RELEASE SCENARIOS

SCENARIO #11: 1-INCH PIPE LIQUID

A. A 1-INCH, SCHEDULE 80 PIPE IS SHEARED OFF. (LIQUID CHLORINE ONLY - INFINITE SUPPLY)

B. HEIGHT OF RELEASE = 3 FEET

C. THE LIQUID CHLORINE FALLS ON A CONCRETE SLAB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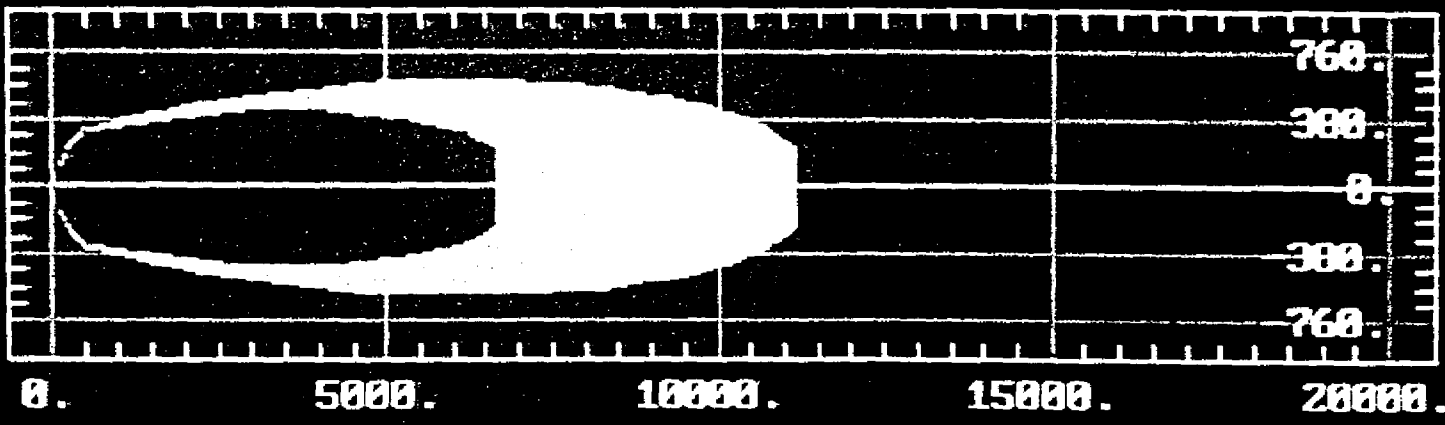
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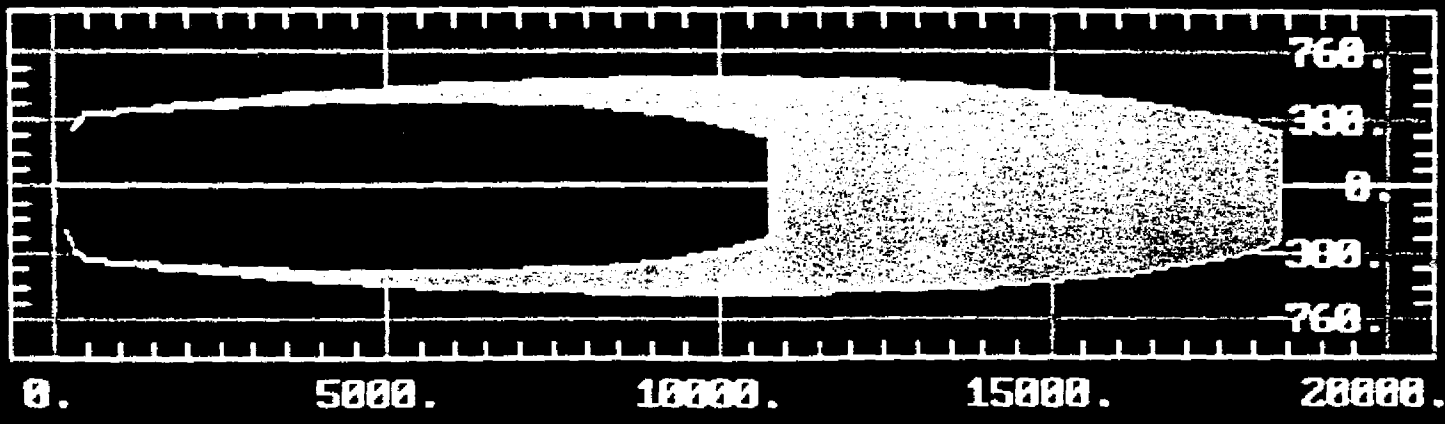
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CHLORINE RELEASE SCENARIOS

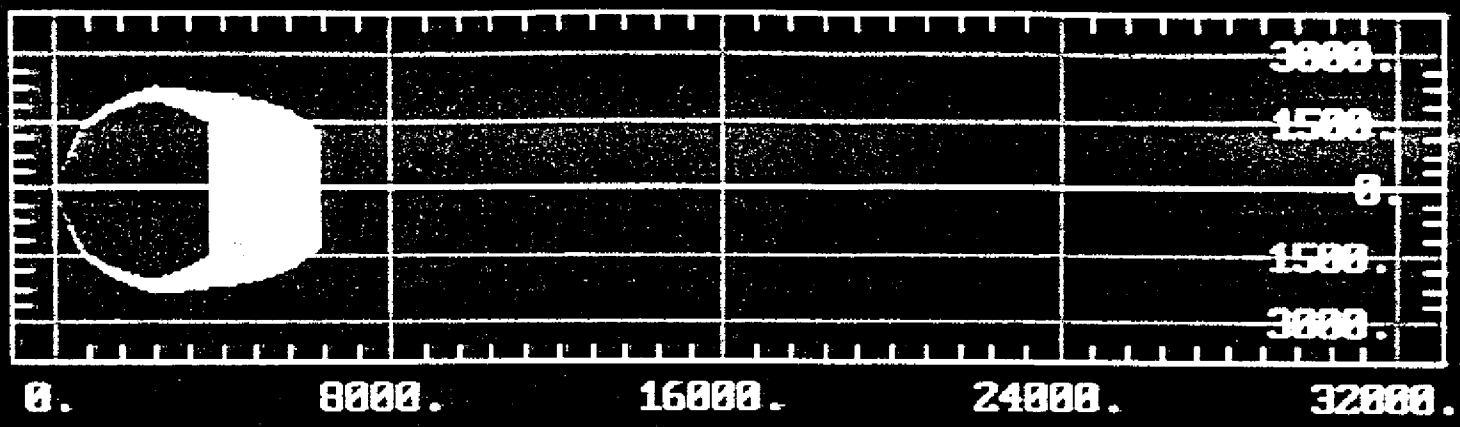
SCENARIO #12: 90-TON RAIL CAR

A. A 90-TON CHLORINE TANK CAR DERAILS

B. THE TANK CAR IS FULL - 90 TON OR 180,000 LBS.

C. THE INNER SHELL IS PUNCTURED AND HAS A 9-INCH HOLE HALFWAY BETWEEN THE CENTER LINE AND THE BOTTOM OF THE SHELL

D. THE TANK CAR IS RESTING ON NORMAL SOIL, AND THE SOIL CONTAINMENT AREA BELOW THE PUNCTURE IS 30' X 40'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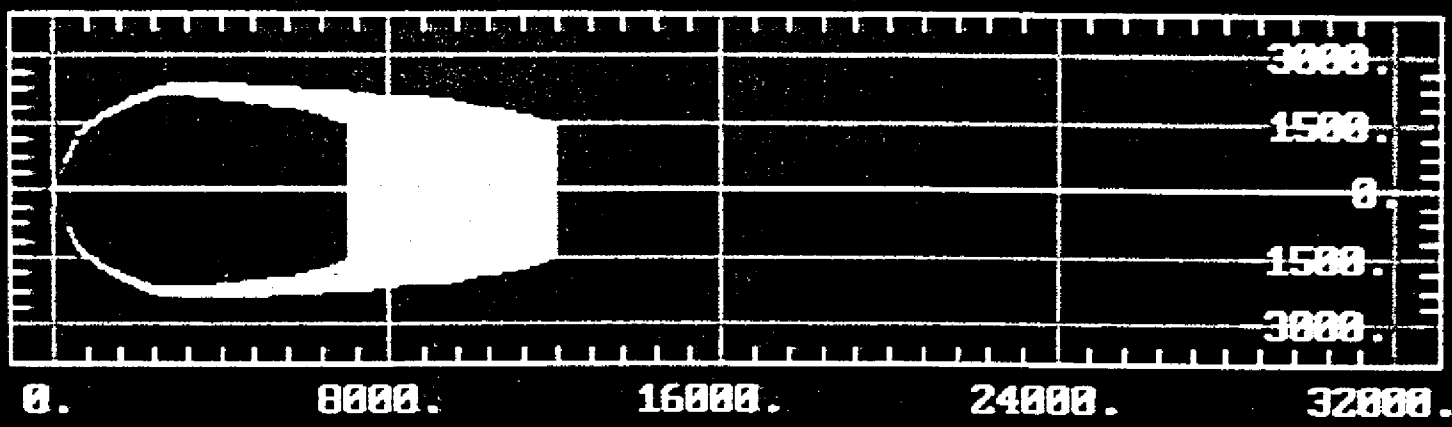
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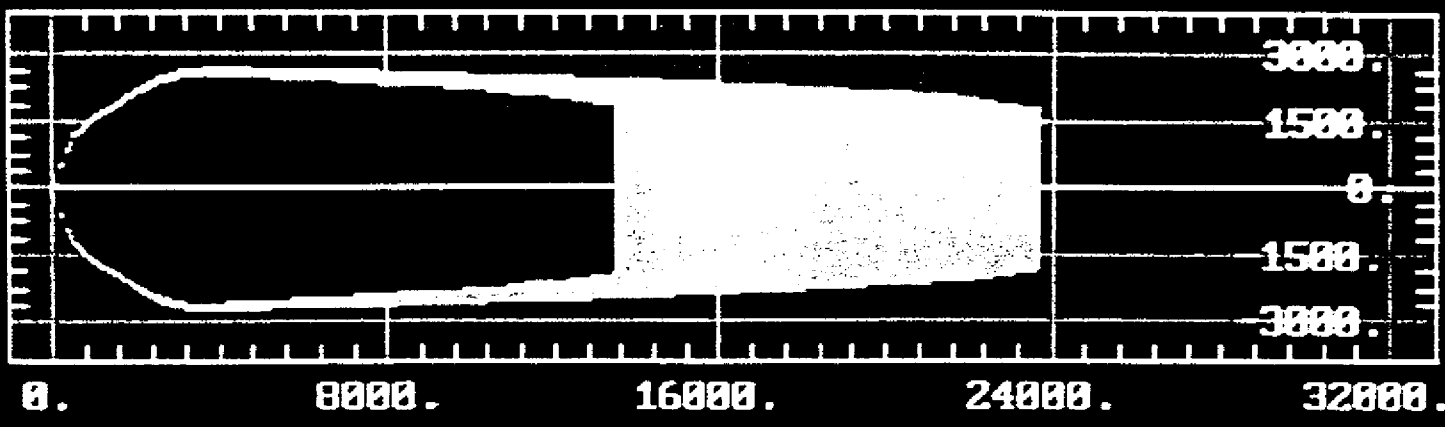
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CONCLUSION

A CHLORINE RELEASE IS A VERY SERIOUS EVENT THAT CAN HAVE FAR REACHING EFFECTS. ALL INVOLVED PARTIES SHOULD TAKE THE APPROPRIATE STEPS TO (1) MINIMIZE THE POSSIBILITY OF A CHLORINE RELEASE AND; (2) HAVE A PLAN IN PLACE TO MITIGATE THE CONSEQUENCES OF A RELEASE IF ONE SHOULD OCCUR.

TABLE I
(By Frequency)

CHLORINE RELEASES FROM CHLOR-ALKALI MANUFACTURING FACILITIES

CATEGORY	NUMBER OF RELEASES	AVERAGE LBS CL_2 PER RELEASE	MAXIMUM LBS CL_2 RELEASED
Emergency Scrubbing System	103	310	8,000
Piping Failure	94	480	13,000
Low Pressure Seals	66	181	2,100
Other Equipment Failure	59	1,846	84,200
Pressure Relief Devices	45	191	3,400
Operating Error	38	173	1,180
Power Failure	34	155	2,800
Less of Air Supply	17	129	900
H_2 Explosion	11	360	1,950
All Others	17	37	100
TOTALS	484	465	

* Survey of North American Chlor-Alkali producers covering chlorine releases of ten pounds or more for 13 years ending December 31, 1991.

TECHNIQUES TO MINIMIZE POSSIBILITY OF A CHLORINE RELEASE

- DOCUMENT OPERATING PROCEDURES

- DOCUMENT SAFETY INFORMATION

- INSURE THAT ALL PERSONNEL ARE APPROPRIATELY TRAINED

- INSURE THE MECHANICAL INTEGRITY OF EQUIPMENT HANDLING CHLORINE

- IMPLEMENT MANAGEMENT OF CHANGES PROCEDURES

TECHNIQUES TO MINIMIZE (CONT.)

- INVESTIGATE ALL INCIDENTS THAT RESULTED IN OR COULD HAVE RESULTED IN A CHLORINE RELEASE

- ESTABLISH AN EQUIPMENT QUALITY ASSURANCE PROGRAM FOR CRITICAL EQUIPMENT

- CONDUCT PRE-START UP SAFETY REVIEWS OF NEW PROCESSES

- DEVELOP A FORMAL EMERGENCY RESPONSE PLAN

- CONDUCT PROCESS HAZARD REVIEWS

TECHNIQUES TO MINIMIZE (CONT.)

- INVOLVE EMPLOYEES

- INVOLVE THE COMMUNITY

- INVOLVE CHLOREP WHEN NEEDED

- INSURE THAT YOUR CUSTOMERS AND SHIPPERS ARE HANDLING AND USING CHLORINE APPROPRIATELY

- CONDUCT INTERNAL COMPLIANCE AUDITS

- **RESPONSIBILITIES OF THE SHIPPER**

- **RESPONSIBILITIES OF THE COMMUNITY**