THE CANADIAN CHEMICAL PRODUCERS' ASSOCIATION RESPONSIBLE CARE®

Key Elements Related to Chlorine Life-Cycle Prevention

PREAMBLE

Canadian chemical producers encourage the responsible development, introduction, manufacture, transportation, storage, handling, distribution, use and ultimate disposal of chemicals and chemical products so as to minimize adverse effects on human health and well-being and on the environment.

STATEMENT OF COMMITMENT

The Canadian chemical industry is committed to taking every practical precaution toward ensuring products do not present an unacceptable level of risk to its employees, customers, the public or the environment. The most senior executive responsible for chemical operations in each member company of The Canadian Chemical Producers' Association has formally accepted these principles and endorsement is a condition of membership.

GUIDING PRINCIPLES

The following list of guiding principles is subscribed to by member companies of The Canadian Chemical Producers' Association.

- ensure that its operations do not present an unacceptable level of risk to its employees, customers, the public or the environment;
- provide relevant information on the hazard of chemicals to its customers, urging them to use and dispose of products in a safe manner; and make such information available to the public on request;
- make Responsible Care[®] an early and integral part of the planning process leading to new products, processes or plants;

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- increase the emphasis on the understanding of existing products and their uses and ensure that a high level of understanding of new products and their potential hazards is achieved prior to and throughout commercial development;
- comply with all legal requirements which affect its operations and products;
- be responsive and sensitive to legitimate community concerns;
- work actively with and assist governments and selected organizations to foster and encourage equitable and attainable standards.

Six codes have been developed focusing on the following areas:

- I Community Awareness and Emergency Response (includes a policy on community right-to-know)
- II Research and Development
- III Manufacturing
- IV Transportation
- V Distribution
- VI Hazardous Waste Management (includes a policy on hazardous waste management)

The following is an overview of those code elements, of the 152 elements of these six codes, which are relevant to chlorine life-cycle accident prevention. Excluded from this overview are those elements which relate more to such issues as long-term environmental impact, waste disposal, product design, etc.

I COMMUNITY AWARENESS & EMERGENCY RESPONSE

1. General

Each member company research and development, manufacturing, distribution and waste management site shall have an <u>active community awareness and emergency response program.</u>
The <u>site manager has the primary responsibility</u> to generate, implement, field-test, audit and

update this program, including its written policies and procedures. This program shall meet or exceed all applicable laws and regulations in letter and in spirit.

Each member company site shall have <u>training criteria commensurate with CAER</u> program requirements, conduct regular <u>performance assessments</u> and maintain <u>employee competence</u>.

Each member company shall work actively, alone or through selected organizations, and, if possible, in consultation with affected stakeholders, to <u>assist governments in developing public policies</u>, legislation and regulations governing community awareness and emergency response.

Some site activities shall be restricted if they cannot be performed in compliance with the emergency response requirements of this code.

2. Community Awareness

There shall be an active community awareness program, consistent with the CCPA's community right-to-know policy which:

- 2.1 <u>identifies and updates a listing of organizations and people which represent community interests;</u>
- 2.4 <u>includes a regular process of communication</u> with the community;
- 2.6 provides a system to measure and assess program activities and results.

3. Emergency Response

There shall be an up-to-date, operational emergency plan which:

- 3.1 <u>is based on a site specific risk assessment</u>, which identifies and evaluates on a regular basis those situations where company materials, processes or equipment could have an impact on site and/or on the community in the event of an emergency;
- 3.2 <u>provides information</u> from this assessment <u>on hazards</u> and associated risks to employees, other people on site and those in the community who have an interest;
- 3.3 is based upon an emergency plan framework developed by site management to both address such emergency situations and to assist authorities in emergency response planning for neighbouring industry and the community;

- 3.4 requires active participation, <u>cooperation and coordination by company personnel</u> with local officials and the media during development and communication of the plan to the community;
- 3.5 <u>integrates the company's emergency response plan</u> with those of industrial neighbours and the community into a community emergency response plan;
- 3.6 is <u>communicated</u> regularly, in its key elements, to <u>the community</u> in a manner which recognizes its <u>right-to-know</u>, in order to gain its cooperation and support;
- in an emergency makes <u>available to first responders</u> and the community <u>company</u> expertise and <u>specialized equipment</u> and materials;
- 3.8 is sensitive to and provides for evaluation with appropriate authorities of the need for immediate and short-term <u>assistance for persons who are dislocated</u> by a company site emergency;
- 3.9 is documented, field tested, audited and updated at least annually.

II RESEARCH & DEVELOPMENT

4. Transfer to Manufacturing

Every member company transferring a new chemical or chemical product, a new process or new equipment from research and development to manufacturing shall ensure that:

- 4.1 <u>hazard and operability studies</u>, or their equivalent, are an integral part of the design process;
- 4.4 <u>material safety data sheets</u> (MSDS) are available for all input, in-process and output materials, and proper procedures for packaging, handling and disposing of these materials, including by-products, are clearly identified.

5. Market Introduction

Every member company introducing a new chemical, chemical product, process or application to the marketplace shall:

- 5.1 ensure that the requirements of all relevant legal and government regulations are met or exceeded in letter and in spirit;
- 5.2 educate employees and contract personnel to ensure responsible product handling and transportation;
- 5.3 provide potential customers with information about <u>hazards and associated risks</u>, and <u>assistance to ensure responsible handling</u>, <u>use and waste management</u>, including reduction/recycling/recovery/reuse opportunities where feasible;
- 5.4 subsequently check back to confirm that customers are following <u>responsible</u> handling, use and waste management practices. Each member company shall require, with due diligence, that customers follow responsible handling, use and waste management practice, if special requirements are determined to apply;

III MANUFACTURING CODE OF PRACTICE

1. General

Each member company shall have <u>written policies</u>, <u>standards and procedures</u> which govern all aspects of the manufacture of chemicals and chemical products. <u>Responsibility shall be clearly defined</u> for generating, implementing, auditing, and updating them, and for taking corrective action. These policies, standards and procedures shall <u>meet or exceed all applicable laws and regulations in letter and in spirit</u>.

Each member company shall have <u>hiring standards and training criteria</u> commensurate with responsible manufacturing requirements, conduct regular performance assessments, take action to <u>maintain employee competence</u>, and ensure with due diligence the equivalent <u>performance from contractors</u> working within the plant environment.

2. Employee, Community and Environmental Protection

Each member company shall have management systems in place to protect the safety and health of its employees and other people on site, the community and the environment from any harmful effects of its materials and operations. The member company shall:

2.1 identify and evaluate on a regular basis potential safety, health and environmental hazards and associated risks, and work to minimize these risks through hazard

- elimination, engineering controls, procedures, education and the use of personal protective equipment;
- 2.2 monitor its safety and health performance as well as the working environment with the objective of identifying and minimizing actual or potential occupational safety and health problems;
- 2.5 be aware of all effluents and emissions to the environment, monitor those for which it is necessary, and implement plans for their control when necessary. Develop and maintain plans and procedures to minimize the effects of accidental spills or emissions;

3. Design and Construction of Facilities

Each member company shall have written policies, standards and procedures for siting, design, construction and commissioning of new facilities. The member company shall:

- 3.1 perform and document a <u>hazard analysis and risk assessment during the design</u> stage of any facility, and act to minimize and control any hazardous situations;
- 3.2 establish <u>site selection criteria</u> which minimize any adverse impact on the community, the environment, industrial neighbours, utilities, and transportation routes;
- 3.3 establish and implement criteria for <u>buffer zone</u> requirements for new or existing sites;

4. Operations

Each member company shall have written operating, engineering and maintenance procedures which specify conditions for the responsible operation of any facility during normal or abnormal circumstances. The member company shall:

- 4.1 perform and document a <u>regular hazard analysis and risk assessment</u> of the operating facility and take action to minimize identified risk;
- 4.2 have written and <u>up-to-date procedures</u> which cover all phases of operation, including start-up and shutdown;
- 4.3 have written and <u>up-to-date procedures</u> which protect personnel during the maintenance of the facilities;

- take action to prevent injury, damage and harm to people and the environment from explosion, fire or uncontrolled releases;
- 4.5 have a management system to <u>control and record changes</u> and modifications to equipment, processes, materials and associated computer hardware and software;
- 4.6 institute <u>security procedures</u> and systems which protect the facilities and address possible security threats;
- 4.7 maintain <u>systems and procedures to minimize risks</u> to safety, health and the environment during the handling and storage of all materials used and produced;
- 4.8 audit and update these procedures on a regular basis.

IV TRANSPORTATION

Each member company shall identify and evaluate on a regular basis the hazards and associated risks to people and the environment from the transportation cycle, and provide information about these hazards and associated risks to employees and transporters.

2. Accident Prevention

Each member company shall have an active program designed to continuously improve safety and to prevent accidents during the transportation cycle which:

- 2.1 establishes <u>criteria for selecting the mode of transport</u>, the <u>specifications for the transportation equipment</u> and container, and inspection and maintenance of these during use;
- 2.2 establishes <u>criteria for selecting carriers</u> which include safety performance and programs, inspection and maintenance procedures for equipment, selection and training of drivers and support staff, and assistance to carriers in meeting these criteria;
- 2.3 <u>identifies alternate transportation modes and routes which minimize the exposure</u> of people and environmentally sensitive areas to the hazards inherent in the transportation mode:
- 2.4 establishes <u>standards</u> for equipment used in loading and unloading containers including containment and emergency response facilities in the event of an accidental release;

- 2.5 provides <u>procedures</u>, <u>training and performance assessment for persons who load</u> or unload the containers;
- deals effectively with the <u>risks involved in the return, cleaning, reuse, servicing and disposal</u> of containers;
- 2.7 clearly identifies the contents of containers;
- 2.8 <u>audits and updates</u> all program components on a regular basis.

3. Emergency Response

Each member company shall have an up-to-date and operational transportation emergency response plan which:

- 3.1 identifies and describes means for dealing with the hazards, whether to people or the environment, and ways of containing and cleaning up the release;
- 3.2 <u>identifies emergency response resources</u> whether in-house, through a mutual-aid plan such as TEAP (<u>Transportation Emergency Assistance Plan</u>) or from a contractor, to be deployed in the case of an accident involving the company's chemicals or chemical products;
- 3.3 provides <u>technical advisors</u> to handle all informational aspects of an accident involving the company's chemicals and chemical products, including media relations;
- 3.4 provides specialized equipment and materials required for responding to an accident;
- 3.5 <u>provides training and regular performance assessment</u> of company emergency response personnel;
- 3.6 provides assistance, through the association, in <u>training first responders along the transportation corridors</u>;
- 3.7 provides for cooperation with government or other agencies at the accident scene;
- 3.8 is sensitive to and provides for evaluation with appropriate authorities of the need for immediate and short term <u>assistance for persons who are dislocated</u> by a transportation accident;
- 3.9 is documented, field-tested, audited, and updated at least annually.

4. Awareness Concerning Transportation

Each member company shall have a program, consistent with the CCPA's right-to-know policy, which enables it to respond to questions from those along transportation corridors.

This program shall include:

- 4.1 key <u>elements of the policies</u>, <u>standards and procedures</u> which reduce hazards, prevent accidents and provide prompt, effective response in the event of an accident;
- 4.2 available <u>information on the hazards and associated risks</u> of chemicals and chemical products moving along the transportation corridors;
- 4.3 identification and training of employees responsible for answering questions;
- 4.4 provision for participation in, and coordination with, a program the association will operate in conjunction with carriers in raising awareness concerning transportation;
- 4.5 periodic assessment and updating of the program.

V DISTRIBUTION

2. Management of Risk - Employees, Contractors, Customers, Publics and Environment

Each member company shall have an active program designed to continuously improve safety through the reduction of incidents and the protection of people and the environment from hazards through hazard reduction, procedures, education and the use of personal protective equipment. The member company shall:

- 2.1 <u>identify and evaluate</u> on a regular basis <u>hazards and associated risks</u> related to the <u>storage</u> and <u>handling</u> of chemicals and chemical products whether on <u>owned or contracted premises</u>;
- 2.4 establish written standards for the proper <u>siting of distribution facilities</u> and for the proper ongoing <u>security of these facilities</u>;
- 2.5 establish written standards and procedures for bulk and packaged storage, including spill containment; proper product segregation; packaging and labelling of chemicals and chemical products in liquid, solid or gaseous form and vehicles used;

- 2.6 provide member company and contract employees with information about the hazards and risks associated with distribution activities, and training in the handling of chemicals and chemical products, including the cleaning of tanks and drums; the proper management of associated waste and empty containers; the transfer of goods from one container to another, including bulk to smaller containers; and, the packaging of chemicals and chemical products;
- 2.7 provide <u>emergency support</u> related to incidents involving member company chemicals, chemical products and services. This support shall be consistent with the code of practice for community awareness and emergency response (CAER) and follow the transportation code of practice;
- 2.8 <u>audit</u> and <u>update</u> the components of this program on a regular basis.

3. Communication of Information

Each member company shall have written procedures in place to:

- obtain, understand, and then provide <u>up-to-date material safety data sheets</u> (MSDS) to the customer's designated representative preceding (or at least accompanying) initial shipment of all chemicals and chemical products, including commercial samples;
- 3.3 <u>provide to the customer that information</u> which the member believes to be <u>vital</u> to the health and safety of the end-user and which is <u>supplementary to the MSDS</u>; and require, with due diligence, communication by the customer of such information to the end-user as a condition of sale;
- 3.4 allow <u>new chemicals</u> and chemical products into the <u>member's distribution</u> network only after all the preceding requirements have been met.

4. Compliance with Legal Requirements

Each member company shall have a program in place to:

- 4.1 <u>meet or exceed the letter and spirit of all legal requirements</u> related to distribution of chemicals, chemical products, services and information;
- 4.2 <u>communicate with its own and contract employees</u> and ensure they are trained to understand and comply with all requirements of the law.

5. Participation - Selected Organizations, Government Bodies and Communities

Each member company should have a program to work actively with and assist selected organizations, government bodies and communities in establishing standards for continuously improving chemical distribution activities. Specifically, each member should:

- 5.2 <u>interact with community groups</u> to raise awareness of existing practices and <u>planned improvements in chemical distribution activities</u> which may not have been covered by the code of practice for CAER;
- 5.4 <u>influence the establishment of chemical distribution public policies</u>, standards and regulations that reflect changing environmental, community, governmental, industry and distribution activities, focusing on the preventative and the proactive, in consultation, if possible, with other affected stakeholders.

6. Requirements Pertaining to Distributors and Resellers

Each member company, if it uses third parties for distribution, shall have a program to educate, assist and assess the distributors of the member company's chemicals, chemical products and services. The program shall:

- 6.1 define a <u>distributor policy</u> which clearly establishes the minimum standards of this code as they apply to distributors;
- 6.2 exercise due diligence in:
 - establishing criteria for the selection of distributors based on their capability to meet the distribution code of practice and other applicable "Responsible Care®" codes;
 - 6.2.2 <u>assessing their performance</u> as appropriate against the criteria;
 - 6.2.3 taking any <u>follow-up actions</u> to cause the distributor to correct shortcomings including, if necessary, termination of supply;
- ensure that <u>distributors understand the expectations</u> of "Responsible Care[®]", its guiding principles and the codes of practice;
- 6.4 <u>respond to requests for information and assistance</u> from any point in the distribution chain concerning chemicals, chemical products and services supplied by the member company.

APPENDIX IV - CASE STUDIES

PRODUCTION SCENARIOS

Case Study 1

At 1:10 am on Monday, 6 May, liquid chlorine began leaking at an elbow on a 2" liquid line feeding production material to a 250 ton storage tank.

The leak was detected by the facility chlorine monitoring system and the alarm sounded. The plant was immediately shut down.

Subsequently, it was learned that the leak was a result of internal corrosion due to a chlorine/water mix flowing to the storage tank.

The employees closed the valve at the storage tank but due to internal corrosion, it did not hold. About 55 tons of chlorine escaped before the leak was sealed at around 7:00 am that morning.

The chlorine cloud did not fully dissipate until 10:30 am because of an atmospheric inversion which is not unusual for the area.

State and county officials report chlorine levels on site as high as 25 ppm; the highest level measured off-site was 17 ppm.

Some 250-300 people were treated at hospitals for chlorine exposure including 16 firefighters, four police officers and two plant workers. Some 30 people were kept overnight. Two exposed people had some residual effects; one was an employee and the other an 11 month baby.

Starting at 2:15 am, 10,000-15,000 people were evacuated, and were permitted to return after 10:30 am.

Nineteen area schools were closed on Monday, all routes into town were closed for nearly five hours; businesses were closed for six hours; and postal service was closed on Monday. Many trees and plants in the path of the chlorine cloud were affected.

- 1. What could have caused water introduction to the liquid chlorine piping?
- 2. What safeguards are in place or should be in place to prevent this?
- 3. Could it still happen?
- 4. What additional safeguards might be considered?
- 5. What equipment is available to seal a leak, or cap a broken or corroded pipe at your facility?

Case Study 2

On Thursday, 20 February, at Plant XX, No 2. chlorine storage module, a 50 mm chlorine vapour padding line was being stress relieved when the pipe failed due to an iron/chlorine fire. A half metre section of pipe was burned away.

The chlorine module was on line and there was a significant release of chlorine for a period judged to be in the region of three minutes. It was estimated that up to 350 kgs chlorine may have been released during the incident.

The approach road to the plant was closed off and the site main gate closed. With the wind from the northeast measured at 1 m/k, the gas cloud drifted towards the site main gate; there were no reports of significant amounts of chlorine from this area.

The gas detection officer measured 0.2 ppm chlorine on a housing estate which is situated to the southwest of the plant.

Questions

- Should this type of work be done on a line containing chlorine?
- What should have been done to prepare the line for this type of work?
- 3. Do the operating personnel in your facility fully understand the implications of heating chlorine-containing equipment and the risks of chlorine/iron fire?
- 4. What safeguards are in place at your plant/facility to prevent this type of incident?
- Could it still happen?
- 6. What additional safeguard might you recommend?

Case Study 3

On 15 November, 1982, a failure occurred in the east chlorine storage tank pump during a barge loading operation. The resulting damage was the complete disintegration of approximately one foot of the shaft and main support column of the two stage Lawrence chlorine loading pump directly beneath the mounting flange in the storage tank.

When the pump was removed, the inside surface of the mounting flange was covered with a layer of ferric chloride crystals, approximately 1 ½ " thick.

The ends of the shaft where the section was missing were reduced down to sharp "icicle" points. When the pump was disassembled, it was found that the shaft had "eroded" back to the bottom ring of packing. All packing rings appeared to be in good condition. No scoring of the shaft at the packing position was found. The bottom lip of the stuffing box was not damaged either.

- 1. What could have taken place to cause this damage?
- 2. There was no chlorine leak at the time of this incident could there have been?
- 3. How serious could this problem have been?
- 4. What safeguards are in place at your facility to prevent this type of problem?
- 5. What has been done in recent years or could be done to reduce the risk?

Case Study 4

In recent years, an explosion occurred at a chloralkali plant that caused serious damage to the chlorine liquefier units and blow gas absorber, as well as to the disposal tanks and pipe work.

There was a significant chlorine emission at the time but no one was injured and no one required treatment for chlorine inhalation either at the plant or off-site, due, to a great degree, to quick action by the operators and foremen in isolating the damaged equipment and the proper use of protective equipment.

The explosion was later determined to have been caused by elevated levels of hydrogen in the system.

Questions

- 1. What could have caused this condition that resulted in a powerful explosion?
- What safeguards are in place at your facility to prevent this condition?
- 3. Could it happen at your facility and are the chances very minute or is the risk significant?
- 4. Are there further things to be done to reduce or eliminate the risk?

DISTRIBUTION AND TRANSPORTATION SCENARIOS

Case Study 5

A Chlorine packaging facility operator is in the process of filling a ton container with liquid Chlorine.

Midway through the act of filling, the ton container ruptures so violently that it is thrown off the filling scale.

There is a significant loss of liquid and gaseous Chlorine.

Questions:

- How could such an incident be mitigated?
- Do Responsible Care initiatives and standards adequately cover such a situation?
- Could this incident happen again?
- What would you recommend to prevent it from happening again?

Case Study 6

A Chlorine packaging facility is in the process of off-loading a 90 ton tank car into cylinders and ton containers.

On the plant site, a full tank car has been disconnected from its delivering freight train, and left standing at the top of a 2-3% grade.

Eventually, gravity starts to pull the car down the hill. It rolls through the derail mechanism, hitting the connected car with such force that the Schedule 60 piping is sheered, and the car is driven 30-40 feet down the track.

There is significant loss of liquid and gaseous Chlorine.

Questions:

- How could such an incident be mitigated?
- Do Responsible Care initiatives and standards adequately cover such a situation?
- Could this incident happen again?
- What would you recommend to prevent it from happening again?

Case Study 7

A Chlorine packaging facility has a 90 ton tank car connected to a cylinder and ton container packaging operation. It is late in the afternoon, so the filling operation is not operational, the tank car valves have been closed, and the connecting lines are under vacuum. Approximately 70 tons of Chlorine remain in the car.

Outside of the plant site, school children are tampering with the rail spur switch-box, damage it, and it becomes locked in the "open" position.

A freight train moving down the main line at 30-40 miles per hour is unexpectedly routed onto the private siding. It passes through the derail hitting the connected tank car sheering all connections and driving it 200 feet and off the wheels.

Fortunately, no product is lost.

Questions:

- How could such an incident be mitigated?
- Do Responsible Care initiatives and standards adequately cover such a situation?
- Could this incident happen again?
- What would you recommend to prevent it from happening again?

Case Study 8

This pulp mill uses a sodium hydroxide scrubbing system to neutralize various vent streams containing chlorine. The facility is located in an urban area in North Western United States. In 1990, the following event occurred at the facility:

During a planned shutdown, maintenance work was performed on the scrubbing system. After the shutdown was completed, the scrubbing system was started up and placed into service. During the start up phase, the operators were notified that chlorine was being detected by other facility personnel downwind of the scrubber tower vent. The operators knew that only a small amount of chlorine gas was being vented into the scrubber from a chlorine unloading vent line.

Within minutes, the facility stopped the release. No off-site evacuation was necessary and no one was injured. Because of the facility's location, as part of its emergency response plan, it immediately notified a local radio station. It also notified the appropriate local, state and federal

agencies and emergency responders.

While the quantity of chlorine released was very minor (seven pounds), because of the media coverage, the Chief Executive Officer of this very large corporation was required to file an Accidental Release Prevention Questionnaire with the Environmental Protection Agency.

Questions

- 1. What are the possible causes of such an event?
- Is this a serious problem?
- 3. What safeguards can be put in place to prevent this event from happening?
- 4. If the company had not notified the radio, the event would have soon been forgotten. Should the company consider delaying any notification to the media or emergency responders?

Case Study 9

In October 1990, 48 pounds of chlorine was released from a chlorine user site in Southern United States. The release occurred in an unloading hose after a railcar had been unloaded and was being disconnected. No injuries occurred. In this facility, the unloading hoses have valves on the ends of them which must be closed before disconnecting the car allowing a mixture of chlorine gas and air in the hose to be released into the atmosphere.

The facility has a written procedure for this job. It was last reviewed with the involved employees 14 months prior to the incident. Prior to the incident the employee had worked in the unloading operations for the last three years, and had unloaded an average of 1-2 cars per week during this period.

Questions

- 1. The cause of the incident was operator error failure to follow established written procedures. Is this a serious problem or an isolated case?
- 2. Who is responsible for this event?
- 3. Should these prevention steps be applicable to just the unloading operation?

Case Study 10

A chlorine user facility has a carbon tetrachloride absorption system to remove and recover chlorine from various tail gas streams. Such a system serves as alternative to a sodium hydroxide scrubbing system and allows for recovery instead of destruction of the chlorine.

The system operates as follows:

Vent streams containing various amounts of chlorine are passed through a carbon tetrachloride absorbing column. The carbon tetrachloride, now containing chlorine, is fed to a stripping column where the chlorine is stripped off the top and recycled to the process. The chlorine free carbon tetrachloride is cooled and recycled to the absorbing column. The chlorine-free gas venting off the top of the absorber column is passed through a carbon adsorption column to remove carbon tetrachloride vapours prior to it being vented to the atmosphere.

A malfunctioning temperature control valve on the stripping column did not allow the chlorine rich carbon tetrachloride to be heated sufficiently to strip out the chlorine. As a result the recycled carbon tetrachloride was not chlorine free and could not absorb any more chlorine. The chlorine containing vent stream fed to the absorber column still contained chlorine when exiting at the top and entering the carbon adsorption column.

As a result an exothermic reaction/fire occurred in the carbon bed liberating chlorine, carbon tetrachloride and some phosgene. The phosgene was formed due to the high temperature in the carbon bed. It was determined that 101 pounds of chlorine, 70 pounds of carbon tetrachloride, and 10 pounds of phosgene were released. No injuries occurred.

Questions

- 1. What steps might be taken to prevent reoccurrences?
- 2. Most chlorine users do not have such a carbon tetrachloride system in their facilities. Does this situation have any application to these facilities? Explain.
- 3. How should chlorine users address process upsets causing problems due to chlorine's reactivity?

Case Study 11

On 11 September 1990, at approximately 4:00 pm, two city waterworks crew members were changing two chlorine "tonners" (bottles of liquified chlorine) in the chlorine room at the Lakeview water treatment plant. These empty tonners had been taken off line by the night shift on the previous evening and the two parallel tonners had been put on line in their place. Often when empty tonners are taken off line there is some residual chlorine that remains in the bottle (i.e. approx. 20 kg).

Since there was only a three man crew on the previous night shift, the standard safety procedure at the plant had been to simply take the empty tonners off line and let the next day shift complete the change-over.

When one of the crew double-checked to see if all of the valves had been completely turned off, he noticed that the valve at the very end of the flex hose on the feed line had been left open by 1/8 of a turn. He immediately closed this valve and then proceeded to open the yoke. When the worker cracked open the yoke to disconnect the hose, chlorine escaped into the room. Both workers immediately left via the exit to the outside on the north wall of the chlorine room.

Once the two men were outside, the chlorine alarm sounded. One of the crew acknowledged it immediately and then turned on the ventilation system. Since the leak was considered normal for a chlorine bottle change procedure, the two crew waited about 6 or 7 minutes, then reentered the room and walked over to the leaking tonner. Since neither could smell any chlorine, they recommenced the switching procedure. One crew member walked over to one corner of the room to retrieve a hoist control. When he bent down to pick it up, he inhaled some chlorine. The worker started to cough and gag, followed almost immediately by the second crew member, but both managed to escape the room. Both personnel did not report for work the next day.

<u>Questions</u>

- 1. What might have caused the above incident?
- 2. How could such an incident have been prevented from occurring?

- 3. What measures would be most effective?
- 4. Is it possible to mitigate such an event. e.g. alarms, ventilation?
- 5. What improvements would you recommend for this chlorine tonner replacement procedure?
- 6. What opportunities may exist here for additional training?
- 7. Should protective equipment such as masks be worn during such routine procedures?
- 8. Are there Responsible Care procedures or standards which could have been applied for this end use and were they?
- 9. Were the emergency response procedures adequate?
- 10. What are the chances of a similar event happening again?

Case Study 12

At 9:30 am on 10 September 1991, a worker at the Metropolitan water treatment plant informed the shift supervisor that he could smell chlorine outside at the north end of the maintenance shop. Subsequently, the supervisor and a second employee walked around the area and noticed a bit of a smell. The covers on two valve chambers were pulled but no odours were detected. It was then thought that an adjacent private environmental laboratory might have been mixing sodium hypochlorite but this proved to be unfounded. Pre-filter chlorine lines at the treatment plant were checked, along with the blanked chlorine lines to the high lift building, the chlorinator and eductor, but everything was found to be isolated. A check was made of the plant's chlorine and chlorine diozide chlorinators, eductors, feed rate and residuals but all systems were found to be normal. Two contractor workers located in an excavation on site were overcome with chlorine fumes, became ill and were taken home. Sanitary sewer lines beside the high lift building reportedly smelled like chlorine. Engineering staff then tried to trace sanitary drain lines inside the building and discovered a purge drain valve had been left open.

Questions:

- Could this incident have been prevented from happening? How?
- 2. Is it possible to mitigate such an event and what measures would be most effective?
- 3. What changes or improvements if any would you recommend to the purge system?
- 4. What about chlorine management in general at the site and the length of time it took to track down the problem? Can it be more effectively managed and what suggestions would you make?
- 5. Would additional training for plant personnel have made a difference?
- 6. Are there Responsible Care procedures or suggestions in the Generic Management Framework which could have been applied here and were they?
- 7. What are the chances of a similar event happening again?

Case Study 13

On 24 August 1989, approximately 0.35 tonnes of chlorine was released over a 25 minute period from the main wastewater treatment plant when a pressure relief valve failed. An evaporator was out of service and valved off. A jacket water heater was on to test an electrical repair made earlier in the day. The evaporator had been evacuated to zero pressure in accordance with shutdown procedures prior to the repair. According to later reports, a small amount of chlorine was trapped in the evaporator piping, which expanded to high pressure after the jacket water heater was turned on. The pressure relief valve failed and the inlet riser pipe burst at the side. Recoil of the burst caused the inlet pipe and valve assembly to snap off

at the supply manifold allowing the supply container to empty unchecked. The city Fire Department's hazardous materials unit subsequently entered the area and valved off the supply containers with the assistance of plant personnel. Five plant workers were affected by the release and taken to hospital, while 50 people in the vicinity downwind of the facility were evacuated as a precautionary measure.

Questions

- Could this incident have been prevented from occurring?
- Since this happened during a maintenance procedure, what improvements would you recommend?
- Could the system design or materials of construction be improved upon?
- 4. Should there be more frequent testing of pressure relief valves?
- 5. Can we say whether the emergency response procedures were adequate to deal with this incident?
- 6. What Responsible Care procedures or other standards could have been applied here and were they?
- 7. Could a similar event happen here again? Why?

Case Study 14

On 7 September 1986 at 12:35 pm, a train derailed twenty-four cars from a forty-six car train. Amongst the cars derailed were nine tank cars closely bunched together in a swampy area alongside the tracks, some half buried in mud with other cars on top.

Based on assessment of the scene following the arrival of the chlorine producers' emergency response team at 5:45 pm, the status of the tank cars was determined to be as follows:

A loaded chlorine tank car, A-86474, was partially buried in the mud and had a ¾" by 1" hole in the west end head plate, about one foot above the lower side of the car.

Lying next to A-86474 on each side were loaded chlorine tank cars U-27963 and 0-11121. Both cars were one half buried in mud and chlorine bubbled up through the mud beside them.

Two residue chlorine cars and a residue alcohol tank car were on top of a loaded chlorine tank car 0-11088 and liquid could be seen running down the side of 0-11088.

Local residents were evacuated including some business. A highway and local roads were shut down. Over the following 6 day period, almost the entire contents of the loaded chlorine car A-86474 was lost to the atmosphere. A small amount remaining in the car was eventually neutralized with sodium thiosulphate pumped into the car which initially intensifies the rate of flash. The car was finally secured at 2:00 pm on September 12th.

There were no leaks from the other chlorine cars. The chlorine bubbling up alongside the tank cars U-27963 and 0-11121 proved to be from liquid spilled from A-88474 in the initial hours of the crash and had sunk in the mud to flash off slowly over the next few days. On September 8, arrangements were made for evacuated chlorine cars to be sent to the scene, along with dilute caustic cars.

These cars arrived on the scene and preparations were made to transfer chlorine from 0-22088 to an evacuated car which was connected to vent to the dilute caustic car. Transfer commenced 5:00 pm on September 12 but had to be shut down at 2:00 am to cool the caustic. Transfer complete 3:00 pm on September 13. The rail line reopened shortly after.

Notes

The on-scene commander was the local fire chief. The state director of the wildlife protection agency was also present and part of the command post decision team. Major area and local news media were present. The chlorine producer and their emergency response team personnel were under a great deal of pressure and were heavily criticized during the incident and after because of their inability to stop the chlorine release and for the extended period that the rail line and highways were shut down and people kept from their homes.

Questions

- What could have caused this derailment?
- 2. What safeguards are in place to prevent train derailments?
- 3. What would you recommend to reduce the risk of train derailment?
- 4. Do you believe that tank cars are designed for the products in mind?
- 5. Why did the tank car release products?
- 6. What can be done to prevent tank car punctures?

Case Study 15

One Sunday evening in March, a Chief Rail Traffic Controller received a call from the conductor of train 342 advising him that his train had an emergency.

Members of the train crew proceeded to inspect the train. Their inspection revealed that 5 cars, positioned 44th to 48th behind the locomotives, had derailed, including tank car GATX 18174 on its side in a ditch. The car was not leaking.

From the placards displayed on the tank car and the documents available to the conductor, it was determined that GATX 18174 was a residue tank car which last contained chlorine.

Although railway practice is to handle all cars of dangerous goods as if they are loaded, no one at the accident site knew that the tank car still had a large amount of chlorine until they began loading it onto a flat car.

It was later determined that the tank car still had 18,200 lbs of chlorine. Usually, it is expected that a residue tank car which last contained dangerous goods does not contain more than 2 or 3% of product.

Questions

- 1. What if the car had leaked?
- 2. Is this a regular practice by chlorine end users?
- 3. Is this an acceptable practice?

Case Study 16

On a hot July afternoon, a train approaching a small community and travelling at approximately 30 MPH derailed 23 cars. 10 of the 23 derailed cars contained dangerous goods.

- 3 tank cars of chlorine withstood the impact of the derailment and suffered minor damage.
- 2 tanks cars of caustic soda and 3 tank cars of methanol leaked small quantities of product.
- 2 tank cars of acetic anhydride, both of which were severely damaged and spilled 68,000 litres of product into the surrounding field.

Approximately 1 hour after the accident occurred, over 400 residents of the small community were evacuated because of the high level of acetic anhydride vapours in the air. They were not allowed to return for six days.

Questions

- Does the fact that more than one dangerous goods were involved alter the approach taken at an accident?
- 2. Was the evacuation necessary?
- 3. Who then makes the decision to lift the evacuation order?
- 4. Why were people not allowed to return for six days?
- 5. Should all derailed tank cars be transhipped before being rerailed?

Case Study 17

At a major railway yard early on a December morning, a yardman detected an odour of chlorine in the vicinity of tank car ACFX 82508.

The Railway Emergency Response Plan was activated and the shipper notified. A shipper representative who was located nearby, came to the yard and found a minute leak of vapour at the base of a liquid valve.

Bolts securing the valve to the manway cover were tightened and the car released for its destination.

CROSS SECTORIAL SCENARIOS

Case Study 18

On 24 September, Chemtrec called out the Chlorep Emergency Response Team from Sector 22 to respond to a reported leaking chlorine tank car ACFX 85286 on the Illinois Central Gulf rail line near Jackson, Mississippi.

On 25 September, Chemtrec again called out a Chlorep Team to respond to a leaking chlorine tank car. This time the car ACFX 86244 was located on the CSX rail line near Milan, Tennessee. The Chlorep Team from Sector 13 responded to the incident. In both cases, there were serious chlorine leaks from the safety vent valve located in the tank car dome. In one case, a railroad employee was overcome by gas, 150 local residents were evacuated, streets and highways closed down and the other incident resulted in environmental damage and a fish kill.

Both cars had been loaded and shipped from the same plant.

- 1. What could have caused these incidents and could they have been even more serious?
- 2. What safeguards are in place to prevent this type of incident?
- 3. What could we recommend that would reduce the risk of this type of incident?

Case Study 19

The Chlorine Emergency Response Team from Section 1 was called out to assist with locating and sealing a chlorine leak from a cylinder in the back of a semi-trailer truck parked in the yard of a distributor warehouse near Vancouver, B.C.

The leak had been discovered by the truck driver when he opened the back door of the truck for unloading. The truck was full of chlorine cylinders on pallets that had been shipped by a package company nearby. The Chlorep Team arrived and using S.C.B.A. (the chlorine gas was very thick) and a hand operated hydraulic hoist, removed the pallets one by one and carefully checked each cylinder for leaks. About midway through the load they discovered a cylinder that was white with frost, about half way down.

The fusible plug had blown out and was emitting a steady stream of chlorine gas. The response team members installed a capping device, the leak was stopped and the cylinder removed from the truck.

The Team Leader contacted Transport Canada to request a permit to transport the cylinder via their Emergency Response Vehicle to the producing plant where the remainder of product in the cylinder could be safely evacuated.

A Transport Canada inspector responded to the scene, issued the permit and escorted the Emergency Response Vehicle to the producing plant with the cylinder.

The cylinder was evacuated at the plant and as requested, the Transport Canada official was called to inspect the empty cylinder. When the inspector arrived, the cylinder was disconnected and was found to contain about 1½ gallons of water.

Questions

- How might this have happened?
- How serious a problem is it?
- 3. What safeguards are normally in place to prevent this from happening?
- 4. What further safeguards could we recommend that may help to assure this does not happen?

Case study 20

On 21 November 1990, Industrial Scrap Corp. workers were shearing a one ton chlorine cylinder for scrap when an estimated ten pounds of chlorine gas escaped to the atmosphere.

The accident caused 31 workers from that company and a tank car manufacturing facility next door to be treated for gas inhalation and skin irritation.

- 1. How might this incident have happened and who should be responsible?
- 2. Is this a rare, freak accident or is it likely to happen again?
- 3. What safeguards are in place that should prevent this and what recommendations might we have that could reduce or eliminate the risk?

Case study 21

In February 1992, a CHEMTREC call was received from a fire department located in a city in Southern United States. It was reported that a 150 pound cylinder of chlorine abandoned in a yard was leaking. CHEMTREC immediately notified the CHLOREP team responsible for the area. The CHLOREP responder calls the fire department and talks to a supervisor. The supervisor advises that the abandoned cylinder is located in a area of fishing camps along the lake. He does not know any more about the severity of the leaks or whether anyone has been injured. His Fire Chief is en route to the scene.

When asked by the CHLOREP responder whether the department had any chlorine training, the supervisor said yes, but he would welcome any advice. What advice would you offer?

After the incident had ended, it was subsequently determined that there were three additional chlorine cylinders on the property site. They were traced to xxxx.

- Who is responsible for the abandoned cylinders? (Consider both legal responsibility and the responsibility in light of public opinion)
 Discussing this issue in terms of responsible care:
- 2. Is this a serious incident or an isolated case?
- 3. How can such a event be prevented?
- 4. Is it feasible to implement any of the prevention steps?

Appendix V Survey of Participants following the CLAP Workshop

Industry

- A participant from an operation located in downtown Fort Francis, where safe management of chemicals is necessary for the safety of the inhabitants, gave the following example of applying the knowledge gained in the workshop:
 - The company normally looks at all processes in process safety. Now, in addition, it is looking at the life-cycle of the chemical Cl₂, from the time it arrives in railcars until it leaves the premises, and beyond. The total approach will be applied to all chemicals and will include verifying the PINs, checking the maintenance program and equipment files. A management file for each chemical will be produced. By the end of 1993, the highest risk chemicals. Chlorine, hydrogen peroxide (H₂O₂) and sulphur dioxide (SO₂) will be managed. The company is applying the information to its Responsible Care initiatives.

Transportation

In transportation, approximately 35% of all Transportation Safety Board Reportable Rail Accidents involve cars carrying dangerous goods. In 1992, a total of 304 accidents involved dangerous goods, a decline of 13% from the 1991 total of 350. Main track collisions and derailments increased in 1992. Derailments, in particular, increased to 121 from 106 during the previous year. Track and equipment play a large role in such occurrences.

Operations

- 3. A municipality has:
 - Updated Operations and Emergency manuals;
 - Modified the loading/unloading procedures of Cl₂ in tonners (at E.L. Smith water treatment plant, operators will use SCBA or other Respiratory protective equipment to prevent exposures to residual Cl₂ in lines);
 - In mid-1993, the municipality will conduct Risk Assessment/Hazard Evaluation of Cl₂ handling at Parks/Recreations' swimming pools, to assist them in developing a producers' manual and to update their employee training.
- 4. A municipal staff participant wrote a summary of the workshop for an association bulletin, and stated he had gained an appreciation of the "cradle-to-grave" (life-cycle) management of chlorine.
- 5. Others have applied workshop material to:
 - Plant layout;
 - Cl₂ handling procedures;
 - Opening communications with fire department;
 - Operations and emergency manuals; and
 - Assisting the management of Cl₂ by identifying small volume users, and users
 of Cl₂ for swimming pools, and making contact with municipal users to advise
 them about safely managing Cl₂.

Training

- 6. Participants have applied workshop concepts to:
 - Training and Standing Operating Procedures.
 - A Municipal Operator Training Course.
 - Accident prevention and countermeasures in TIPS Manuals.

General

7. Participants indicated in the survey that they are applying the principles of the workshop to other chemicals besides Cl₂.

MIACC CHLORINE LIFE-CYCLE ACCIDENT PREVENTION November 16 - 17 1992 **DELEGATE LIST**

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