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Project Summary

Prevention Reference Manual: Chemical Specific, Volume 9: Control of Accidental Releases of Chlorine

D. S. Davis, G. B. DeWolf, J. D. Quass, and K. P. Wert

Recent headlines of accidental releases of toxic chemicals at Bhopal and Chernobyl have created the current public awareness of toxic release problems. As a result of other (perhaps less dramatic) incidents, in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Chlorine has an IDLH (immediately Dangerous to Life and Health) concentration of 25 ppm, which makes it a substantial acute toxic hazard.

Reducing the risk associated with an accidental release of chlorine involves identifying some of the potential causes of accidental releases that apply to the processes that use chlorine. In this manual examples of potential causes are identified, as are measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigration measures are provided.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research report that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The accidental release of a toxic chemical, methyl isocyanate, in Bhopal, India, in 1984 was a milestone in creating an increased public awareness of toxic release problems. There have been other less dramatic incidents of toxic chemical releases in the past, and the chemical industry was aware of this problem long before this event. Safety and loss prevention have long been standard parts of industrial activity, and over the years industry has made many advances in this area. There is renewed interest, however, in reviewing technology and procedures for preventing, protecting against, and mitigating accidental releases.

As an aid to regulators and industry personnel charged with reducing the probability and consequences of accidental toxic chemical releases, technical manuals have been prepared that address prevention, protection, and mitigation measures for releases. This chemical specific manual on chlorine is part of that series.

Chlorine is a major commodity chemical in industry. The major industrial uses of chlorine are: numerous organic and inorganic chemical syntheses, bleach manufacture, cooling tower water treatment, drinking water treatment, wastewater disinfection, and repackaging for resale.

Potential Causes of Releases

Potential chlorine releases may be either liquid or vapor. Liquid spills can occur when chlorine is released at or below its boiling point of -34°C (-29.3°F), or when a sudden release of chlorine at temperatures above -34°C results in vapor flashing. Direct releases of vapor gas can also occur.

Chlorine is frequently stored in 68 kg (150 lb) cylinders and 1 ton (907 kg) containers. These containers are equipped with fusible plugs as a form of pressure relief. Although fire is not the most frequent hazard, it may be the most serious, since fire can melt the fusible plug of a container at 70°C (158°F), allowing most of the chlorine in the container to escape. Defective fusible plugs have also failed to melt, allowing fire to rupture the container. Corrosion or poor bonding between the lead alloy plug and the plug retainer allows moisture to accumulate, causing corrosion at the connection, leading to the chlorine leak. One frequent cause of chlorine emissions is failure of the copper tubes commonly used to connect cylinders and containers to process equipment.

Process causes of a chlorine release include: (1) excessively high chlorine feed rate to a bleach reactor leading to excessive exothermic reaction, combined with failure of the cooling system; (2) backflow of chlorination water to a chlorine cylinder; (3) loss of agitation in batch reactor systems; (4) excess chlorine feed leading to overfilling or overpressuring equipment; (5) photo-lamp failure in photochemical reactor; and (6) overpressure of a chlorine storage vessel caused by overheating from reactions.

Equipment causes of accidental releases result from hardware failure such as excessive stress caused by improper construction or installation, mechanical fatigue and shock, thermal fatigue and shock in bleach reactors, brittle fracture (especially in carbon steel equipment), creep failure in equipment subjected to extreme operational upsets, and corrosion.

Operational causes of accidental chlorine releases involve incorrect operating or maintenance procedures, or operator error. Examples are overfilled storage tanks, errors in loading and unloading procedures, inadequate maintenance, and lack of inspection and nondestructive testing of vessels and piping to detect corrosion weakening.

Hazard Prevention and Control

The prevention of accidental releases relies on a combination of technological, administrative, and operational practices applied to the design, construction, and operation of facilities where chlorine is stored and used.

The most important process design considerations are aimed at preventing overheating and overpressuring systems containing chlorine. Temperature monitoring is important, not only because of potential overpressure or equipment weakening caused by overheating, but also because chlorine can react with many metals above a certain activation temperature. Chlorine can also cool itself while off-gasing and potentially reach temperatures below the safe operating range of some metals.

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Equipment construction materials must be chosen to prevent deterioration or product contamination. Steel, cast and wrought iron, copper and nickel alloys, some varieties of stainless steel, and lead are common construction materials in chlorine processes. On vessels, relief devices provide overpressure protection against catastrophic rupture or explosion by controlling the release of the overpressured contents. Vessels larger than cylinders or 1-ton containers are usually equipped with pressure relief valves and rupture disks. Even with these devices, however, a catastrophic sudden release could occur. Further protection can be gained if the relief device is routed to a caustic scrubber.

Overfilling can be prevented by using level sensing devices, pressure relief devices, and adequately trained personnel. Relief devices for chlorine overfilling may be the same as or similar to those used for gas pressure relief.

According to guidelines developed by the Chlorine Institute, chlorine tanks, usually constructed of normalized carbon steel, should be designed to accept a tank car dome assembly. In addition to vents, containers should have valves that can isolate the vessel from the process to which the chlorine is being fed. As a protection against corrosion, moisture must be excluded from the tank, and it should not be left in standing water or exposed to moist air.

Another concern is the backflow of material into a storage vessel. When chlorine is being mixed with a liquid, the liquid can be drawn back into the chlorine container. Such backflow can be prevented by a vacuum-breaking device, or a barometric leg, check valves, and positive-displacement pumps.

A chief concern in liquid chlorine pipe domes and valves is overpressure caused by thermal expansion of the chlorine, or pressure pulses caused by shutting valves rapidly. These pressures can rupture pipes. An expansion chamber, consisting of a rupture disk and a receiver chamber, can be installed to prevent thermal expansion ruptures. Pressure pulses can be avoided by selecting valves that do not shut abruptly. Ball and plug valves should be designed so that excess pressure in the body cavity will relieve spontaneously toward the high pressure side. Pipes and valves and process machinery such as pumps and compressors must be constructed of materials resistant to chlorine at operating temperatures and pressures.

Facilities and equipment should be sited to minimize personnel exposure in the event of a release. Large inventories of chlorine should be kept away from sources of fire or explosion hazard. If possible, chlorine piping should not be located next to other piping under high pressure or temperature. Storage facilities should be segregated from the main process and away from control rooms, offices, utilities, and laboratories.

Protection technologies for facilities that use or manufacture chlorine include enclosures and scrubbers. While enclosures for secondary containment of chlorine spills or releases do not seem to be widely used, they can be considered for areas near especially sensitive receptors. Enclosures capture and contain any chlorine spilled or vented from storage or process equipment, preventing immediate discharge of the chemical to the environment. If enclosures are used, they should be equipped with continuous monitoring equipment and alarms. For chlorine, concrete block or concrete sheet buildings or bunkers are most suitable.

Scrubbers, which absorb toxic gases from process streams, can be used to control chlorine releases from vents and pressure-relief discharges from storage equipment, process equipment, or secondary containment enclosures. Spray towers, packed bed scrubbers, and venturis are appropriate for chlorine discharges. An alkaline solution is needed to achieve effective absorption because absorpotion rates with water alone would require unreasonably high liquid-to-gas ratios. In an emergency, however, water scrubbing can be used in a makeshift scrubber if an alkaline solution is not available.

If chlorine is released in spite of all precautions, the consequences may be reduced by mitigation measures such as physical barriers, water sprays and fogs, and foams, where applicable. The purpose of a mitigation technique is to divert, limit, or disperse the chemical that has been spilled or released to the atmosphere. The choice of a mitigation technology for a particular chemical depends on that chemical's specific properties (flammability, toxicity, reactivity), as well as its dispersion characteristics in the atmosphere. Secondary containment systems, such as impounding basins and dikes, reduce the evaporation rate of a released liquefied gas, as do flotation devices and foams. However, even when measures such as these are employed after a chlorine release, a hazardous vapor cloud will probably form. The primary means of dispersing as well as removing chlorine from the air is with water sprays or fogs. The effectiveness of water sprays depends on wind direction, on the distance of the nozzles from the point of release, on the fog pattern, and on nozzle capacity, pressure, and rotation. If the right strategy is followed, a "capture zone" can be created downwind of the release into which the chlorine vapor will drift and be partially absorbed. In some cases, it may be possible to use fans and blowers to disperse a vapor cloud.

Operation and maintenance practices that can reduce the probability of a large chlorine release include training employees in proper handling and storage procedures. To prevent corrosion, chlorine should be analyzed for water several times a week, and pH readings of cooling water and condensate can be taken several times a day to detect internal leaks.

D. S. Davis, G. B. DeWolf, J. D. Quass, and K. P. Wert are with Radian Corporation, Austin, TX 78766.

T. ***Kelly Janes*** *is the EPA Project Officer (see below).*

The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 9. Control of Accidental Releases of Chlorine," (Order No. PB 87-228 664/AS; Cost: $18.95, subject to change) will be available only from:

National Technical Information Service
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Springfield, VA 22161
Telephone: 703-487-4650

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