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Project Summary

Prevention Reference Manual: Chemical Specific, Volume 2: Control of Accidental Releases of Chlorine (SCAQMD)

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The South Coast Air Quality Management District (SCAQMD) of southern California is developing a strategy for reducing the risk of a major accidental air release of toxic chemicals. The strategy, aimed at guiding industry and communities, includes monitoring activities associated with the storage, handling, and use of certain chemicals. Its purpose is to aid in identifying and controlling release hazards associated with certain toxic chemicals. This manual presents information on the uses and hazards of chlorine specific to the SCAQMD.

Chlorine is a highly reactive and corrosive liquid that boils at room temperature. It has an IDLH (immediately dangerous to life and health) concentration of 25 ppm, making it an acute toxic hazard. Examples of potential causes of accidental releases of chlorine are identified, and specific measures that can be taken to reduce the risk of such releases are listed. Such measures involve design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Conceptual cost estimates of these measures applied to some example systems are also 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 project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In 1985, the South Coast Air Quality Management District (SCAQMD) conducted a study to determine the presence, quantities, and uses of hazardous chemicals in the SCAQMD, which comprises Los Angeles, Orange, San Bernardino, and Riverside Counties. The study resulted in a report, "South Coast Air Basin Accidental Toxic Air Emissions Study," outlining an overall strategy for reducing the potential for a major toxic chemical release incident. The strategy includes monitoring industry activities associated with the storage, handling, and use of certain chemicals in the SCAQMD and obtaining technical information that will guide industry and communities in reducing the potential for accidental releases and the consequences of any releases that occur. This manual provides some technical information on the prevention of accidental releases of chlorine as it is used in the SCAQMD.

Chlorine is a major commodity chemical in industry. The major industrial uses of chlorine in the SCAQMD include chemical synthesis of chlorinated chemicals, and disinfection of drinking water and wastewater. Other uses include cooling tower water treatment, bleach manufacture, chemical synthesis, and repackaging. Though chlorine is not manufactured in the SCAQMD, its uses there require the storage of large quantities of the chemical.

In the SCAQMD, chlorine is stored in small cylinders, 1-ton cylinders, railroad tank cars, and bulk storage tanks.

Potential Causes of Releases

Potential chlorine releases may be in the form of 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 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 a 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 and leading to the chlorine leak. One frequent cause of chlorine emissions is failure of the copper tubes commonly used to connect cylinders and 1-ton containers to process equipment.

Possible process causes of a chlorine release include:

- Excessively high chlorine feed rate to a bleach reactor leading to excessive exothermic reaction, combined with failure of the cooling system;
- Backflow of chlorination water to a chlorine cylinder;
- Loss of agitation in batch reactor systems;
- Excess chlorine feed leading to overfilling or overpressuring equipment;
- Photo-lamp failure in photochemical reactor; and
- Overpressure of a chlorine storage vessel caused by overheating from reactions.

Equipment causes of accidental releases result from hardware failures 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 iron, wrought iron, copper alloys, 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 allowing a controlled 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 venting provisions, containers should have valve arrangements that allow the vessel to be isolated 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 situated 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, it is possible for the liquid to 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 rapid valve closure. These pressures can rupture pipes. An expansion chamber, consisting of a rupture disc and a receiver chamber, can be installed to prevent thermal expansion ruptures. Pressure pulses can be avoided by selecting valves that do not close 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, 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 absorption rates with water alone would require unreasonably high liquid-to-gas ratios. In an emergency, however, water scrubbing could be used in a makeshift scrubber if an alkaline solution were not available.

If a chlorine release occurs in spite of all precautions, the consequences of the release may be reduced by employing mitigation measures such as physical barriers, water sprays, 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 liquified 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 effectivensss 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.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific—Volume 2: Control of Accidental Releases of Chlorine (SCAQMD)," (Order No. PB 87-227 054/AS; Cost: $18.95, subject to change) will be available only from:

National Technical Information Service
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