6.8 Mitigation Systems

Introduction

Mitigation systems are used to reduce the overall impact of an accidental release. The methods listed below provide varying degrees of mitigation from complete mitigation to unquantified partial mitigation systems. Mitigation of phosgene is difficult because of its chemical properties.

In relative terms, phosgene is slow to hydrolyze when exposed to water whereas other halogen compounds tend to react very quickly with water. This characteristic represents a key understanding for emergency response and HAZMAT personnel's awareness.

Systems handling phosgene need to be properly designed, constructed and maintained. See Sections 6.1 – 6.7 for design guidance.

Another concern is that hazardous concentrations of phosgene may not be visible because the vapor tends to be transparent unless the concentration is very high. This issue depends on the atmospheric conditions at the time of the release.

Phosgene also tends to accumulate in low-lying areas. For instance, phosgene will often be found in drainage systems located in affected areas of a release.

The following methods have been used in large-scale applications. There may be other methods for the mitigation of phosgene. The information provided in this section should not be considered as a directive or as an industry standard. Instead, the information is intended to provide helpful ideas and guidance that users may wish to consider in a general sense (See Section 1.1 *Preface and Legal Notice*). Also included is a reference list of useful resources.

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6.8.1 Fugitive Collection Systems

6.8.1.1 Vacuum Systems

Generally, there are two different types of vacuum systems employed for handling of fugitive phosgene emissions.

6.8.1.1.1 Spot Ventilation Systems

A spot ventilation system typically consists of a circuit or header of “elephant trunk” drops connected to a large volume-blower, and discharges to a phosgene mitigation device. The flexible hose of an elephant trunk drop is positioned near the fugitive source, pulling the emission away to a mitigation device. This system of pipes and hoses is temporarily used for the following purposes:

- Capture, contain, and mitigate low levels of fugitive phosgene resulting from a minor loss of containment event (*e.g.,* a small valve-packing leak).

- Capture, contain, and mitigate low levels of fugitive phosgene which may result during the process of verifying equipment is clear prior to any maintenance breaking and entering activity.

The flexibility and ease with which the system can be used to capture and contain fugitive emissions also introduces potential risk. In the event an in-service elephant trunk drop is inadvertently removed or becomes disconnected, the potential exists to expose personnel in the vicinity.

As with all ventilation systems, design is crucial. Relevant considerations used in system design include the number of drops that will be in use at one time, and whether the design capacity can accommodate the maximum use.

Improper positioning of the flexible duct or lack of mechanical integrity of the duct hose can render the system ineffective. Consider the effect of positioning distance, on capture velocity and duct velocity and also include consideration of positioning of the duct relative to any work or line opening being done.

Care must be taken to limit liquid build-up especially at reduced temperatures in this vapor containment system. Evaluate use of a means for detecting and/or removing liquid in this system.

Liquid can seal off the vacuum source during use and actually lead to a more severe incident.

Potential risks can be reduced through frequent inspection of the flex duct and replacement as necessary.

Consider the potential for backflow in the ventilation system in the event of a loss of the vacuum source due to loss of power or shutdown while in use.

Avoid the use of fixed connections to spot ventilation.

6.8.1.1.2 Permanent Ventilation Systems

The second vacuum system is typically associated with clearing contaminated process equipment prior to any maintenance disassembly activities. This vacuum system has consisted of either temporary or permanent piping connected to process equipment, with a vacuum pump capable of pulling deeper vacuum. (See Sections 6.1– 6.7 for design guidance for mechanical systems) As part of the overall strategy for clearing and maintenance preparation, phosgene and other contaminants are vaporized under a deep vacuum, captured in the vacuum system and discharged to a phosgene mitigation device.

6.8.2 Phosgene Neutralization Systems

6.8.2.1. Caustic Scrubbers

Caustic (sodium hydroxide solution) scrubbers provide a method for mitigation of a phosgene release. Within the category of caustic scrubbers, there are several different types of scrubbing towers.

The basic caustic scrubbing system is comprised of a caustic source feeding a scrubbing tower. The tower is either an open-contact type tower or a packed tower.

Key operating parameters for operation of a caustic scrubber include: the maximum flow rate of phosgene expected from the process; the maximum duration of the release to the scrubber; the concentration of caustic available for scrubbing; and the circulation or flow rate of caustic into the scrubbing tower. Well-designed systems will consider the capacity of the system to neutralize the gases while having sufficient volume to absorb the heat of reaction. See Section 6.2.8.2 for Process Design Considerations to ensure adequate capacity of the caustic scrubbing system.

6.8.2.1.1 Caustic Spray Towers

In a spray tower, the caustic supply is sent to the tower at several locations from the bottom to near the top of the tower. Spray-rails are installed to control the spray pattern of the caustic into the tower. Phosgene would be introduced near the bottom of the tower and as the gas rises it is neutralized with the caustic spray.

A drawback to this type of scrubber is any change in the caustic spray pattern will affect the scrubbing efficiency of the scrubber. Phosgene would still have a chance to break through the scrubber untreated.

6.8.2.1.2 Packed Caustic Towers

The purpose of the phosgene scrubber unit operation is to treat acid gas from the phosgene containing section of the plant prior to discharging the resulting treated gas streams to the atmosphere. A scrubber unit operation often contains: a vent header, a disengagement vessel, the scrubber tower, caustic storage tanks, and the tower feed and return pumps. Caustic solution from the tower feed pumps flows to the top of the scrubber to a liquid distributor and over the top packed bed. Acid gas enters the scrubber below the lower packed section from a gas collection header. A disengagement vessel (knockout pot) on the vapor feed line to the tower helps ensure that no liquid phosgene is sent to the scrubbing system. Caustic is returned back to the feed tank supplying the scrubber tower with return pumps or by gravity. A heat exchanger on the caustic return line removes the heat generated from the neutralization of phosgene. Vents leaving the primary scrubber are normally free of phosgene and HCl and may be further treated to destroy any carbon dioxide or Volatile Organic Compounds in the exit gas stream with devices including flares, thermal oxidizers or other treatment units. Typical streams feeding the scrubber system may include: emergency process vents from relief devices or equipment de-pressuring, vents resulting from plant startup or shutdown, and vents resulting from clearing process equipment in preparation for maintenance.

Phosgene neutralization with caustic is a mass transfer limited operation and is a function of the rate of absorption of the phosgene into the caustic and the rate of chemical reaction to neutralize the phosgene. The height of a mass transfer unit (HTU) required can vary greatly depending on caustic strength and the maximum amount of phosgene to be absorbed.

6.8.2.1.2.i Caustic Scrubber Process Design Considerations: *The following items may assist during process design activities**:***

Worst-Case Design Scenario: Items including the following may be relevant in defining the design basis for the phosgene scrubber: the highest flow instantaneous vent feeding the scrubber, the highest instantaneous concentration of phosgene feeding the scrubber, the total amount of phosgene and HCl to be neutralized during the worst-case scenario, and total inventory of phosgene and HCl during normal plant operations. For the worse case design, inert loadings dramatically effect capacity and mass transfer calculations. Higher inert loading from the vent collection system or from off-gassing during the scrubbing reaction may reduce scrubbing efficiency to the point of phosgene or HCl breakthrough.

*Tower Scrubbing Performance**:*** Consider whether an adequate amount of tower packing height is available to adequately neutralize the worst-case design scenario feeding the system, and the maximum allowable permitted release of phosgene.

*Tower Liquid Loading***:** The tower diameter is determined primarily by the amount of liquid caustic loading on the packing. As phosgene concentration in the feed stream increases, the heat of reaction increases. Higher liquid loading serves to carry away the excess heat resulting from the phosgene reaction and prevent the tower packing from exceeding design limits.

Tower Temperature: Consider whether the caustic flow rate supplying the tower is maintained in a region that does not negatively impact the vapor-to- liquid mass transfer rate of phosgene. The reactions of phosgene and HCl with caustic are exothermic and can adversely impact the scrubbing effectiveness by raising the partial pressure of water and inhibiting contact of the acid gas with the caustic solution at the liquid film interface. In addition, caution may be needed to prevent the tower temperature from exceeding the mechanical limits of the materials of construction.

*Tower and Tank Caustic Concentrations***:** Evaluate the caustic concentration and inventory available to the primary tower with consideration to the highest instantaneous HCl/Phosgene concentration and vent rate. In addition, consider scenarios resulting in large total quantities of HCl / Phosgene vented when determining the available caustic inventory because the available caustic must be enough to completely carry-out the necessary scrubbing at the highest total HCl and Phosgene load. The concentration of the caustic leaving the tower is very important because it must be kept high enough so as to prevent phosgene break- through.

*Utility Failure Scenarios***:** Incorporating layers of protection can be used to guard against major utility failure scenarios (*e.g.,* electrical power, instrument air) and allow for continued operation of the phosgene scrubber system.

6.8.2.1.2.ii Caustic Scrubber Operational Considerations:

The phosgene scrubber system represents a critical element for process equipment consideration. When process equipment contains phosgene, evaluate whether the emergency vent scrubber system is in service and capable of neutralizing a phosgene vent stream. This evaluation may include the operating procedures for maintenance and 'out of service' time for spare equipment (pumps, blowers, and instrumentation).

Consider the emergency relief device on phosgene containing equipment and connection of the discharge outlets to the phosgene scrubber system. Consider if the capacity of the scrubber system is sufficient to address potential relief scenarios. (See Section 6.6 *Relief Devices*)

Operation of the production facility without the phosgene scrubber system running and being capable of neutralizing a phosgene vent stream raises risk concerns.

Frequent verification of the caustic concentration helps ensure adequate neutralization inventory (*e.g.,* some companies use once/shift samples and/or online analyzers) as does increasing the frequency of analysis during known process activities that consume caustic at a higher rate.

Upon reaching the defined minimum caustic concentration, taking the spent caustic tank off-line and replenishing it in an expeditious time frame can be a useful practice.

The practice of replenishing, “sweetening” or “juicing” the caustic tank to raise the caustic concentration, versus dumping the spent caustic and making a fresh batch, has the negative impact of accumulating carbonate salts and reducing the neutralization efficiency. In addition, the accumulation of carbonate salt species can reach saturation, precipitate and plug the tower packing, and associated piping, resulting in ineffective scrubbing performance. For example, greater than 20% initial caustic allows the possibility of solid salt precipitation as the caustic concentration is fully depleted.

6.8.2.1.3 Dispersion Stacks

A robust phosgene destruction system design, installation, and operating procedures represent the primary option of controlling phosgene emissions. (See Sections 6.1 – 6.7 for design and installation guidance) However, an elevated dispersion stack may be used to provide an additional layer of defense in the event of phosgene breakthrough from the primary phosgene destruction system. In the event the destruction system is unable to completely neutralize the phosgene, the exit gas can be dispersed at an elevated location with the intention of reducing the risk to personnel in the general vicinity. Dispersion modeling software can be employed to estimate any potential impact of a fugitive phosgene emission, taking into consideration environmental conditions, such as wind speed and direction. Materials capable of withstanding corrosion resulting from mixing phosgene with moisture in the air are available for dispersion stacks and related equipment.

In addition, an online phosgene analyzer can be used to help ensure appropriate regulatory limits are not exceeded. See Section 6.*6 Instruments* for further information.

References

Control and Mitigation Systems for Accidental Releases of Toxic Chemicals, US EPA, EPA Number EPA/600/D-88/099, 5/24/2004.