State-of-the-Art Techniques for Chlorine Supply Release Prevention

By

Peter S. Puglionesi
Sr. Section Manager
Roy F. Weston, Inc.

Richard A. Craig
Project Director
Roy F. Weston, Inc.

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For more information, please call:

Corporate Communications
Roy F. Weston, Inc.
Weston Way
West Chester, PA 19380
Phone: (215) 344-3509
Fax: (215) 430-3124
INTRODUCTION

Chlorine is one of the most widely used toxic gases worldwide. The acute hazards of chlorine have long been recognized and the means of safely handling chlorine have been detailed by numerous industry groups and associations. Efforts to reduce the risk of toxic gas releases have been redoubled in recent years as awareness has increased and risk management legislation and regulations have been enacted requiring all facilities using such materials to evaluate and reduce these risks. State programs, such as New Jersey's Toxic Catastrophe Prevention Act (TCPA) of 1986, will soon be followed by a nationwide program driven by OSHA requirements and the Clean Air Act reauthorization. The regulations expected to result will require comprehensive risk management programs at each facility handling extremely hazardous substances. These programs will encompass design, operations, maintenance, training and emergency preparedness. They will also establish requirements for performing process hazard analysis and safety reviews.

The state-of-the-art of hazardous material release prevention has evolved in recent years and new techniques are being more widely applied in the design of new facilities and in upgrading existing facilities. In some applications, this has resulted in extensive and expensive systems to contain and capture released gases. Equally important features and techniques are available to reduce potential release frequency and quantity, typically at lower cost. These latter measures may also be more easily applied at existing facilities.

This paper reviews the techniques historically utilized, and examines recently developed approaches, for prevention and minimization of chlorine release from chlorine storage and supply systems. Included are measures applicable to low pressure water chlorination feed systems, and high pressure chlorine vaporization systems. Alternative approaches are presented which minimize releases by flow limitation, chlorine vapor detection, automatic shutoff and liquid pool isolation.

Consideration of the safety issues involved in storing, handling, and using liquid chlorine must begin at the earliest stages of process design and continue through the operating life of the installation. This evaluation of safety aspects begins with selection of the site and the establishment of the design philosophy.

SITING AND DESIGN PHILOSOPHY

In the early stages of process design for a new facility, a Preliminary Hazard Analysis (PHA) can be useful in identifying major risk issues and in significantly reducing the ultimate risk.
Where the use of highly toxic materials are planned, chemical substitution or alternative processes should be considered. Substitution has been implemented recently most often for small water supply disinfection and cooling tower biocide applications where sodium hypochlorite solution has been substituted for chlorine cylinders and ton containers. While some risk management measures discussed in this paper are applicable to these smaller installations, this paper principally focuses upon larger installations.

Substitution may not be practical or cost effective for very large water chlorination systems or for chemical process industry reaction applications. In these cases, the PHA should screen for the degree of hazard based on the size of potential release scenarios. Two main factors limit the size (and effects) of potential releases:

1. Quantity in storage, and
2. Maximum utilization (or feed-forward) rate.

The largest quantity release scenarios occur in unloading and storage system failures. The probability of these kinds of releases can typically be lowered to acceptable levels using available state-of-the-art technology and management practices. It is typically more difficult to reduce the probability of chlorine release scenarios downstream, in quantities at or below the forward flow rate, due to leaks in longer runs of piping, flanges, vessels, etc. and reduced probability of early detection/response. Based on criteria developed by New Jersey under the TCPA regulations, if the rate of release for this type of scenario exceeds 2,500 lbs/hr of chlorine, the resulting ground level concentrations are more likely to cause serious injuries or deaths off-site. If the feed rate exceeds this quantity, the facility siting should be most carefully evaluated in order to minimize population exposure and maximize buffer zones.

The volume in storage should be minimized to the extent practical, given shipping container size, delivery time and rate of use. For intermediate rates of chlorine use, feed from multiple one-ton chlorine containers is an alternative to using a single rail car. This lowers the maximum worst-case release quantity; however, the cost is an increased probability of smaller releases due to the frequent changeout of containers which will be required.

Once the minimum requirements for chlorine storage and feed rate are established, the first objective of the system design should be to lower the maximum potential release quantities by:
• Minimizing the length of liquid chlorine lines to reduce the quantity of chlorine in pipelines. The chlorine vaporizer should be located as close as possible to the liquid chlorine source (1).

• Limiting the maximum feed-forward flow of chlorine as early as possible in the process.

The next objective of reducing the probability and size of a release can be achieved by:

• Operating at lower temperatures and pressures.

• Providing continuous leak detection and automatic shutoff valves (with appropriate expansion protection on every isolated line segment or device).

If the probability of significant release occurrences can be sufficiently reduced by these means, the necessity for containment and mitigation for major releases is thereby reduced. For high rates of chlorine unloading and use, however, consideration of containment and mitigation measures are often warranted. Such measures could include one or more of the following:

• Enclosures
• Vent controlled spill collection sumps.
• Ventilation and scrubbing.

Siting of the chlorine unloading and storage area within a facility requires balancing several priorities. Siting should consider:

• Rail cars must be at a dead end and guarded against damage from other rail cars and motor vehicles.

• The area must be accessible to operating and emergency personnel.

• The area should be located away from area residences and the facility boundary.

• The area should preferably be located downwind of most operations and support areas, based on prevailing wind patterns, to facilitate evacuation and corrective action.

• If the site has significant slopes, the area should not be uphill of operations and support areas because the dense chlorine gas will flow downhill.
The storage area should be isolated from incompatible materials, and sources of corrosion, fire and potential explosion (2).

ESTABLISHED STATE-OF-THE-ART DESIGN CRITERIA

The established state-of-the-art transport and storage design criteria are readily available in publications of the Chlorine Institute (1,3,4,5,6,7), AWWA (8,9), NFPA (2), and the Federal government (10,11,12,13). Applicable regulations have been published by U.S. DOT (14) and OSHA (15). All cylinders, ton containers, road tankers and rail cars used for transportation and storage of chlorine must meet DOT requirements. Other authoritative publications include White's Handbook of Chlorination (16) and publications of regional and professional associations (17,18,19). These references, particularly those of the Chlorine Institute, should be fully reviewed prior to design. Pertinent criteria for design and operation are summarized below.

Chlorine Rail Car Facilities

Rail cars are the most commonly used shipping containers for large and intermediate chlorine users. Road tankers can be used but are less common. Chlorine rail cars are designed and maintained by suppliers in conformance with U.S. DOT and Chlorine Institute requirements. These vessels are considered to be state-of-the-art and their design should not be altered. Given their design and intensive maintenance for transport accident release prevention, they are considered to be more reliable as storage vessels than most stationary storage systems. State-of-the-art unloading area design features include:

- Car should be positioned for unloading at the dead end of a dedicated rail siding.
- Storage or use areas should not contain combustible or incompatible materials.
- Storage areas should be isolated from hydrocarbons per NFPA No. 49 (2).
- According to DOT regulations, unloading operation should be continuously monitored "throughout the entire period of unloading." The Chlorine Institute cites a DOT interpretation of this requirement which allows for automatic monitoring and shutoff to be substituted for continuous attendance by an employee.
• Unloading area should have easy access for emergency response and should be well lit and ventilated (if indoors).

• Remote monitoring and isolation capability should be provided in case of disconnection or failure of the unloading system.

• Vapor release mitigation equipment should be provided commensurate with the results of hazard analysis.

• Padding gas should be supplied from a dedicated source and should not be taken from the plant air system to avoid pressure variability and potential chlorine backflow.

• Padding air pressures should be kept as low as possible.

• Padding air must be oil-free and dried to a dew point of \(-40^\circ\text{F}\) or below.

• A suitable operating platform should be provided for easy access to the rail car connections.

• It is desirable to purge lines to the process or to an adsorption device prior to disconnection of lines.

• All liquid chlorine pipelines which may be blocked (closed-in) by valves or other means must have appropriate protection against buildup of hydrostatic pressure due to temperature change.

• The quantity of gas vaporized from large liquid chlorine releases depends upon heat transfer from the ground. This can be minimized by engineering liquid containment which minimizes surface contact with the ground and air, such as curbs, dikes and collection sump.

Operational requirements include:

• Handbrakes and chocks should be set prior to unloading. The rail car and safety systems should be inspected before connecting to the transfer or distribution system.

• Derails should protect the open end and be located at least 50 feet from the rail car being protected.

• Caution signs should be placed at each derail.

• Car should be inspected at least daily for leaks.
Chlorine Vaporizing Equipment

Chlorine vaporizer design information is available in Chlorine Institute literature. Generally applicable design criteria include:

- Provide automatic gas line shut-off valve.
- Minimize the length of liquid lines to the vaporizer.
- Isolate the vaporizer from potential damage by vehicle, fire or explosion.
- Provide gas pressure-reducing valve downstream of the vaporizer in order to minimize condensation in the chlorine vapor line.
- Provide a pressure relief valve between the evaporator and any gas shut-off valve.
- Provide gas temperature and pressure gauges.
- Provide gas flow control valve.
- Provide heating system temperature measurement and interlocks to shut down liquid feed on low vaporizer temperature. If set properly, this will prevent liquid from entering the chlorine gas lines.
- Provide alarms at continuously manned control room to warn of improper conditions.

RECENT DEVELOPMENTS

According to G.C. White (16), the two most critical causes of chlorine accidents, ranked by frequency and magnitude of release, are fire and flexible connection failure. The largest releases will occur at the rail car storage and vaporizer areas. Excluding catastrophic transport accidents, the largest releases are of liquid at the pigtail connection (i.e., in the flexible connection). The excess flow valve internal to the rail car is typically designed to close when more than 15,000 lbs/hr of liquid chlorine is flowing. This may vary with the size of the rail car. It will not close if a partial liquid line failure results in release of less than that flow. This equipment is typically removed for inspection and maintenance each time a rail car is prepared for refilling. It is, therefore, an extremely reliable safeguard. Thus, 15,000 lb/hr is the maximum release scenario with a significant probability of occurrence for in-plant chlorine storage and use. The serious effects of such a release warrants focusing
prevention efforts on reducing the probability of this scenario.

Unloading To Stationary Storage Tanks

Most large quantity chlorine users will have permanent stationary storage tanks. Chlorine is transferred at a relatively high rate from rail cars or road tankers using dry compressed air from a dedicated compressor system. State-of-the-art features in one 1976 installation (20) included:

- Enclosed building for the transport vessels during unloading.
- Location of the storage tanks in a basement which is partially open to the atmosphere.
- Concrete secondary containment for the transport and storage tanks.
- Relief vessel to accommodate possible thermal expansion if tanks are overfilled and/or blocked in by valves.
- Load cells to determine rail car and storage tank levels with appropriate alarm points.
- Leak detectors in storage, vaporizer, and chlorine use areas with high (5 ppm) and high-high (15 ppm) air concentration set points. Control room, access road, and local audible and visible alarms.
- Emergency ventilation automatically turned on based on high chlorine area concentrations to aid in dissipating small releases and to facilitate corrective action. Ventilation would be turned off at high-high concentrations (indicative of a major release) in order to prevent spreading the release.
- Automatic closure valves installed on the storage tank liquid inlet and outlet lines. These were closed on high-high area chlorine concentrations but could be overridden remotely.
- Water sprays to "disperse" gas clouds and foam injection points to blanket liquid chlorine spills.
- Windsocks, portable radios, and personal protection equipment to aid in emergency response.
- Off-site siren activated only by the emergency coordinator to warn nearby residents.
This facility is depicted in Figure 1. It used hot water bath chlorine vaporizers to generate chlorine gas at 2.5 atmospheres for feed to water chlorination injectors.

The best location for automatic shutoff valves is not at the storage tank inlet, however. Since leakage in the unloading line is more likely, the shutoff valve should be placed directly on the rail car. This will provide positive protection against the most probable failure mode.

Discussions with chlorine manufacturers have indicated that building enclosures for the chlorine unloading and storage areas have been used in several instances by both manufacturers and large consumers. One serious potential flaw in such building enclosures is ignoring the potential for overpressure failure of the building in the event of a large liquid spill due to rapidly vaporizing chlorine. Another effect of a tight building enclosure is excessive triggering of sensitive chlorine detectors due to small valve stem leaks. Other design issues to be considered are materials of construction and layout as it effects access, scenarios for personnel exposure and escape.

One proposal for minimizing the boiloff rate of released liquid chlorine provides drainage to an enclosed insulated sump (see Figure 2). Released liquid chlorine is initially vaporized if its temperature is above the boiling point, as it is in many storage systems. The boiling point of chlorine is \(-34 \, ^\circ\text{C}\) at atmospheric pressure. The initial vaporization cools the remaining liquid to the boiling point. The subsequent release rate of gas is governed mainly by heat transfer from the surrounding environment, and mass transfer factors including:

- Degree of liquid spread.
- Heat transfer characteristics of soil or containment.
- Wind or air velocity.

The proposed sump would be insulated and isolated from the effects of wind, minimizing heat and mass transfer. A flapper valve would allow the liquid to enter, but then close, containing the boiling chlorine with the fumes drawn through a caustic scrubber (11). This would result in a reduction of the total release quantity. However, a high initial rate of vaporization and resulting pressure would still occur due to the volatility and heat capacity of the liquid chlorine and heat transfer from the base of the containment area.

Another proposal for a safer bulk storage system would minimize the initial chlorine release by refrigerating the chlorine to lower its vapor pressure to below atmospheric pressure (21). This scheme would also use insulated containment, enclosed
unloading area, chlorine monitors and an emergency scrubber system (see Figure 3). This would require a large capacity refrigeration system to cool the chlorine as it is unloaded and a smaller output to maintain the low temperature while in storage. Obtaining shipments of cold chlorine would reduce the refrigeration load somewhat. Receiving precooled shipments would also minimize the effects for one of the most frequent release causes, flexible connection failure during unloading. This proposed system appears to provide the best protection against the rapid release of chlorine gas to the environment once a leak has occurred. The incremental reduction in risk due to lower release quantity from this protection scheme must be weighed against cost and the effect of low temperature on the reliability of system components.

For many existing facilities, retrofitting with the above systems may be infeasible. The most readily retrofitted and most cost-effective modification to minimize unloading releases should be considered as a minimum: area chlorine monitors coupled with automatic shutoff valves located at the rail car.

Unloading Directly To A Vaporizer

Many users of intermediate quantities of chlorine unload directly from a rail car to a vaporizer. The rail car is, in effect, a very capable storage device. Many of the techniques applied to stationary storage devices could potentially apply to these systems, but the costs are high and the situation may allow for alternatives which are more cost effective.

Consider, for example, a case where chlorine is used at a rate of 300 lb/hr (108 tons/month). By utilizing a design philosophy which limits feed forward flow as early in the feed system as possible (i.e., directly on the rail car), the quantity of release for higher frequency failures (e.g., flexible hose leaks, pipeline leaks, etc.) is low enough to prevent serious off-site effects. The probability of high quantity releases is reduced to acceptable levels by the flow limiting devices and redundant safety shutoff devices. The proposed system would include:

- Automatic shutoff valve located directly at the rail car. This valve would automatically close on instrument signal failure (i.e., if the flexible feed and/or instrument lines are severed).

- Excess flow valve or constant flow orifice located directly at the rail car limiting flow to a fractional safety factor above the design requirement.

- Provide area Cl₂ monitors with high and high-high set points to alarm and to close the automatic shutoff valve.
Provide sufficient partial enclosure of the unloading and vaporizer areas to minimize the effects of wind dispersion on the performance of area monitors.

Provide a low pressure alarm and interlock on the liquid chlorine feed line to close the automatic shutoff valve.

Provide flow limitation on the air pad (if used) to act as a secondary limitation on the quantity which might be released if a leak occurs in the liquid Cl₂ lines.

Provide a scrubbing system for vapor releases and for purging liquid lines prior to disconnection for rail car changeover.

These measures, depicted in Figure 4, would provide for redundant protection against releases above 300 lb/hr and provide for detection and mitigation of releases under 300 lb/hr.

Additional measures are suggested at the vaporizer and downstream in order to further limit the potential for both larger and smaller releases:

- Limit the heat input capacity of the vaporizer to a fractional safety factor above the design requirement. For presized commercial package units, this may be accomplished by limiting the power input.

- Use as low a gas feed pressure as practicable by increasing chlorine gas line size. Lower chlorine gas line pressure has a secondary benefit of lowering the chlorine gas dew point and thus minimizing condensation. This reduces the potential for downstream malfunctions and releases which can result from slugs of liquid chlorine entering process equipment.

In addition, the established protective measures for unloading and vaporizer areas, discussed previously, would be used to minimize the quantities and probabilities of release.

OTHER ELEMENTS OF RISK MANAGEMENT

Other important considerations which are integral to the successful execution of the design are emergency preparedness and good management practices. The facility must have facilities and an emergency response plan which provides for:

- Personal protective equipment.
- Capping kits and other necessary tools.
Communications equipment and procedures.
Wind speed and direction monitoring.

Good management practices include providing for the equipment to be properly operated and maintained. This requires:

- Detailed standard operating, safety and emergency procedures.
- Training - both initial and refresher.
- Preventative maintenance, including removal, inspection, repair and replacement of critical components and associated recordkeeping.

These elements are detailed in the numerous references previously cited. In order to ensure that the facility operates as intended, periodic performance audits should be conducted. This would determine that:

- The design basis has not changed.
- Safety features in the design have not been compromised.
- Operating procedures are being followed.
- Experience gained with the operation is incorporated into design or operating procedure revisions.

CONCLUSIONS

Overall risk management for liquid chlorine handling and use requires considerable advanced planning and must incorporate design elements and operating procedures which take into account the level of hazards. Publications of many organizations such as the Chlorine Institute should be consulted in developing such a design to ensure conformance with appropriate consensus standards. These requirements, summarized here, provide a basis for designing a state-of-the-art system from a safety and accidental release prevention viewpoint. However, each design will, of necessity, consider individual site conditions and in so doing must account for the hazards of chlorine and incorporate adequate emergency response planning and other good management practices.
REFERENCES


FIGURE 2 COLLECTION SUMP WITH VAPOR CONTAINMENT

Source: Reference 11
Emergency Shutoff Based on:
- Area Cl₂ Detector High-High Concentration
- Low-Low Pressure in Liquid Cl₂ Line
- Low Temperature in Cl₂ Vaporizer
- Operator Response

FIGURE 4 PROPOSAL FOR REDUNDANT FLOW LIMITING AND AUTOMATIC SHUTOFF SYSTEM FOR LOW RATE CHLORINE UNLOADING