

Safety Bulletin

U.S. Chemical Safety and Hazard Investigation Board



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Emergency Shutdown Systems for Chlorine Transfer

Summary

The U.S. Chemical Safety and Hazard Investigation Board (CSB) issues this Safety Bulletin to emphasize the importance of installing, testing, and maintaining chlorine detection and emergency shutdown devices on chlorine railcar transfer systems.

This bulletin compares two chlorine releases investigated by the CSB. In both, a railcar unloading hose failed and chlorine was released. In the first incident, an emergency shutdown system malfunctioned, resulting in a release of 48,000 pounds of chlorine and a significant community impact. In the second, the emergency shutdown system worked to minimize the release, and the community was not impacted.



Figure 1. August 14, 2002, chlorine release at DPC Enterprises in Festus, Missouri

Uncontrolled Release Event

In 2002, the CSB investigated a chlorine release at DPC Enterprises (DPC) in Festus, Missouri, that resulted when a chlorine railcar transfer hose ruptured. The CSB determined that although the supplier's manufacturing records and identification tag indicated that the metal braid on the failed hose was made of Hastelloy C, as specified by DPC, it was actually made of stainless steel. Neither the manufacturer nor DPC confirmed that the hose was constructed of the proper material before it was put into chlorine service. Chlorine rapidly degraded the braid and the hose ruptured¹ (CSB, 2003).

¹ The braided metal hose was Teflon-lined.

DPC had an emergency shutdown system to stop chlorine releases from the railcar, which included remotely activated emergency shutdown valves installed at each end of the chlorine transfer hose. These valves were supposed to close automatically when detectors identified chlorine in the area or if operators pushed an emergency shutdown button. However, on the day of the incident, even though the chlorine detectors detected the release and the operators pushed the shutdown button, the valves remained open.^{2, 3} Furthermore, the excess flow valve (internal to the railcar) did not close.

Consequently, 48,000 pounds of chlorine was released into the neighboring community, resulting in hundreds of residents being evacuated or sheltered-in-place. Sixty-three local residents sought medical evaluation; three were admitted to the hospital. The chlorine caused tree leaves and vegetation around the facility to turn brown.

The CSB recommended that DPC develop a quality assurance system for chlorine hoses, and implement procedures and practices to ensure that the emergency shutdown system operates reliably. The CSB also recommended that the hose fabricator implement a materials' verification procedure to improve quality and ensure that hastelloy chlorine hoses are readily identifiable.

Controlled Release Event

On August 11, 2005, a chlorine transfer hose ruptured at Honeywell International's (Honeywell) Baton Rouge chemical plant.⁴

² The CSB determined that the valves were not adequately maintained or tested by DPC to ensure they would operate when needed.

³ Employees pressed the remote emergency shutdown button to close the isolation valves every day during the transfer system shutdown. However, DPC did not require employees to verify that the valves actually closed.

⁴ Microscopic examination of the hose revealed that corrosion of the wire hose braid at the failure site had reduced the diameter and pitted the failed wires. The CSB investigated the operating and environmental conditions the hose was subject to prior to the failure, but did not identify a likely cause of the corrosion.

Chlorine began to escape from the railcar. A newly installed chlorine detector alerted control room operators of the release; a shift supervisor who was outside saw the escaping chlorine and sounded the evacuation alarm. A control room operator stopped the release by remotely closing the emergency shutdown valves on the chlorine transfer hose. The release lasted less than one minute.

Although contractors working in the area heard the alarm and evacuated, some inhaled chlorine and were taken to the hospital where they were treated and released. All returned to work the next day. Immediately after the release, Honeywell tested for chlorine at the facility property line and found none.

In contrast to the 2002 incident at DPC, the rapid and successful activation of the emergency shutdown system at Honeywell prevented a major release and off-site impact.

The August 2005 incident at Honeywell demonstrated that properly maintained chlorine detection and emergency shutdown systems are critical for protecting workers, adjacent communities, and the environment.



Figure 2. Honeywell ruptured chlorine transfer hose

Since 1994, the CSB and the Chlorine Institute have recorded at least five hose failures that resulted in chlorine releases. Additionally, one hose manufacturer reported that 6 of 2,781

chlorine hoses had been returned for failure analysis between January 2000 and September 2006. This data indicates that chlorine hoses are susceptible to failure, and that emergency shutdown systems are needed to prevent human exposure to chlorine that is released during a hose failure.

Chlorine Background

Chlorine Properties

Molecular Formula – Cl₂
Boiling Point – 29.2 °F
Vapor Pressure – 53.5 psi at 32 °F

Chlorine is highly toxic and corrosive. It irritates the mucous membranes of the nose, throat, and lungs, and exposure to relatively low concentrations can be fatal. The National Institute for Occupational Safety and Health (NIOSH) and OSHA have determined that 10 ppm is immediately dangerous to life and health (IDLH). Table 1 summarizes the health effects of acute chlorine inhalation.

Chlorine is used for water and wastewater disinfection, and to manufacture products such as household bleach, pesticides, medicines, plastic

Table 1: Health effects of short term chlorine inhalation

Concentration (parts per million)	Health Effects
1-3	Mild mucous membrane irritation, tolerable up to one hour
5-15	Moderate irritation of upper respiratory tract
30	Immediate chest pain, vomiting, dyspnea, and coughing
40-60	Toxic pneumonitis and pulmonary edema
430	Death within 30 minutes
1,000	Death within a few minutes

Source: Ellenhorn and Barceloux, 1988.

pipework, silicon chips, and automotive parts. Facilities that use chlorine are located throughout the country, sometimes close to residential communities. Many of these facilities receive chlorine in railcars; according to the Surface Transportation Board Carload Waybill Sample almost 3 million tons of chlorine was shipped by railcar in 2005 in the United States (Surface Transportation Board, 2005).

Chlorine Railcar Unloading Systems

The most basic chlorine railcar unloading system consists of hoses and manual valves. Pressurized nitrogen or dry air is fed to the railcar through one hose to force liquid chlorine through a second hose. The railcars themselves are equipped with an internal excess flow valve (EFV) designed to close if the rate of chlorine flow becomes excessive (7,000 to 32,000 pounds per hour depending on the design parameters for the specific application). For instance, excessive flow might occur if the manual valve breaks off during an accident in transit.^{5, 6}

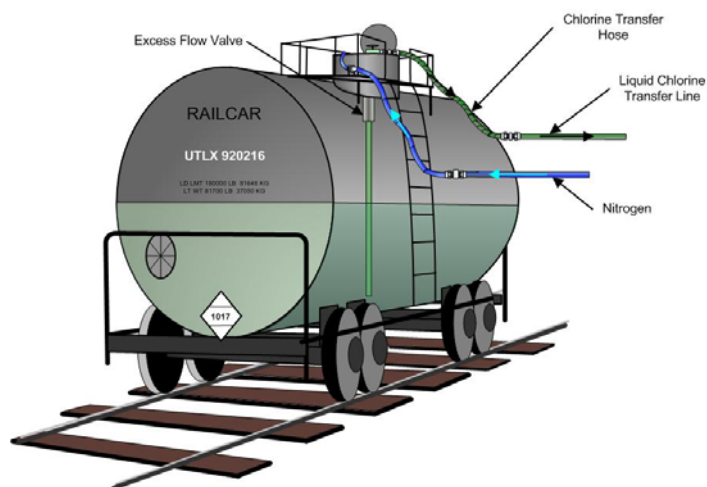


Figure 3. Basic unloading system

⁵ DOT Hazardous Materials Regulations (49 CFR 173.314 (k)) require that chlorine railcars be equipped with excess flow valves (HMR, 2006).

⁶ The Chlorine Institute Pamphlet 66, "Recommended Practices for Handling Chlorine Tank Cars," contains recommendations for excess flow valve design.

With this basic system, the EFV is the only physical safeguard to prevent a large chlorine release into the atmosphere if an unloading hose ruptures. However, the design of EFVs requires a compromise: they must be designed to allow a reasonable flow such as what may occur during routine unloading, but close if the flow becomes very large. Hence, an EFV is unlikely to stop a small to moderate leak from a ruptured hose. The Federal Railroad Administration (FRA) warns that when unloading equipment is attached to a railcar, product flow “will not be sufficient to activate the EFV” (FRA, 2003).

Numerous incidents have demonstrated that EFVs should not be relied upon solely to stop a hazardous material release during unloading.⁷ As an example, the National Transportation Safety Board (NTSB) investigated a July 2001 methyl mercaptan release from a railcar at ATOFINA Chemicals, Inc. (ATOFINA), and found that reliance on the excess flow valve to stop a leak contributed to the size of the release. The release started when “a pipe attached to a fitting on the unloading line of a railroad tank car fractured and separated” (NTSB, 2002). The methyl mercaptan, which is both toxic and flammable, ignited, causing a large fire. Three ATOFINA employees were killed, and several other employees and local residents were injured.

In response to an NTSB recommendation, the U.S. Environmental Protection Agency (EPA) issued a Chemical Safety Hazard Alert titled “Failures of Excess Flow Valves in Hazardous Materials Service” (EPA, 2004). The Hazard Alert describes four significant incidents where excess flow valves failed to stop hazardous material releases. The Hazard Alert noted that the National Propane Gas Association, Chlorine Institute, National Fire Protection Agency, and Compressed Gas Association either “recommend or require” that additional protections be used to supplement EFVs (EPA, 2004).

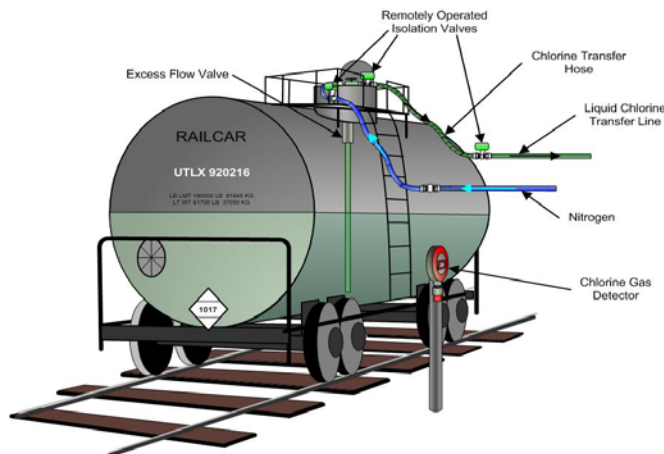


Figure 4. Chlorine railcar unloading system with an emergency shutdown system

Despite these warnings, the CSB investigators found that approximately 30 percent of the bulk chlorine users contacted during this investigation continue to rely only on excess flow valves to stop chlorine flow in the event of a transfer hose rupture.⁸

At a minimum, chlorine railcar unloading systems (Figure 4) should include the following components:

- Automatic shutdown valves, which are capable of isolating the unloading system within 8-10 seconds, located on the nitrogen or dry air hose-to-railcar connection, and at both ends of the chlorine transfer hose.
- Emergency shutoff switches, to activate the shutdown valves, installed in at least two easily accessible remote locations.
- Leak detection equipment that either automatically activates the shutdown valves or alerts personnel to manually activate them. This equipment may include atmospheric monitoring systems, video monitoring, loading line pressure monitoring, or railcar derailer position sensors.

⁷ Excess flow valves will not close if the flow rate through them is less than the design rate, or if some foreign material prevents the ball from seating.

⁸ The CSB investigators contacted approximately 30 bulk chlorine users.

Furthermore, these systems should be designed to be highly reliable⁹ to ensure that they will function when required. The emergency shutdown system should be regularly tested and maintained.¹⁰ Chlorine transfer and emergency shutdown procedures should be in writing and employees should be trained on them.

OSHA and EPA Regulations

The OSHA Process Safety Management (PSM) standard (29 CFR 1910.119) and the EPA Risk Management Program (40 CFR 68) require that facilities handling significant amounts of chlorine (more than 1,500 pounds for PSM and more than 2,500 pounds for the Risk Management Program) implement comprehensive management systems to prevent or minimize the consequences of a release (OSHA, 2006),(EPA, 2006).

These regulations require:

- “[T]hat equipment complies with recognized and generally accepted good engineering practices” [29 CFR 1910.119(d)(3)(ii); 40 CFR 68.65 (d)(2)];
- A comprehensive process hazards analysis that addresses “[e]ngineering and administrative controls applicable to the hazards...” [§ 1910.119(e)(3)(ii); §68.67(c)(7)]; and that
- Equipment “inspections and tests shall be performed...” [§ 1910.119(j)(4)(i); §68.73(d)(1)].

Because these are performance-based regulations, neither have specific requirements for chlorine railcar unloading systems.

DOT Regulations

The Department of Transportation (DOT) Hazardous Materials Regulations (HMR; 49 CFR 171 through 180) govern transportation of hazardous materials by rail, aircraft, vessel, and motor vehicle tank truck (DOT, 2006). The HMR requires emergency shutdown equipment for motor vehicle tank truck chlorine transfer systems but not for railcar chlorine transfer systems.

On October 30, 2003, the DOT issued a final rule clarifying the scope of the HMR, which defines transportation as “the movement of property and loading, unloading, or storage incidental to the movement.” The final rule explained that transportation, and therefore DOT regulatory authority, ends when the consignee takes possession of the material (DOT, 2003).

When hazardous materials are delivered to a facility by tank truck, the carrier usually unloads the material for the consignee, who then takes possession after unloading. When hazardous materials are delivered by railcar, the consignee commonly takes possession when the railcar is placed onsite; the material is later unloaded by the consignee. As a result of this distinction, the HMR covers tank truck unloading but not railcar unloading.

The NTSB identified this as a regulatory gap in its investigation of the 2002 ATOFINA incident and recommended that the DOT develop safety requirements that include “emergency shutdown measures” for railcar unloading (NTSB, 2002).¹¹ However, the DOT did not implement the recommendation; the NTSB classified the DOT response “Open-Unacceptable Response,” and asked the DOT to reconsider.¹²

⁹ For more information about safety integrity levels for critical components, see International Electrotechnical Commission (IEC), 2004. 61511, “Functional Safety Instrumented Systems for the Process Industry Sector.”

¹⁰ For detailed information, see The Chlorine Institute, Inc., 2003. “Emergency Shut-off System for Bulk Transfer of Chlorine,” Pamphlet 57, 4th ed., October 2003.

¹¹ During the 2001 ATOFINA investigation, the NTSB interviewed nine companies that handled hazardous materials and found that six relied solely on excess flow valves to stop leaks (NTSB, 2002).

¹² As of the writing of this bulletin, the NTSB recommendation to DOT remains classified as “Open-Unacceptable Response.”

The Chlorine Institute Recommendations

The Chlorine Institute, Inc. is a trade association that represents companies that manufacture, distribute, and use chlorine. The Chlorine Institute members produce 98 percent of chlorine manufactured in the United States and Canada (Chlorine Institute, 2007). The Chlorine Institute develops and publishes technical and safety pamphlets with recommendations for handling and distributing chlorine, which include requirements for railcar unloading. Its members agree to adhere to these recommendations and to a signed safety and security commitment.

The Chlorine Institute requires its members to also ensure that their customers:

- Are adhering to The Chlorine Institute safety recommendations,
- Have a risk management program in place, and
- Are in compliance with the “Chlorine Customers Generic Safety and Security Checklist” in The Chlorine Institute Pamphlet 85, “Recommendations for Prevention of Personal Injuries for Chlorine Production and Use Facilities” (Chlorine Institute, 2005).¹³

Pamphlet 85 specifically requires “a remotely operated or automatically actuated emergency shutoff valve system in place which can safely isolate both ends of transfer hoses/flexible piping.”

Lessons Learned

- Excess flow valves should not be relied upon as the sole means to stop chlorine releases during railcar unloading.
- Effective emergency shutdown systems are critical in preventing major chlorine releases.
 - Emergency shutdown systems should be designed in accordance with industry best practices, such as those published by The Chlorine Institute.
 - Procedures for using emergency shutdown systems should be in writing, and personnel should be trained on their use.
 - Emergency shutdown systems should be maintained and tested periodically to verify their operability.

¹³ Bulk chlorine customers (those that receive chlorine by railcars, barges, or tank trucks) must comply by December 31, 2007. Packaged chlorine customers (those who receive chlorine in 2,000 pound containers or cylinders) must comply by December 31, 2008.

Recommendations

US Department of Transportation

2005-06-I-LA-R1

Expand the scope of DOT regulatory coverage to include chlorine railcar unloading operations. Ensure the regulations specifically require remotely operated emergency isolation devices that will quickly isolate a leak in any of the flexible hoses (or piping components) used to unload a chlorine railcar. The shutdown system must be capable of stopping a chlorine release from both the railcar and the facility chlorine receiving equipment. Require the emergency isolation system be periodically maintained and operationally tested to ensure it will function in the event of an unloading system chlorine leak.

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