

Chlorine Leakage from Control Valve in Charging Station Pipeline: A Case Study

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Abstract

This paper describes accidental release of chlorine gas from control valve through a chlorine charging system in a green color pigment manufacturing chemical industry. The chlorine gas dispersed over the entire reactor floor and nearby area at night time shift work. This paper presents root cause analysis of the incident. Corrective and preventive measures are also discussed. Finally, conclusions reached with recommendations are drawn for industrial facilities for handling and prevention of chlorine.

Keywords: Chlorine, control valve, leakage

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INTRODUCTION

Human exposure to chlorine results in large number of deaths and injuries. Inhalation is the primary mode of exposure; direct skin contact with gaseous and liquid chlorine may result in chemical burn as the chlorine reacts with moisture on the skin [1].

Chlorine is a toxic, corrosive gas; it is greenish-yellow non-flammable liquefied compressed gas packed in cylinders under its own pressure. It forms fumes on contact with moisture in the air. It is also an oxidizer and will support combustion. Products of combustion gases are generally toxic in nature. Chlorine is extremely irritating to muscles, membrane, eyes and respiratory tract. In extreme cases, lung tissues may be attacked resulting in pulmonary edema. Prolonged exposure or high concentrations is fatal. The threshold values are as follows:

Odor threshold : 0.31 ppm

OSHA : PLE = 1 ppm

ACGIH : TWA/TLV = 0.5 ppm

NIOSH : IDLH = 10 ppm

Chlorine is widely used in making a large number of every day products. Here, it is used for color pigment manufacturing. The potential for leak and spills of chlorine is present with its use [2]. MHIDAS database indicated that 96 accidents of chlorine release

to atmosphere occurred in the period 1964–1996. These resulted in 39 deaths and over 2700 injured. Contribution to human error cause was 26% of incidents resulting in chlorine release.

The pigment manufacturing plant is situated in Raighad district (Maharashtra). Around 40 ton of chlorine is used per month for pigmentation. Pigmentation is done in three 4 kL glass line reactors. Per batch of production, around 2 ton of chlorine is used till the required drop test is observed. All the flow is controlled and measured through SCADA system. Liquid chlorine cylinders/tonners are made of mild steel sheet 21 mm thick with an overall length of 12548 mm and inside diameter of 2743 mm. On top, there is a manhole cover on which six valves are fitted with necessary pipe connections. Out of the six valves provided in each storage tank, two are for outlet liquid chlorine one for inlet of chlorine, one for safety valve and one each for equalizer and air pressurization. There is one safety relief valve and one rupture disc. One temp gauge and one pressure gauge are fitted on each tank. Three liquid chlorine cylinders are attached to the chlorine pipe line. The liquid is passed through a strainer to the vaporizer tank where controlled steam supply is provided at 100 °C. The vaporized chlorine gas then flows to cushion tank of 5 m³ and from then on to chlorine reactor at the plant.

INCIDENT DETAILS

Plant : B/G production
 Location : "12" meter Bx. making area
 Date : 10/10/2013
 Time : 15:45 h

Activity

Product 2707 W # 270 – Chlorination of batch was in progress, at around 15:45 h. Batch operator observed that chlorine addition had stopped due to high pressure developed in chlorine charging system and chlorine gas nuisance was noticed on the reactor shop floor, i.e., third floor of the building.

Incident Narration

At around 15:30 h, chlorination process was in progress. After addition of 2300 kg chlorine in the process, drop test is essential to check final product quality. To take sample for this drop test, the operator closed the control valve (before Rotameter) manually. This drop test activity takes 10 min approx. In such cases, the pressure of chlorine addition system is maintained by PCV 22404 (as shown in Figure 1). Setting of PCV 22404 is between 0.4 and 0.6 kg/cm². At 15:45 h, the operator closed the valve for drop test. During drop test, pressure developed in the system was around 6 kg/cm². After drop test, as operator opened the valve,

due to rise in pressure, the float in rotameter got stuck to the outlet of rotameter which stopped the chlorine addition in K22105. Pressure rose to 6–10 kg/cm² due to which chlorine leakage was observed through flange joint of the pipeline near chlorine vessel. The operator immediately raised the siran and rushed to SCADA room control cabin and shutoff the valve manually [3].

Nature and Extent of Damage

Inside the factory third floor (12 m) at chlorine reactor:

Casualties : Nil

: Minor injuries to 8 people by inhalation of chlorine gas. Admitted to hospital; after about 72 h, all were discharged from the hospital. None of the admitted cases was of a serious nature. No person died.

Probable Causes of Failure

Control Valve (PCV 22404) Failure

PCV 22404 set at 0.4 to 0.6 kg/cm², which regulates the pressure of chlorine during drop test, failed and could not maintain the pressure between 0.4 and 0.6 kg/cm². The control valve was badly corroded and selected MOC of the control valve was not suitable.

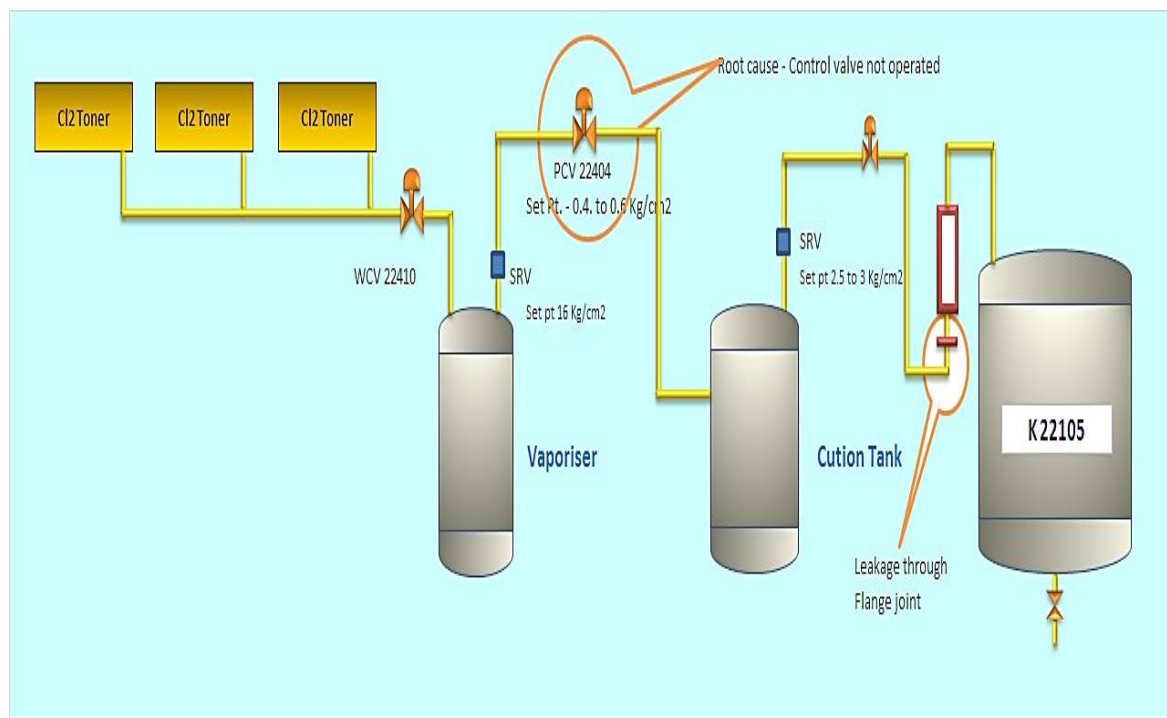


Fig. 1: General Setup.

Root Cause and Analysis

1. Valve actuator got stuck and it remained in open condition due to which chlorine pressure could not be controlled.
2. Valve actuator wheel had some play and there was no lubrication of actuator so that it got stuck.
3. Preventive maintenance of control valve was not followed as per PM schedule.
4. Material of construction of the valve was not of suitable standard.

Safety Relief Valve Failure

In case of rise in chlorine pressure, provision of safety relief valve is available; released Cl₂ line is connected to scrubber. Safety relief valve is set at 2 to 2.5 kg/cm² pressure but it is not operated during rise in pressure up to 6 kg/cm². As preventive maintenance of SRV is not followed as per PM schedule, calibration of safety relief valve was not done.

Alarms system is available in SCADA system. In case of rise in pressure of Cl₂, alarm or indications are displayed on SCADA screen. After that, the operator will close liquid Cl₂ charging control valve from SCADA. Alarms are generated during rise in pressure (as per history stored in PC) but operator did not close the control valve of liquid chlorine due to lack of awareness. The man engaged in the process had no knowledge regarding the hazards of chlorine.

Preventive Actions

Engineering Control

1. Prepare schedule for preventive maintenance of chlorine system on monthly basis (including control valve).
2. Proper selection of MOC for control valve with teflon coating inside the valve.
3. Provide secondary control in case of control valve failure.
4. Hazop and LOPA for the entire system will be revisited along with the team consisting of PE, Maintenance, Manufacturing, and Safety.
5. Alarm annunciator to be installed in SCADA room for extra alertness.
6. Provision of mechanical PRV and collection pot to be installed (these provisions are available in new Cl₂ charging system).

7. Maintain spare control valve for cushion tank to reduce MTTR.
8. Whole chlorine system to be checked by a competent person.
9. Calibration of safety relief valve on regular interval by competent authority.
10. Provide separate emergency scrubber system to take care of the worst case scenario for chlorine tonner area.
11. Provision of pressurized system for DCS room.
12. Fusible plug safety device on container should be tempered.

Administrative Control

1. People to be trained for usage of SCADA.
2. Mock drill to be conducted once bi-monthly.
3. Provision of CCTV monitoring of chlorine tonner area and batch making area.
4. Third party audit of chlorine system by competent person after every six months.
5. Once cylinder is connected to the process, it is to be opened slowly and carefully.
6. Establish an emergency response plan for responding to leaks and spills of chlorine at the work site.

Other Observations

1. Provision of emergency exit is not available at DCS room.
2. Escape plans from areas where there might be a chlorine emission not observed.

Emergency Response

Leak in System/Piping

- Piping arrangement should be as simple as possible (i.e., minimum elbows and bends).
- Piping should have suitable thermal expansion allowance for pipes.
- Piping system should be well supported, adequately sloped to allow drainage and flange joints should be kept to the minimum.
- Low spot (vertical U bends in piping should be avoided). Such bends generally retain gas/liquid when the supply is shut off and is a potential source of leak.
- In case of leak in piping, approach affected area from upwind direction to prevent being confronted with leaked gas,

shut off valves and other systems in the prescribed manner.

- The leak in equipment/piping should be contained using HAZMAT response kit.
- Leaked chlorine should be neutralized using alkaline medium such as caustic soda, lime slurry, etc.

Disaster Management Plan

Disaster management plan is totally based on hazard identification, prediction and prevention [4]. Several techniques are available for identification and evaluation of hazard in chemical process industries. For example:

1. Safety audit is to be carried out as per statutory requirement.
2. Procedure for hazard operability study (HAZOP) at every stage of critical operation is required.

Following are general points to be included in the disaster management plan of chemical industry.

- Preparation of onsite and offsite emergency preparedness plan.
- Identification of critical zones.

- Identification of hazardous chemicals, processes and operations.
- Release scenarios, consequences in term of heat generation over pressure and toxic release.

Rescue and Evacuation

In the above case of incidents, emergency escape route is to be provided for rescue operation. Shop floor operators and supervisors should close their indoors with doors, windows and other ventilators and shut off air conditioning systems [5].

The evacuation must be carried out as quickly as possible. An emergency plan is required to achieve this.

Public Information

The district collector or his representative will act as chief coordinator. Onsite emergency control room should inform the district authority, pollution control officer, police superintendent, divisional fire officer and district medical officer about the incident and probable damage [6]. Figure B shows the network of communication between various agencies.

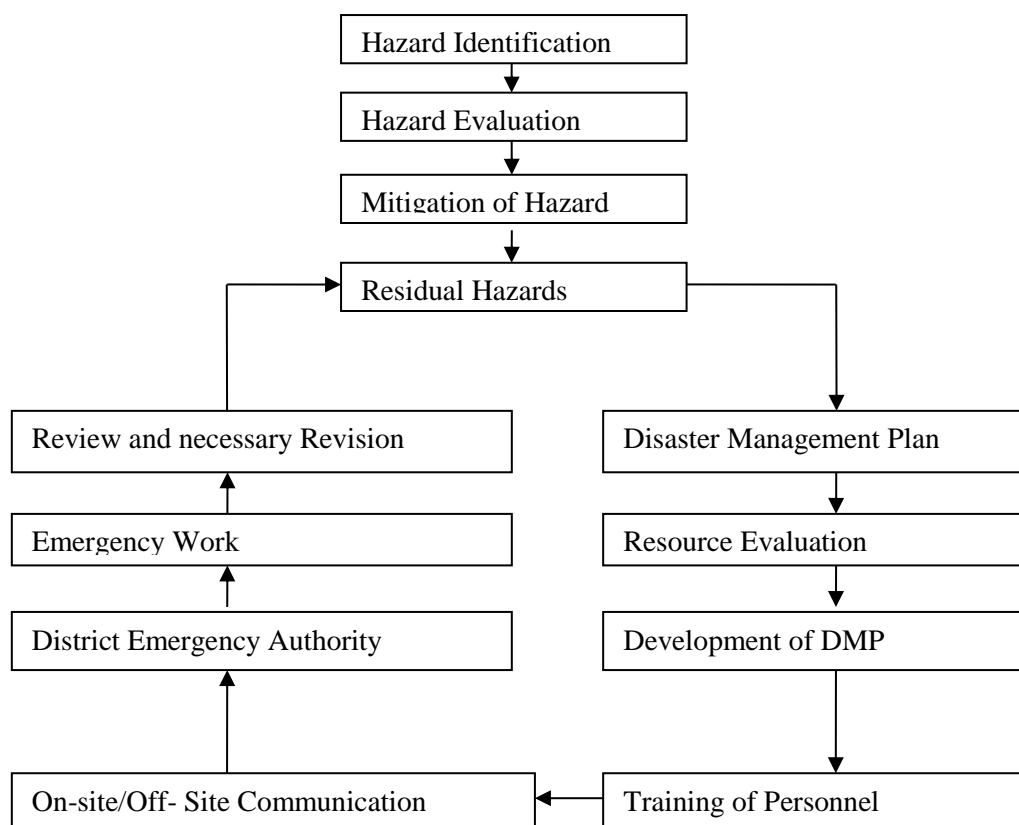


Fig. 2: Comprehensive Disaster Management Plan.

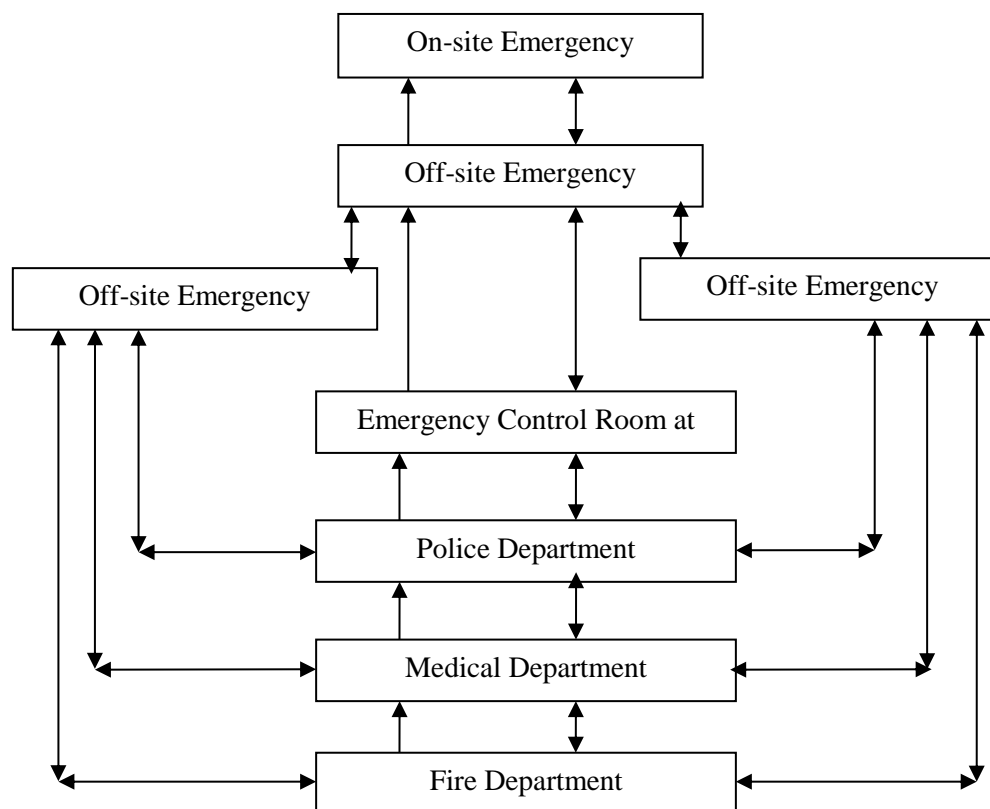


Fig. 3: Network of Communication.

CONCLUSIONS AND RECOMMENDATIONS

Chlorine release is an extremely serious accident that can have severe consequences under less favorable circumstances. It is observed that these accidents take place due to lack of awareness at operator level regarding the potential hazard related to handling hazardous chlorine gas. Recommendations:

1. A proper system of periodic inspections of all safety relief valve, control valves and equipment including pipelines, flange joints, degassing system, vaporizer tank is followed by process and maintenance department.
2. Regular preventive maintenance checks are needed with periodic shut down of equipment and plant.
3. An adequate number of self-contained breathing apparatus should be provided and maintained in the factory. It should be periodically tested by a competent person and record should be maintained.
4. Suitable level indicator and gauges should be provided and maintained in liquid chlorine storage tank to prevent overfilling.
5. The control room should be equipped with instruments for automatic detection of small amount of chlorine smell.
6. Periodic safety audit by internal and external audit team should be undertaken by the management.
7. An emergency disaster management plan should be available and the plan should have HAZOP study to detect all modes of failure.

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