Liquid chlorine leak in an industrial gas plant

27th May, 2009

Martigues (Bouches-du-Rhône) France

Chemistry
Chlorine
Piping / valve
Organization / human factor
Process failure

THE FACILITIES INVOLVED

The site:

Located adjacent to the Lavéra petrochemical complex, this facility was responsible for packaging and distributing industrial gases, mainly chlorine (170,000 tonnes) and ammonia (100,000 tonnes). This site had been assigned an upper-tier Seveso rating.

View of the site

Liquefied gas bottles

The specific unit involved:

The relevant unit comprised 3 distinct installations implicated in the accident: the chlorine tanker car transfer station, the liquid chlorine bottle packaging plant, and the air compressor utility room.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

On 27th May at 9:45 am, the plant manager discovered 2 chlorine puddles, one in the packaging workshop the other in the compressor utility room.

The triggering event had occurred the previous day at 2 pm; two experienced technicians had connected a chlorine tanker car in accordance with the "Tanker car acceptance and connection" procedure, involving: removal of flanges from the fixed installation as well as the car; positioning of the moving head on the car's liquid valve (in red); connection of the high-pressure compressed air "inflation" intake (i.e. pressurised drainage system) onto the car's gas valve (yellow); and lastly repositioning and tightening of the flanges.

Chlorine tanker car transfer station (chamber no. 2)

Car - moving head valve connection

Between 3 and 4 pm, the technicians installed an air intake on the tanker car's valves, then opened manual valves on the low-pressure air circuit. During verification of the seal on the moving head-car connection by means of an alkali test, they detected a chlorine leak. In the event of leak detection, the emergency shutdown system was supposed to be activated; one of the technicians however, instead of starting up this system, acted out of reflex and adjusted the closest air control valve (see arrow in photograph) to shut the tanker car's liquid valve (in red). The automatic chlorine detection chain placed all installations in secure mode; the two technicians, wearing self-breathing apparatuses, clamped the flange and stopped the leak. The pipe containing liquid chlorine was subsequently drained and degassed towards the bleach tanks, before being filled with inert air by opening the car's high-pressure inflation system. The compressors were turned off and the technicians scheduled a flange joint change for the following morning.

At 7:30 am the next day, the depressurisation step was initiated on the liquid chlorine line as of the tanker car outlet prior to disassembling the moving head. The chlorine was channelled towards the soda lye - bleach neutralisation tanks. At 9:30 am in observing frost on the tank degassing rods, the workshop manager made his way to the tanker car in order to verify closure of the liquid chlorine valve. He had the control rod safety nut removed and noticed that the control rod, when partially reassembled, allowed some of the liquid chlorine to escape. When he activated the air supply valve to bleed the circuit, the valve shut entirely.

Around 9:35 or 9:40, the workshop manager recorded a chlorine leak on the high-pressure air inflation system in the packaging workshop (1st puddle). Upon entering the compressor utility room to insulate the air distribution network, he then observed the formation of a liquid chlorine puddle inside the network at the level of an air dryer (2nd puddle).

The internal emergency plan was launched at 9:45 am, and a team of first responders verified site confinement in addition to operability of the neutralisation tower. Once notified, plant personnel remained indoors; a second team set up water curtains. No trace amount of chlorine was recorded downwind at the site's property boundary. Fire-fighters were at the scene by 10 am and established a safety perimeter; moreover, street and highway access was blocked, employees from neighbouring companies were kept indoors, and a crisis management unit assembled. Local media were informed and reported onsite. The premises were cleaned from 10 am to 9:45 pm, at which time the emergency plan was lifted.

Consequences of this accident:

The liquid chlorine leak formed 2 puddles on the ground that subsequently vaporized. The quantity of chlorine lost was equal to what had been trapped inside the high-pressure air inflation pipe, i.e. for a DN15 diameter and 100-m length, a volume of 17.7 litres, corresponding to 25 kg of chlorine. No impact on the environment was observed as the strong southern wind helped disperse the chlorine. Measurements recorded at the site boundary indicated contents of less than 0.17 ppm. This incident produced no injuries.

The European scale of industrial accidents

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the '*SEVESO*' directive on handling dangerous substances, and in light of information available, this accident can be characterised by the four following indices:

During the incident, 25 kg of chlorine were released into the atmosphere. The Seveso threshold for this substance stands at 25 t. The quantity lost therefore corresponds to 0.1% of this threshold, i.e. equal to a 2 on the index relative to quantities of dangerous substances released (see Parameter Q1). The incident did not give rise to any human, social or environmental consequences; hence, the values of the two corresponding indices were scored a "0". Since property damage costs remained unknown, the index relative to economic consequences could not be rated.

The parameters composing these indices and their corresponding rating protocol are available from the following Website: http://www.aria.developpement-durable.gouv.fr.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

Triggering event no. 1:

On the day prior to the incident, the technician instinctively closed the nearest air control valve when noticing a chlorine leak at the level of the moving head-tanker car connection, so as to close the chlorine car's valve, instead of activating the emergency shutdown system. In reality, this air control valve contained no outlet and the entrapped air pinned the control rod in an intermediate position, meaning that the tanker car's valve remained partially open.

Triggering event no. 2:

During inerting of the liquid chlorine circuit, the technician opened the high-pressure air inflation system, in assuming that chlorine was only present in its gaseous phase, which should have been the case. In addition, a pressure drop had occurred in the compressor despite operability of the safety system by differential pressure (ΔP). Opening of the air network, coupled with this pressure drop, introduced liquid chlorine into the high-pressure air circuit. The inerting process was then stopped, the manual air circuit valves closed and the compressors shut off, which in turn closed their supply valves. The high-pressure air network thus remained pressurised and subject to chlorine pollution.

The incident:

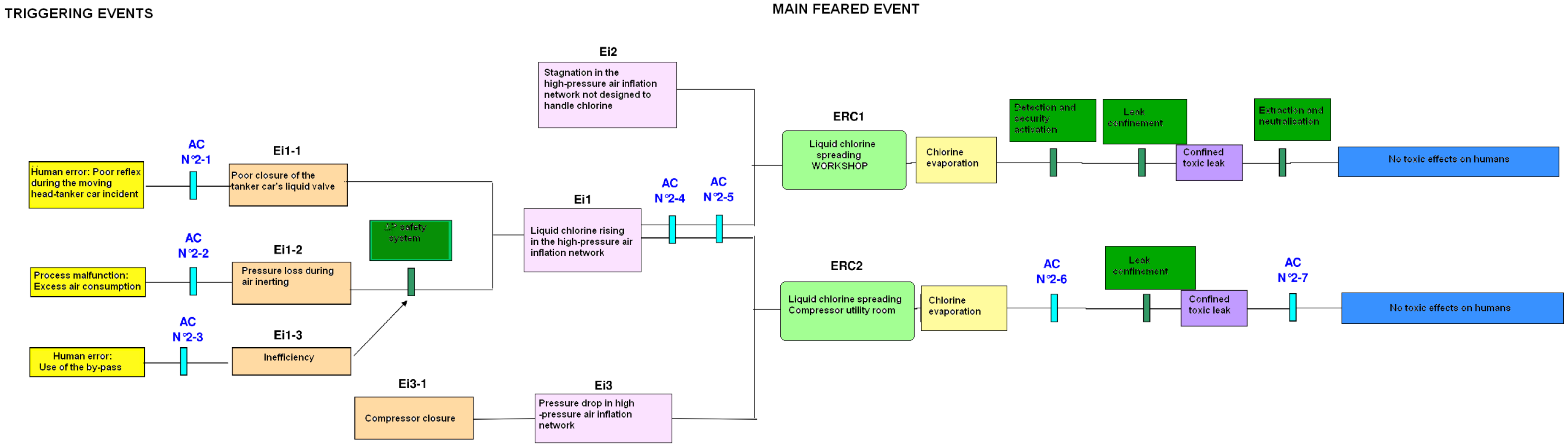
The next day, on 27th May, during the depressurisation step carried out on the liquid chlorine network, the Cl_2 trapped inside the high-pressure air circuit spread throughout this circuit and wound up leaking at the level of the workshop and compressor utility room.

In order to reduce pressure in the chlorine pipe via the air ejection system, technicians used the high-pressure process air circuit, a step that led to liquid chlorine migration. Once suctioned into the gaseous chlorine pipes, the liquid chlorine was then trapped by the buffer cylinders before being rerouted to the bleach tanks. The liquid chlorine expansion caused the formation of frost on the tank degassing rods. Being trapped inside the high-pressure pipe, the Cl_2 migrated towards the packaging workshop along the line's contour and then leaked at the level of the workshop, thereby forming an initial puddle. After the compressor was shut off by the workshop manager, the trapped chlorine then moved towards the compressor and began leaking at the level of a dryer, thus forming the second puddle.

Remarks:

The inoperability of the differential pressure (ΔP)-based safety system was due to a handling error and not to any equipment malfunction; tests performed on 17th June demonstrated the system's good working condition. As a matter of fact, when the automatic safety device was triggered by the detection of chlorine on 26th May, the ΔP cut-off valve had been in the closed position. To open it, the ΔP system had to be reset in the workshop. At the time of inerting however, once the flange had been tightened, technicians elected to use the ΔP valve by-pass (composed of 2 manual valves) instead of re-engaging the system from inside the workshop.

Causal tree analysis for the chlorine leak incident on 27th May, 2009



corrective measures

existing measures

AC	Description of the corresponding corrective action (causal tree analysis)
N°2-1	Installation of new 3-way manual valves on the low-pressure air circuit controlled upstream of the instrument console
N°2-2	Modification of high-pressure air networks with the creation of 2 independent circuits, each with a dedicated air supply tank: [high-pressure inflation network] / [high-pressure process network + control low-pressure network]
N°2-3	Secure mode for "technical" manual valves by means of padlocking
N°2-4	Installation of 2 "liquid trap" buffer tanks on each of the 2 high-pressure air networks
N°2-5	Installation of a chlorine detection devices on both of the high-pressure compressed air networks, with servo-controlled closure of guided valves
N°2-6	Installation of a chlorine detection device in the compressor utility room
N°2-7	Placement of an air extraction duct in the compressor utility room connected to the neutralisation tower

The sudden pressure drop in the air circuit was due to a process malfunction. In reality, the consumption of compressed air exceeded normal levels following partial opening of the tanker car's liquid valve, which in turn caused a longer high-pressure air inerting process. Site consumption compounded matters: tap removal, brushing booth, etc. This total consumption pushed pressure down to a level below that of the tanker car (the saturating vapour pressure of chlorine at 20℃ = 5.7 bar).

This incident thus resulted in a rise of liquid chlorine within the high-pressure inflation circuit due to a combination of the 3 following factors:

- poor closure of the car's liquid valve subsequent to the initial incident on the car's moving head (closure of the wrong valve when the technician acted out of reflex);
- pressure drop during the air inerting step (air circuit designed too small given the exceptional operating conditions);
- inoperability of the differential pressure ΔP safety system (by-pass of the safety ΔP by technicians instead of responding to the malfunction).

ACTIONS TAKEN

A Prefecture order to proceed with emergency measures was adopted on 29th May, requiring that the installations remain shut down as long as the operator proved incapable of identifying incident causes and moreover enacted compensatory measures for remediation purposes. The service restart of these facilities would only be allowed upon decision of the Classified Installations Inspectorate.

Once the causes of this incident had been identified, the operator undertook several corrective measures:

- update, revision or creation of safety management system procedures to improve the organisational supervision of suspect operations, along with a training session specifically adapted to technicians;
- installation of new 3-way manual valves on the low-pressure air circuit controlled upstream of the instrument console for the purpose of bleeding the tanker car valve air supply and thereby avoiding the operational error due to air valve closure that resulted from an inappropriate reflex action;
- (reversible) locking of the ΔP safety by-pass, given that this by-pass was only necessary for installation maintenance (padlocked manual valves);
- separation of the high-pressure air circuits (i.e. process and inflation) by introducing a compressor for each circuit in order to both avoid disturbances between the two and increase air supply capacities, which were inadequate at the time of the incident. Installation on both circuits of 2 "liquid trap" buffer tanks.

Installation of 3-way valves

Independant air circuits with distinct identification

Installation of "liquid traps" in both high-pressure circuits

Afterwards, complementary measures were implemented:

- enhancement of the chlorine detection network by, among other things, the coverage of the compressor utility room and setting up chlorine detection devices on both high-pressure compressed air circuits (inflation and process), with a servo-controlled valve closing in the event of detection;
- installation of an air extraction duct in the compressor utility room hooked up to the neutralisation tower;
- periodic verifications of technician training efficiency (i.e. safety management system procedure);
- application of safety management system guidelines to secure by-pass use conditions.

The installations were then approved for restart under the proviso of strictly applying all of these remedial measures.

LESSONS LEARNT

Controls, training and modification oversight

Beyond the technical modifications described in the previous section, especially separation of the two high-pressure air circuits and reinforcement of the means of chlorine detection, the revision of existing safety management system procedures relative to tanker car operations (connection/disconnection, loading, shutdown) planned by the site operator were intended to avoid such an incident from ever recurring. In particular, the operator set out to detail the protocols and introduce an improved valve identification procedure, plus a number of additional controls (establishment of an inspection checklist).

The revised personnel training programme relative to procedural modifications was also intended to prevent a technician from activating a valve out of reflex instead of the emergency shutdown system purposely designed for this type of situation. The periodic verification of technician training efficiency was a useful approach to avoiding the missteps that led to technician preference for a seemingly relevant, yet totally inappropriate, operating routine.

Feedback return management

This incident revealed that a more comprehensive risk analysis associated with a more extensive and better adapted chlorine detection network would have made it possible to foresee this malfunction and thereby avoid the chlorine leak, or else to act more quickly once the leak had occurred. Moreover, the incident raised doubts over the operator's choice to push the chlorine with air despite the existence of alternative methods (e.g. expulsion by gaseous chlorine, by nitrogen).

An analysis of the incident led to identifying the causes and adopting appropriate corrective actions. All these measures would be subsequently mandated in a supplemental Prefectural order. They would be used for review purposes and serve to complete the safety report conducted prior to establishing the technological risk prevention plan for the Lavéra petrochemical site.

Bibliography:

Prevention of accidents involving chlorine - INERIS / SHD / BARPI - October 2004.