

Accidental release of phosgene

14 May 2012

Le Pont-de-Claix (Isère)

France

Chemistry
Phosgene
Leaks
Heat exchangers
Corrosion
Confinement enclosure
Organisation / Human
factor

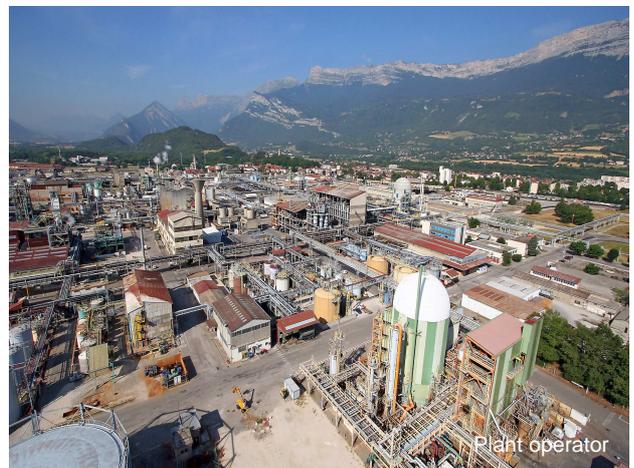
THE FACILITIES INVOLVED

The site:

This plant is part of the Pont-de-Claix chemical complex, an industrial park that includes several firms with close ties due to their respective manufacturing activities. The site is located in a densely urbanised environment on the outskirts of the Grenoble metropolitan area.

Park activities are based on producing chlorine and phosgene for subsequent use in the synthesis of isocyanates (intermediate compounds for polyurethane foams and paints) and several products intended for crop protection.

This upper-tier Seveso site is subjected to Prefecture oversight as prescribed in regulations governing classified facilities for the manufacturing, storage and use of hazardous substances, i.e. mainly chlorine, phosgene and isocyanates.



The specific unit involved in this accident:



The accident occurred inside an isocyanate production workshop. The process implemented consisted of generating a reaction from a phosgene solution on an amine compound under conditions of high temperature and pressure.

The number one hazard during workshop operations is the accidental release of a phosgene cloud. Phosgene gas, which is heavier than air and highly toxic, was notably used as a combat weapon during World War I (with a threshold for significant lethal effects after a 30-min exposure = 3 ppm - source: INERIS).

Given the hazard potential associated with the substances employed, this reaction was carried out within a confined enclosure held in a low-pressure state and featuring a safety column (for soda absorption), which served to dissipate the phosgene cloud emitted during an accidental situation.

This enclosure housed 2 tubular heat exchangers, one of which became the source of this accident.

Operations of the faulty equipment:

To proceed with isocyanate synthesis, the two tubular exchangers warm the phosgene solution prior to its reaction. This solution circulates inside the tubes, with the caloric contribution being generated at the level of the tubular shell by overheated steam. Pressure rising to several tens of bar around the dissolved phosgene by far exceeds the vapour pressure introduced. Drains at the base of exchangers collect the condensates, which are then channelled to a soda tank located outside the enclosure. The gaseous phase is directed to a chimney via the safety column.

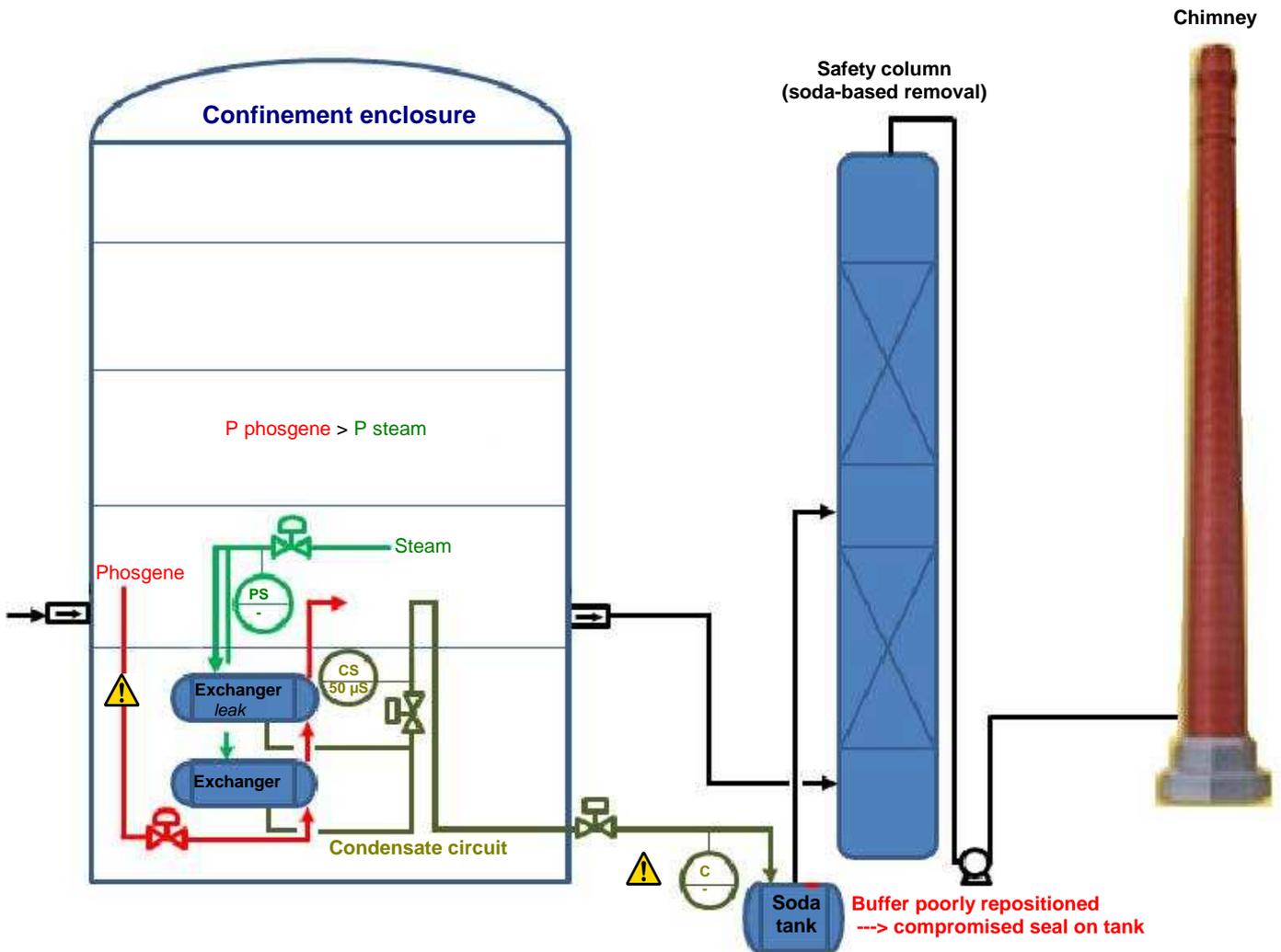
During normal operations, phosgene and water are never in contact with one another. However, in the event of an exchanger tube leak, the phosgene solution spills into the steam circuit. Pressure increases in the circuit, and a portion of the phosgene

reacts with the water vapour in forming hydrochloric acid. Both the phosgene and hydrochloric acid are then discharged through the condensate circuit to the soda tank on the safety column outside the confinement zone. To avoid such a scenario (identified in the safety report), 2 technical safety barriers had been designed, namely:

- a conductivity measurement on the condensate circuit, which triggers isolation of this circuit and shuts down the phosgene solution supply pump once threshold value tops 50 µS;
- a pressure switch on the steam circuit, which upon recording a "high pressure" measurement also isolates the condensate circuit and shuts down the phosgene solution supply pump.

Moreover, the installation contained an additional conductivity meter on the condensate circuit dedicated to system supervision, i.e. without any associated programmed action, as well as an automatic valve closure device for the confinement should the low-pressure state not be maintained.

Simplified diagram of a portion of the HDI (isocyanate) workshop process
(State of the installation on the day of the accident)



- Sensor measuring condensate conductivity with a safety action programmed at 50 µS → isolation of the condensate circuit and shutdown of the phosgene pump
- Sensor measuring condensate conductivity without triggering any safety action
not operational on the day of the accident
- Sensor measuring the condensate circuit pressure with programmed safety action → isolation of the condensate circuit and shutdown of the phosgene pump

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

The accident occurred during the night of May 14th to 15th, while the isocyanate production unit was in operation:

- Subsequent to a seal defect on one of the tubes in an exchanger (due to a hole the size of a pinhead), a portion of the phosgene solution penetrated into the tubular shell and mixed with steam.
- Upon this contact, a portion of the phosgene reacted with water vapour to form hydrochloric acid, which eventually corroded the outer wall of the tube where the leak began and, to a lesser extent, the walls of adjacent tubes.
- The phosgene and hydrochloric acid were then conveyed, along with the condensates, to the soda tank, whose seal had been compromised due to faulty buffer repositioning following its most recent drainage. The tank pressure drop however was still sufficient to direct the gas to the safety column, thereby avoiding any direct phosgene release to the outside.
- In the presence of hydrochloric acid and phosgene, condensate conductivity increased to a point of reaching the 50- μ S threshold. As expected, the programmable safety controller automatically isolated the condensate circuit and shut down the phosgene solution supply pump → activation of the 1st technical safety barrier.
- The 2nd conductivity meter, which was not operational on the day of the accident and whose replacement had been scheduled by the maintenance department, indicated a value of 0 μ S. Technicians on duty at the time, who had not been notified of the device malfunction, decided to sample the condensate in order to confirm their reading.
- The sample was sent to the plant's onsite laboratory, informing the on-call manager that the safety controller had been activated.
- Following a discussion with technicians, yet without waiting for the laboratory to return its analyses, this manager approved circumventing (by-passing) the technical safety barrier that initially triggered installation shutdown and authorised restart of the production line.
- The installation was once again operational, and the phosgene release continued within the steam circuit. The ensuing hydrochloric acid very quickly corroded the steel composing the tubes, given the favourable temperature and pressure conditions. The quantity of phosgene increased in both the condensate circuit and the soda tank outside the enclosure. Due to this considerable inflow of phosgene, the pressure drop created in the tank had become inadequate to route all of the gas to the safety column. Some phosgene escaped into the atmosphere via the poorly-sealed tank buffer, thereby causing the external analysers to rise until reaching a state of saturation.
- Corrosion at the level of the tube where the leak was initiated was such that the tube's residual thickness was no longer sufficient to resist the pressure. The tube ripped open abruptly, with a large quantity of phosgene instantaneously flowing into the steam circuit, whose pressure then suddenly jumped. Once the pressure threshold had been reached, the safety controller isolated (as was programmed) the condensate circuit and turned off the phosgene solution supply pump → activation of the 2nd and final technical safety barrier.
- As a result of this pressure surge in the condensate circuit and the sudden valve closure, a "water hammer" phenomenon broke one of the bleed valves at the base of the exchanger.
- The released quantity of phosgene immediately flowed into the confinement enclosure, causing a loss of depressurisation in the enclosure and subsequent closure of its check valves.
- The phosgene cloud was effectively trapped.
- The laboratory returned its results, confirming the high level of conductivity detected in the condensate sample.



Consequences:

This event was not responsible for any impacts beyond the chemical complex boundary; 4 onsite workers, who felt ill from the release, were taken to the plant's infirmary, but all quickly resumed their work shifts.

The maximum volume of phosgene released into the confinement was evaluated at between 580 kg and 960 kg.

In all, prior to isolating the enclosure, the low level of continuous degassing around the soda tank via the leaking buffer, as well as the undetected degassing once the tube had torn (for just a few seconds prior to closure of the shutoff valves), was estimated to have amounted to less than 14 kg.

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 II' directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

Dangerous materials released		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Human and social consequences		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Environmental consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Economic consequences		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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

The "hazardous substances released" index was rated a "4" to account for the release of at least 0.6 tonnes of phosgene.

The "human and social consequences" index was given a "1" score due to the 4 employees adversely affected by the release.

The "environmental consequences" index could not be rated, since no consequences of this type were actually recorded.

The "economic consequences" index was assigned a "1" as a result of the property damage sustained by the unit as well as the significant operating loss, whose total amounted to between €100,000 and €500,000.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

This accident stemmed from the perforation of one of the tubes on an exchanger. The expert appraisal conducted by the chemical complex's certified inspector revealed that:

- Phosgene / steam contact followed the internal corrosion of a tube, which caused a "pinhead"-sized hole (diameter: 0.5 mm);
- This phenomenon likely happened due to the presence of deposits that had become corrosive after insufficient cleaning of the exchanger and then "activated" once the three following conditions had occurred:
 - presence of phosgene under the deposits during exchanger downtime;
 - partial elimination of deposits at the time of cleaning;
 - water retention under the deposits despite completion of a drying step (nitrogen flushing) after cleaning.



The presence of phosgene and residual water under the deposits led to the formation of hydrochloric acid.

The phosgene release in the direction of the exchanger's tubular shell subsequently induced external corrosion on the tube that eventually leaked and, to a lesser extent, on adjacent tubes. For the originating tube, the level of corrosion was such that the residual steel thickness was no longer adequate to resist the differential pressure, which in turn caused the tube to burst and a major release of phosgene within the shell.



Phosgene release into the atmosphere resulted from poor repositioning of the soda tank buffer following its most recent drainage; its seal however would have allowed eliminating phosgene via the safety column.

Event management response by the team on duty was another contributing cause of this accident. The post-accident investigation indicated a succession of errors and negligence that could have been avoided, namely:

- poor assessment on the part of assigned employees regarding proper operations of the conductivity meter that had placed the facility in safety mode due to the conflicting "0" reading on the "supervisory" meter, whose sensor was out-of-order;
- decision to circumvent the technical safety barrier, even though it was operational, without waiting for the laboratory's analysis results relative to condensate conductivity, in order to confirm the good working order of the safety barrier;
- non-compliance with both internal procedures and Prefecture orders regarding installation operations, as no compensatory measure was implemented to guarantee an equivalent level of security after bypassing the safety barrier;
- a misinformed approach adopted by the onsite team, proof of denial of the inherent risk.

ACTIONS TAKEN

This accident gave rise to a joint inspection by the Classified Facilities inspector and the staff member assigned to monitor the "Pressurised equipment" activity, in a step that enabled observing the violations noted in the previous section.

Following the accident, the facility operator undertook a number of remedial actions:

- of a technical nature:
 - evaluation of condensate circuits for those exchangers exhibiting the same problem in the event of perforation (other workshop instruments and other isocyanate workshops);
 - repositioning of the soda tank buffer into its proper place and verification of its seal;
 - repair of the defective conductivity meter, increased calibration frequency (quarterly instead of semi-annually);
- and of an organisational nature:
 - modification of the exchanger cleaning procedure and establishment of criteria for evaluating the quality of exchanger drying;
 - change in the soda tank pumping operations procedure so as to avoid opening the tank buffer;
 - availability of basic instruction sheets to formalise appropriate workstation practices and decision-making regarding technical safety barriers, supplemented by detailed information provided by individual teams;
 - revision of the safety "bypass" procedure: standardisation across workshops, specification of roles, bypass conditions, etc.;
 - feedback from the incident and enhanced awareness by all production staff of the safety bypass procedure: plant technicians, shift foremen, workshop managers, etc.;
 - awareness building training dedicated to the bypass procedure also offered to on-call personnel, followed by a formalised commitment by this personnel category to strictly comply with the revised procedure;
 - modification of the technician certification training programme, with an additional process safety module;
 - disciplinary actions taken against onsite employees present on the day of the accident.

LESSONS LEARNT

This incident reveals that a succession of human errors and negligent conduct can lead to an industrial accident. The infrequency of such accidents and the routine nature of these operations are just two of the factors that over time had resulted in risk underestimation. This event provides a reminder of the need for regularly training plant employees so as to ensure that the required level of vigilance, commensurate with the presence of major risks, is always maintained.

The operator wound up expanding onsite process safety training by undertaking the actions set forth in the previous section. For year 2012, a total of 4,600 hours of training were devoted to safety and the environment for all 550 site personnel.

The management procedures applicable to technical safety barriers were reviewed and standardised. The operator renounced the notion of "replacement" safety equipment, which had been applied to justify, in certain cases, overlooking one barrier due to the simple existence of a second barrier.

This accident has also confirmed the relevance of confinement for such installations, which handle highly toxic gases at high pressures. For the second time, this constructive measure has proven its efficiency. A similar phosgene leak (850 kg) had previously been successfully trapped following corrosion of an arm guard (due to an inappropriate alloy) on 11th July 1988 shortly after the workshop's inauguration (ARIA 390). On two occasions, this measure has served to avoid the consequences of accidents that could have been disastrous, especially given the densely urbanised environment around the Pont-de-Claix facility.