# Phosgene discharges in a chemical plant

## 12 August 2017

## Le-Pont-de-Claix (Isère)
## France

**SEVESO**
**Isocyanates and by-products**
**Chemical manufacturing**
**Subcontracting**

## THE ACCIDENT AND ITS CONSEQUENCES

At around 11:00 p.m., phosgene ($COCl_2$) and chlorobenzene began leaking inside the containment building of a chlorinated chemicals plant. The leak was detected at levels between 13 and 22 ppm by analysers inside the containment. The analysers' control system automatically directed the air inside the containment towards the caustic scrubber. Technicians began looking for the cause of the leak.
While one of them was suiting up to enter the containment, the analysers detected an even larger leak (500 ppm) at 12:20 a.m.

The technicians placed the circuit in a safe position by shutting off the pump (which stopped the leak) and isolating the containment, but not before 400 kg of phosgene and 600 kg of chlorobenzene spread inside the containment. Although the analysers did not detect anything unusual, there was a noticeable odour outside, near the containment.

Phosgene is a gas used under pressure. It is a dangerous substance classified as "Acute toxic, category 2, all exposure routes".

Chlorobenzene is a category 3 flammable liquid, and other flammable liquids with a flash point of < 60°C, stored at high pressure or temp.

Both are SEVESO substances.

At 2:00 a.m., the technicians began cleaning the containment by injecting air inside the scrubber. They could smell something in the air although none of the analysers in the surrounding production facilities and labs detected any phosgene. At around 2:40 a.m., outside analysers detected phosgene at levels between 0.12 and 0.2 ppm.

The operator estimated that 4 – 5 kg of phosgene escaped to the atmosphere via the containment's stack.

## THE ORIGIN AND THE CAUSES

The analysis revealed that the releases to the atmosphere were caused by a long string of events.

### Release of gases inside the containment

The initial leak inside the containment was caused by a leak on the pressure sensor of a pump and a leak on a flange's seal upline of a flow meter connected to this pump. The flange's seal had been replaced by a subcontractor called to assist an other subcontractor shortly before the accident. However, it had been incorrectly fitted. Seal installations are supposed to be inspected and inspected seals have to be identified with a label. As no label was on the valve in question, there was no way of knowing if an inspection had indeed been performed.


*© Site operator*
*Flange's seal upline of the flow meter*

It was not clear who was responsible for performing inspections (the contractor, its subcontractor, or the operator). In addition, the subcontractor called as additional help had only been recently trained in the fitting of seals. Perhaps they lacked sufficient knowledge about the risks related to incorrect fitting, the inspections to be conducted, and the consequences of leaks on the facility. Lastly, a number of operating procedures for sensitive equipment were not written out.

A helium leak test conducted before the facility was restarted did not reveal these leaks. The operator called into doubt the reliability of the helium leak test for this type of equipment, pointing out in particular technicians' inexperience due to training issues and the choice of material used.

### Release of chlorinated gases outside the containment

The bypass very closed valve on the scrubber also had a leak, but the leak had not been found because the valve is located between two very closed pipes, making it difficult to access. A portion of the gases to be treated by the scrubber therefore was directly discharged to the stack.

Three phosgene analysers are fitted on the stack's outlet. They use 2/3 voting logic, meaning that phosgene must be detected by two of them in order to activate risk management measure and close the valves leading to the stack. On the day of the accident, phosgene was detected by just one analyser. The flow rate of the sample loop was too low for the second analyser and the third analyser was sampling the ambient air, not the air inside the stack. This 2/3 voting logic did not allow the technicians to stop the flow of phosgene to the stack.

The analysers were calibrated but the sample loop had never been checked.

The access hatches on the containment's valves also leaked, making total containment impossible. Before the accident, these valves had been opened for maintenance. However, the seals, ordered from the maintenance department, had not yet been repaired. Though valves are under the responsibility of the central maintenance department, their integrity is the responsibility of sectoral maintenance. A resealing notice had been issued in June, but nothing had been done. This fact revealed a lack of coordination among maintenance crews and a lack of interdepartmental communication when defining priority actions. In addition, the operator did not have software to track assigned maintenance tasks.

### Lack of detection outside the containment and no-triggering of the gas leak alert

The outside analysers did not detected phosgene because they were not placed where they could detect a loss of containment. Instead, they were positioned to detect leaks from the low-pressure phosgene synthesis unit next to the containment. In addition, the instructions to be followed in case of a gas leak at the facility had not been revised whereas the plant's internal emergency plan had been modified subsequent to previous events. The gas leak alert was supposed to be given when the phosgene level detected by at least one analyser in the containment exceeded the upper limit. In the present case, the limit had been exceeded but the facility's employees were unaware of the procedure to follow. As a result, the gaz leak alert was not given and the proper steps were not followed. Nevertheless, the crew on duty responded appropriately by shutting off the phosgene pump.

## FOLLOW-UP ACTIONS TAKEN

The inspection authorities for classified facilities visited the plant and the incident was added to a study conducted by BARPI and the French National Institute for Environmental Technology and Hazards (INERIS). This study, which went beyond the present event, examined how the operator analysed and applied feedback following various accidents that had occurred at the plant in 2016 and 2017. The aim was to take a critical look at the operator's analysis of the incidents/accidents. It highlighted the need to look more closely for organisational causes when conducting analyses and showed which risk factors were liable to cause accidents, in particular :

- the existence of bias when analysing risks (financial/technical biases, focus on major accident scenarios, difficulties in factoring in transitional phases);
- the potential for errors due to inadequate, non-existent, or multiple procedures and instructions.

## LESSONS LEARNT

### Improved reliability of critical elements

After the accident, the operator replaced all its defective equipment and began implementing corrective measures, particularly on the tracking and coordination of maintenance tasks among the various maintenance crews.

It audited the safety devices installed at its facilities.

In particular, it began implementing:

- weekly testing of the sample loops used by the phosgene analysers in the stack and other critical analysers around the plant;
- testing, under a pressure of 20 mbar, of the containment after each opening of the hatch and at least once a year.

The closure effectiveness of the valves was also investigated. The operator also began enhancing the reliability of helium testing.

### Revised practices regarding critical elements

The operator revised the procedures to be followed if gas is detected inside the containment so that they are consistent with the procedures in the internal emergency plan, and distributed them to each facility.

A working meeting was held with the contractor in order to:

- redefine inspection rules;
- clarify inspection responsibilities;
- introduce sealing checklists;
- establish rules of communication with the contractor.

A safety moment was then held to once again go over everyone's responsibilities and the safety rules that apply to contractors and their subcontractors. A multiple-choice quiz on sealing and a practical test were conducted before operations on the site to check whether the relevant instructions and procedures were well understood. The number of people authorised to assess workers was increased.

The operator implemented operating procedures for general work performed on critical elements.

The calibration standards (training, procedure, plan) were revised.