Hydrochloric acid (HCl) vapour emissions

13th May, 1993

Port de Bouc (Bouches-du-Rhône) France

Maintenance / building works
Cleaning
Organisation / procedures
Risk analysis
Acid
Media impact

THE FACILITIES INVOLVED

The site:

The plant was producing disulphur dichloride (S_2Cl_2, also called sulphur monochloride, which is an intermediate product in the halogenated sulphur chain), by means of spraying gaseous chlorine into liquid sulphur. Manufactured in the plant at a rate of 3,000 tonnes/year, this chloride output was either used in-house or sold.

This product was being stored in two 50-m^3 reservoirs not subjected to any of the prevailing regulations specific to gas pressure apparatuses.

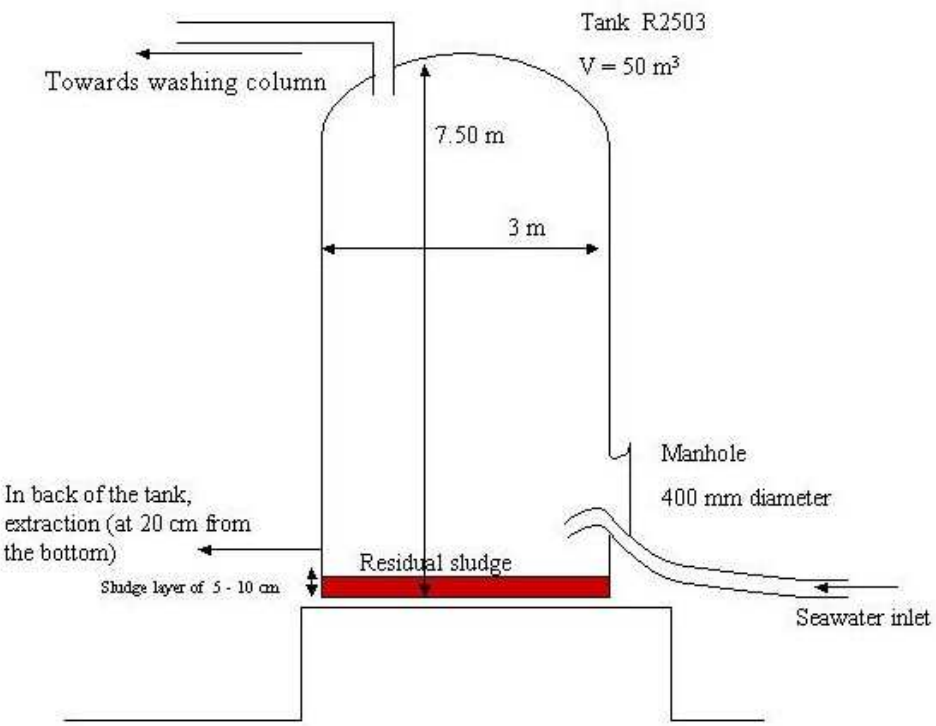
The specific unit involved:

The onset of cracking on the shell-bottom junction weld was detected on Reservoir R 25.03. A regular maintenance call had been scheduled; these works required preliminary drainage of the tank.

The reservoir was thus emptied and then prepared a few days prior to the works:

- The product inlet and drainage pipes were insulated by filled buffers.
- A 400-mm diameter manhole at the base of the reservoir was opened, and the disc held open using a tie bolt.
- A connecting pipe between the reservoir dome and a washing column was kept in place in order to capture the hydrochloric acid vapours.

However, a relatively compact sludge with 60-mm average thickness still remained at the bottom of the device. This sludge contained corrosive products, 50% sulphur monochloride and miscellaneous other impurities.



At the beginning of the afternoon, the site operator decided to rinse the reservoir. A specific set of guidelines, written ahead of time for this particular purpose, described the operation; they did not indicate the composition of sludge to be scraped yet did call for installation of a powerful sprinkling mechanism in order to repel the eventual emission of acid vapours. The sulphur monochloride actually hydrolysed rather violently when placed in contact with water, in forming hydrochloric acid and sulphur dioxide subsequent to exothermic chemical reactions.

In accordance with the operating protocol, the neighbouring industrial facilities as well as a marshalling yard were notified prior to initiating these steps. Water curtains were set up on the three "accessible" sides of the site, spray nozzle on the rail station side, and a 6-cm diameter water nozzle fitted with a vaporization cannon facing north. Moreover, a suction mechanism was installed opposite the manhole by a 4-cm diameter sleeve in addition to the suction placed on top of the reservoir, which had been directed towards the washing column.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

A 25-mm hose set inside the reservoir via the manhole was hooked up to a seawater tank in order to take advantage of the solution's buffering capacity[1]. The cleaning operation began at 1:30 pm at an approximate flow rate of 2 l/s.

One minute later, a thick white smoke surged from the slightly open manhole. The water injection step was halted.

The technicians noted a significant decrease in smoke release 3 minutes after stopping water injection; 5 minutes hence, no further releases were being observed through the manhole. The pipe connecting to the scrubbing column was sufficient to capture residual vapours.

The scrubbing device proved efficient when operating laterally. At the level of the reservoir however, a hot acid vapour column rose into the atmosphere above the site installations. The technicians, while reassured by the impressive dimensions of the device introduced, had not noticed this emanation. Satisfied with their handling steps, technicians had no idea that the acid vapours could adversely affect areas outside the site and felt it unnecessary to alert local fire-fighters or for that matter their superiors.

The cloud that formed moved with wind currents and, once it had cooled, fell back to the ground as fog or fine droplets of acidified water. The quantity of acid vapours emitted would subsequently be evaluated at 80 kg.

Consequences of this accident:


Martigues : fuite de gaz toxique

Nuage acide sur le collège

Vingt-quatre élèves du collège Daumier ont été incommodés par un nuage d'acide chlorydrique échappé de l'usine Atochem de Port de Bouc. Pourtant, aucune alerte n'a été déclenchée par l'industriel...

Le communiqué d'Atochem

A secundary school located 1.15 km north-east of the plant happened to lie in the trajectory of the cloud at the time when children were playing in the schoolyard. Several of these youth were physically bothered (watery eyes, runny nose and sore throat), and 24 of them had to be evacuated by fire-fighters, between 2:20 and 3:30 pm, to the nearest medical centre. A medical exam was administered to conclude that none of the students were exposed to danger.

This accident nonetheless exerted a strong media impact, due in particular to the lack of information circulated and failure of the operator to notify authorities.

[1] The buffering power of a solution is its capacity to resist a variation in pH when adding an acid or a base. Seawater is naturally alkaline, with a pH of around 8.2. Alkalinity measures the capacity to resist an acid attack, thus a drop in pH when mixing water with acid.

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

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

The quantity of acid vapours emitted was evaluated at 80 kg, which corresponds to less than 0.1% of the upper-tier Seveso limit for HCl; the hazardous materials released index was thus scored at level 1.

24 children had to be hospitalised for less than 24 hours (parameter H5), placing the human and social consequences index at level 4.

No notable environmental impact was reported, hence the environmental consequences index equals zero.

Given the lack of information on eventual economic consequences, the corresponding index could not be rated.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

Adding water on sulphur chloride led to a hydrolysis reaction of this chemical product, with the formation of large vapour quantities (in the form of smoke) with a high and uncontrolled hydrochloric acid content.

ACTIONS TAKEN

The operator was sanctioned for failure to inform administrative authorities and coordinate emergency services even though the acid cloud was harming the environment. Administrative authorities were eventually notified by fire-fighters and needed 2 hours to identify the responsible facility.

Service start-up of the sulphur monochloride storage operations was contingent upon acceptance of a new authorising procedure.

The operator also modified its response protocol, in addition to updating its safety report, enhancing personnel awareness of the potential for risk and improving emergency communication channels between the plant and its neighbours.

LESSONS LEARNT

Fortunately, this accident only resulted in limited consequences outside the plant perimeter. Nonetheless, it appears that the potential consequences from the type of neutralisation reaction practiced here had been seriously underestimated when preparing for these maintenance works. Such oversight led to an observation that the normal gas treatment system had been under-designed, as well as to the atmospheric discharge of a hydrochloric acid vapour cloud, despite installation of a water curtain around the site periphery.

Alongside these noted deficiencies in scheduling, preparation and execution of maintenance operations, the influence of erroneous human judgment of the event needs to be added. The poor level of recognition by technicians of the magnitude of these gaseous releases, plus the vulnerability of water curtains and the potential consequences of the cloud drifting beyond the site boundary all prevented triggering an external alarm response.