Chlorine cloud resulting from a failure in handling hazardous substances

5th October 2007

Frankfurt

Germany

Distributor of chemicals
Sodium hypochlorite
Mix up of connections
Generation of chlorine

THE FACILITIES INVOLVED

The site:

The accident happened at a site of a distributor of bulk chemicals such as acids, bases, aqueous solutions of detergents etc. The chemicals are delivered by road or railway tankers and put into tanks. On the demands of customs, the chemicals are then filled in drums or cans which have a volume ranging from 20 to 200 L. At the site there is also a company administration building, a building with laboratories, small scale production rooms and a storehouse. At 100 m away there is a public street.

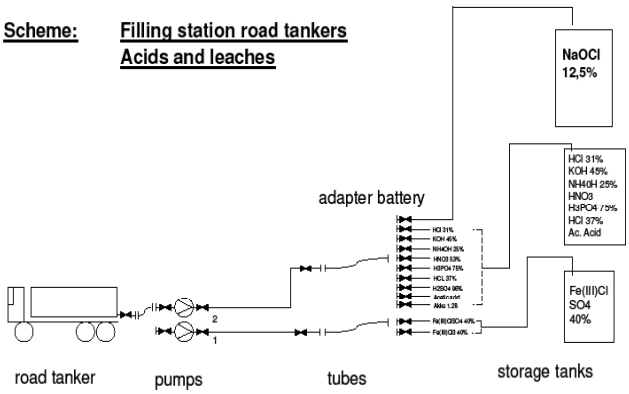
The site is neither under the regulation of the Seveso-II-directive nor the German Federal Immission Control Act (BImSchG). Thus the substances handled on the site are neither inflammable nor toxic.

The involved unit:

The involved unit consists of a storage unit with 13 tanks of 30 m³ volume, a delivery station for road tankers at a distance of about 50 m to the tanks and a filling station for drums and containers from 20 to 200 L volume. The chemicals stored in the unit are acids such as nitric acid, sulphuric acid and hydrochloric acid. Furthermore, caustic soda, FeCl(III)-solution and sodium hypochlorite solution are stored there.

The accident happened during a period of rebuilding of the unit; the filling station and the delivery station were in the process of being renewed.

At the delivery station for tankers there is a connection for FeCl3-Solution and only one connection for all the other chemicals. A pump transports the fluids via pipe to a connection battery / filling station for drums, which is near the tanks. At the battery a worker connects the pipe, by using a hose, to the right tank. Before filling, the road tanker should be weighed, delivery documents checked and a sample of the tanker withdrawn. The sample is analyzed (specific weight) in the laboratory. Then the filling is released.



THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

In the morning of the 5th October 2007 a road tanker with 27 000 L concentrated hydrochloric acid arrived at the site. A sample of the content was withdrawn and analyzed in the laboratory. The driver connected the tanker with the delivery station; meanwhile at the adapter battery the worker of the company connected the end of the pipe by a hose with the filling pipe of a tank, unfortunately the (wrong) sodium hypochlorite tank.

When the filling was started, the content of the hypochlorite tank reacted with the hydrochloric acid and a chlorine cloud was released. The worker was aware of his failure and closed the valve. Whereby he received a serious dose of chlorine and was injured. The headquarter of the fire brigade was alerted at 10:35.

The police closed off the area and ordered the radio stations to send warnings out for the east of Frankfurt. The fire brigade saved the victims around the site and fought the chlorine cloud with water.

Consequences of the accident:

The weighing document shows, that about 1 140 kg of 31% hydrochloric acid were pumped towards the tank. About 200 kg of chlorine was released out of the ventilation system of the tank. The cloud drifted towards the administration building and the public street. Employees of the company left the building because of the chlorine smell. Other people living in the nearby public street were injured by the cloud. Besides the serious injury of the worker, 63 people (5 from the company and 58 from the neighbourhood) were taken to hospital. The worker died within 4 weeks of the accident. Within a distance of 1000 m people were asked to stay inside. A main public street was closed for a short while.

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 the information available, this accident can be characterised by the four following indices:

200 kg of chlorine were formed, which corresponds to 0.8 % of the Seveso-threshold, column 3 (level 2).
It occurred one death and >50 injured (level 4), whereby the exact number of hospitalisation (>24h) is unknown.
No environmental damages have been observed (level 0).
The costs were less than 10.000 € (level 0).

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 THE ACCIDENT

The accident was caused by a human failure, a mix up of connections. Instead of connecting a hydrochloric acid containing road tanker with the right tank, the worker connected it with the hypochlorite tank. Due to the reaction scheme

$$NaOCl + HCl \rightarrow HOCl + NaCl$$
$$HOCl + HCl \rightarrow Cl_2\uparrow + H_2O$$

$$NaOCl + 2\ HCl \rightarrow Cl_2\uparrow + NaCl + H_2O$$

200 kg of chlorine were formed. (pK_a (HOCl) = + 7,5)

The following circumstances contributed to the accident :
Just at the time the accident happened, rebuilding measures were being conducted at the site. As a result of this, there was a provisional and somewhat confusional arrangement of the connections.

Secondly, the fact, that only one pipe led to the storage unit, made it impossible to use special connections for the hypochlorite.
Thirdly there was no four eyes principle established. Although the laboratory`s personnel checked the content of the delivery by analysis, the driver's action was not checked. The driver of the road tanker and the company's worker were too far away from each other, so coordinated control of their actions was impossible.

Furthermore the site is not under the regulation of the Seveso-II-directive. The requirements of the directive such as analysis of hazards, risk assessment, change control and planning for emergencies did not need to be implemented.

ACTIONS TAKEN

The operation of the storage unit, especially the filling with acids and hypochlorite solution, was shut down until appropriate measures were implemented :

1. The delivery station for roadtankers was equipped with a separate filling pipe for hypochlorite. The adapter was equipped with left hand threads.
2. All adapters of the storage unit were locked off.
3. Keys will be released after analysis by the laboratory personnel.
4. All connections were clearly labelled.
5. The hypochlorite pipe is monitored by a pH-electrode.

LESSONS LEARNT

The handling of hypochlorite solution holds a high risk. Mixing up the hypochlorite with acids will lead to a dangerous amount of chlorine. If not appropriate measures are undertaken, a simple failure will lead to great risk of life to personnel and surrounding neighbourhoods.

Other accidents with this compound in Germany forced the legislative to improve regulations. Safety regulations called rules on handling hazardous substances (TRGS 500) was renewed. Requirements on handling hypochlorite solutions as mentioned above were introduced.

Perhaps it should be kept in mind to extend the seveso directive to those chemicals ('any classification with Risk Phrase R 31: in contact with acids, liberates toxic gas'), if the directive is reworked.