Release of sulphur dichloride and hydrogen chloridedrogène

January, the 20th, 2000

Castleford

United Kingdom

Chemistry
Start-up
Exothermic reaction
Water
Quantity of substances
Property damage

LES INSTALLATIONS CONCERNÉES

The site and its history

The company in question is a major chemical site handling a wide range of chemicals that bring it under the COMAH regulations (**CO**ntrol of **M**ajor **A**ccident **H**azards). Using the COMAH aggregation rules and the quantities of materials declared to the Local Planning Authority (Wakefield Metropolitan District Council – MDC) under the Planning (COMAH) regulations1999. In October 1999, the site had a total of 40 times the qualifying quantity for the top-tier COMAH status on the toxic test and 3,5 times the quantity on the flammable test.

The sites carries out a wide variety of chemical transformations, mainly but not exclusively using batch processes. These processes use a wide variety of toxic and flammable chemicals as raw materials. Both the wanted products and the waste materials produced can themselves be toxic, flammable or dangerous to the environment.

The site has been in continuous use for chemical manufacture since 1915 when a factory was constructed at the direction of the War Office. The factory manufactured TNT for use in munitions during the First World War. The original site was 6 acres besides the River Aire giving frontage for quays of some 650 feet and offering facilities for railway sidings direct on the London and North Eastern Railway direct from its Castleford station. The land had previously been used mainly as a cricket field and as allotments. The site has grown since then and now covers 75 ha (175 acres).

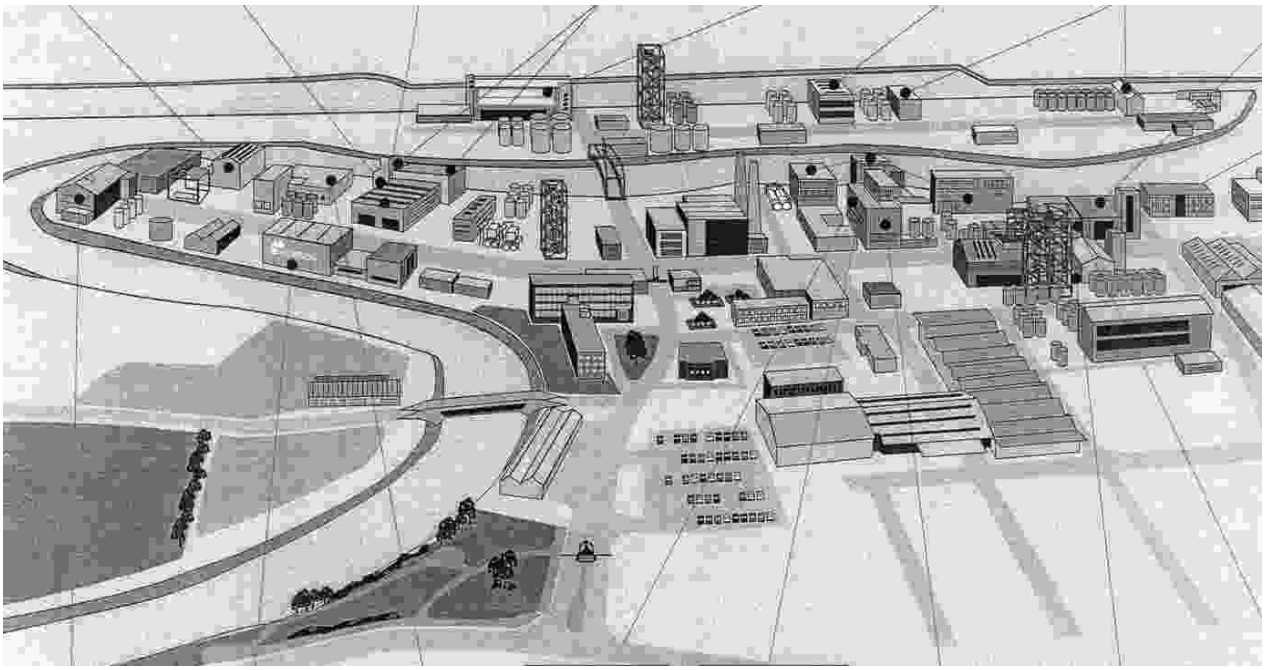
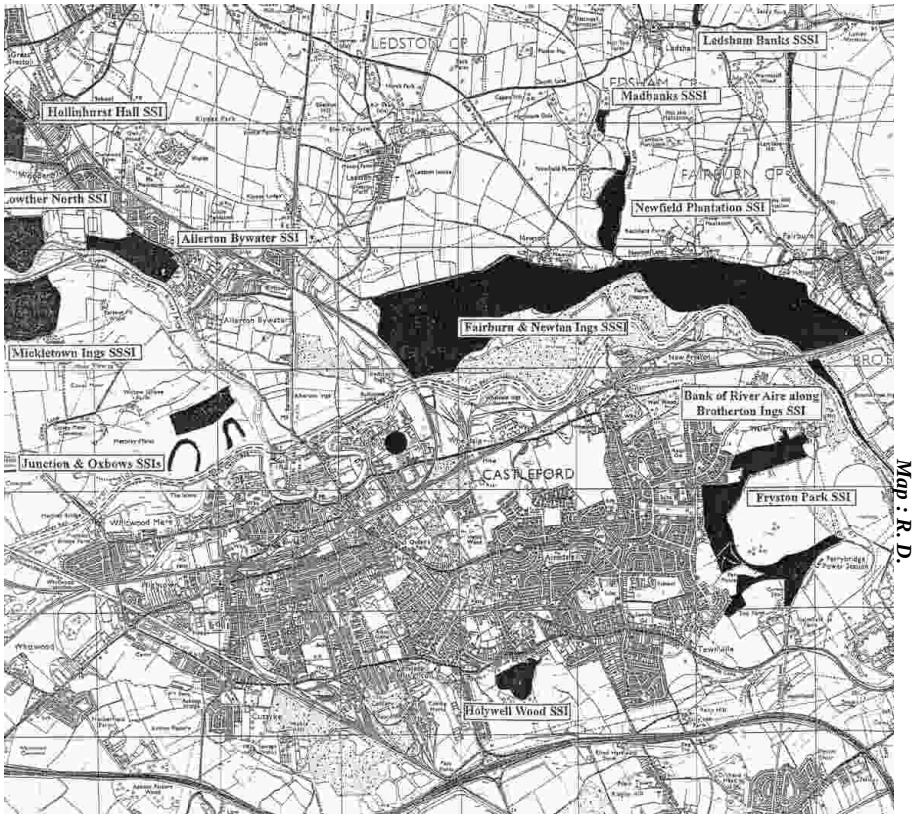


Schéma : R.D.



Map : R. D.

The ten named substances used on the site in significant quantities are as follows. The declared site maximum inventory for each substance is the quantity that was used when applying for Hazardous Substances Planning Consent. It is possible that this quantity may be held on the site.

No other named substances are used on the site. Before the addition of any new named substance to the site inventory, notification will be made under the Planning Regulations in addition to notification under the COMAH regulations. The different substances involved in the process or stored on the site, according to the inventory, are the following ones : arsenic (V) oxide and salts (0,4 t), chlorine (70 t), hydrogen (1,8 t), hydrogen chloride – liquefied gas- (20 t), LPG (100 t), methanol (260 t), oxygen (25 t), phosgene (0,7 t), sulphur dichloride (<1 t), sulphur trioxide (75 t).

The location of the site between an urban area and important waterways near a number of areas of special scientific interest make substance and accident control especially important issues in the operation of this plant.

The installation

The part of the plant involved is the sulphur dichloride unit (called SDC in the following part of the document and whose formulation is SCl2). The following diagram shows the materials involved in the process, the main ones are the following ones : weight system and container venting line, transfer line with its pump, measure pot (T34). In the main lines, SDC, used in the process, is transferred in the ensuing unit from a dedicated vessel : a purpose designed pressurised steel container with nitrogen blanketing in the ullage space. This capacity is connected via a flexible to a transfer system composed with : a capacity located at the top of the reactor and equipped with its own scrubber and venting system. A pump pushes the product through the flexible to the capacity. At this time, it was the first start of this installation, adapted for SDC use. Previously, the part of the line concerned had been flushed with MCB, a solvent and still contained a part of it.

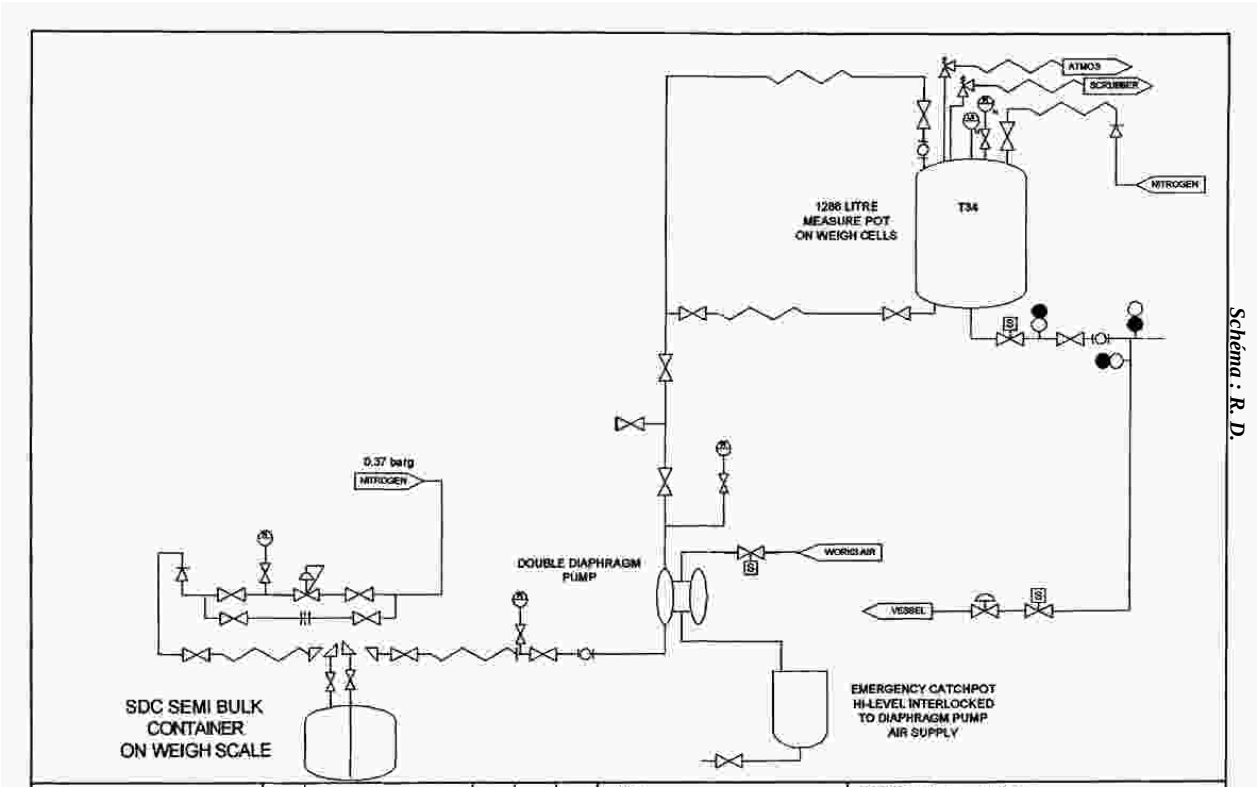


Schéma : R. D.

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident

× It happens on the 20th of January, 2000, in unit 280, for the first transfer operation since the repair of the product suction line. Indeed, previous attempts to start the transfer earlier in the day had been unsuccessful, and it had been found that there was a minor leak, leading to loss of suction on the suction line from the transfer pump to the portable container.

Photo : R. D.

× The leak had been repaired, and the transfer at 20.20 was the first after the repair had been effected. Three attempts were made to transfer the contents by starting the transfer pump and opening the valves : these attempts were unsuccessful.

× At 20.20. on the evening, an attempt was made to transfer the contents of a transportable container of sulphur dichoride to a measure pot (vessel T34).

× The SDC container has connected to it, a supply of gaseous nitrogen which has a supply pressure limited to 500 mbar. This nitrogen supply was opened up to assist in priming the pump (as designed). The pump then successfully primed, and SDC was noted to begin transferring to T34 as evidenced by the increase of recorded weight from the load cells upon which T34 is stationed. The weight in T34 was seen to rapidly rise to in excess of 200 kg by the operatives in attendance. As this was the first transfer of the material after repair of the suction line to the pump, the operatives in attendance « walked » the length of this line to determine whether any further leaks had developed.

× Within 5 minutes of the transfer starting, fumes were seen to be emitted to the atmosphere, from the pressure relief valve system situated on top of T34.

× The transfer pump was immediately stopped, and almost immediately, the emission of fumes from the relief valve ceased. As the operatives re-entered the main plant from the annex where the container offloading station is situated, there was a loud “thud” which was followed by a cloud of fumes being emitted into the plant area, emanating from the gas scrubbing system area for the process.

× The site main control office was contacted by the area personnel and the on site « toxic gas » alarm was raised and the works fire team assembled. No assistance was requested from the off site emergency services.

× At this time, the level of fumes within the plant area was low. The operator team was then instructed to evacuate the plant facility after making the other plant equipment safe (this entailed closing down the adjacent T36 vessel distillation). By this time, the fume density within the plant had increased, but was such that the opposite wall of the plant (about 30 meters away) was still visible. The on site fire team closed the valves on the SDC container. The fire team entered the plant to ensure that all personnel had been evacuated and that no problem was evident.

× A “water curtain” was deployed to the east of the plant to mitigate any downstream effect of the gas cloud.

× The fumes had abated by this time, and technical personnel to ascertain the damage to the equipment then entered the plant. It was quickly noted the main scrubber vessel lid had been displaced during the incident, and some further damage to pipelines in the vicinity of the scrubber lid had been damages. A low level of fuming was seen being emitted from a leak on a flexible line connecting the SDC transfer line to the top of the measure pot T34. An inspection of the plant at 9.30 PM identified that the T34 measure pot contents were approximately 50°C (close to the boiling point of SDC).

The consequences

No personnel on site was injured and an inspection of the roof of the plant immediately below the pressure relief valve found evidence of a very small degree of contamination from material being emitted from the relief valve vent. The estimation of lost SDC quantity is about 71 kg, the mass of SDC transferred was 206 kg (container weights) and the quantity on site at the moment of the incident was 400 kg.

Photo : R. D.

On the material level, the top of the srubber column is ruptured, together with other materials in connection with it.

The cost is not available but the accident losses cover the following operations :

- ✓ Engineering re-installation of the process,
- ✓ Lost materials (cf. photos),
- ✓ Response teams operation costs,
- ✓ Clean up of the installations,
- ✓ Post-accident investigations : both for internal and external investigation inquiries.

On another hand, this kind of accident may involve problems with public confidence as well as on the company reputation with its customers.

The adjacent sports centre to the works was informed of the accidentat this time. There has been no further interest shown from the occupants of the sports centre. There has similarly been no interest shown by any media representatives either local or national.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the ‘SEVESO’ directive, the accident can be characterised by the following 4 indices.

Dangerous materials released	■ ■ ■ □ □ □
Human and social consequences	□ □ □ □ □ □
Environmental consequences	□ □ □ □ □ □
Economic consequences	□ □ □ □ □ □

The parameters that comprise these indices and the corresponding rating method are available at the following address: http://www.aria.ecologie.gouv.fr.

The 71 kg of sulphur dichloride released represent 7.1% of the corresponding Seveso threshold (1 ton – designated product), which equals level 3 of the "quantities of dangerous materials" index according to parameter Q1 (Q1 between 1 and 10x the threshold).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The liberation of HCl and sulphur dioxide gases is the result of a reaction of SDC with water. This reaction occurred in the T34 measure pot as evidenced by the relatively high temperature detected in the measure pot after the incident.

As a result of the investigations, three potential sources of water were determined from the configuration of the plant. The balance of the evidence is strongly in favour of the contaminated drum of MCB being likely source of the water, as described below :

✓ Subsequent investigations into the drums used for the cleaning process showed that one drum of MCB still contained a significant quantity of free water (analysed at 35 % water content, but this only of the sample taken- MCB and water are immiscible). No other drums used were found to contain free water. A structural inspection of the drum containing water showed evidence of internal corrosion suggesting a long-term contact with water. Other drums inspected showed no evidence of this corrosion.

✓ Unfortunately, the MCB used in the washing out procedure is transferred as part of the operation into solvent recovery vessel to be used later in the process. This is a continuing integral part of the process as MCB is a solvent for the later part of the process. The wash out MCB had already been distilled free of water as part of the start up process and therefore it cannot be confirmed that the material was wet when in the measure pot.

ACTIONS TAKEN

The restart of the unit is submitted to the relevant authority agreement, after the operator showed them technical elements they asked for : analysis of the accident, actions taken.

LESSONS LEARNED

Lessons to be learned cover very different fields :

As far as Security management, on a general level, is concerned, the main points are the following ones :

- Increase emphasis on Hazop studies,
- Management of change procedures are crucial,
- Pay particular attention to reducing inventories of dangerous substances in process to limit maximum losses.

Apart from the general methods, it is possible to focus on a few elements concerning the **practices** :

- The check of the quality of materials, particularly of raw ones, must be taken in account and adapt according to the installation risk. In the case of this accident, the reaction with water was well-known. In spite of that, the operator did not carried out special checks on this point.
- Commission must be carried out during normal working hours and in daylight.

Lessons are to learned for the **design operations** too :

- The equipment is not dedicated to one product : this increases the risk of accident.

- Control rooms should normally be manned to allow immediate shutdown action to commence after an instrument indication of a problem. Acting on visual observation is second best.

If we consider the **studies**, it is necessary to underline that a completed COMAH Safety report would not have prevented this accident. But it is seen as useful in identifying adjacent and possible knock-on hazards and plant preparedness for emergencies.