Explosion in a chlor-alkali plant due to a voltage dip

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Germany

chlorine, hydrogen, explosion, power supply, voltage dip, stand by set,

THE FACILITIES INVOLVED

The site :

The accident happened in a chlor-alkali plant based on the mercury-process. The plant is located in an industrial estate which houses among others four chemical plants consuming products of the chlor-alkali-plant. Adjacent to the west there is a commercial area. The estate lies in rural setting alongside a Channel. The shortest distance from the chlor-alkali-plant to an inhabited area is about 750 m, to a school about 1100m. A farmhouse is situated at a distance of 520 m.

The annual capacity of chlorine production is 146 kt. The input salt is shipped via the channel. Chlorine is transported from the site solely by rail. All other products are transported by ship, rail or road. Besides the chlor-alkali plant there are consumers for chlorine and hydrogen on the site (synthesis of sodium hypochlorite, hydrochloric acid, metal chlorides).

The main features of a chlor-alkali plant are the cell room, the chlorine absorption unit, the brine circuit, chorine processing, hydrogen processing, caustic processing and storage tanks for chlorine, caustic soda and hydrogen.

The involved units :

The involved units are the cell room and the standby set as causal units, and parts of the chlorine processing as damaged units.

The cell room contains the low height (a few tens of cm) and large surface (several tens of m²) cells, inside which the electrolysis takes place. A 3 mm thick layer of mercury flows on the slightly inclined bottom of the cells and acts as a cathode, on which the brine (NaCl) previously purified (removal of carbonates, sulphates, calcium, manganese ions and metals traces) runs at a speed of 1 m / s. The anodes made of titanium coated with ruthenium and titanium oxides, are arranged parallel to the surface of mercury at a distance less than 5 mm.

Chlorine gas is directly formed at the anode by redox at high temperature (T = 80℃) and in acid mediu m (pH = 4) to avoid chlorine disproportionation.

$$2\ Cl^- \rightarrow Cl_2\ (g) + 2\ e^-$$

The cathode reaction is divided into two steps in order to separate chlorine and hydrogen : In the cell a sodium/mercury amalgam is formed, which is decomposed to hydrogen and caustic in a separate denuder.

$$Hg + Na^+ + e^- \rightarrow NaHg$$

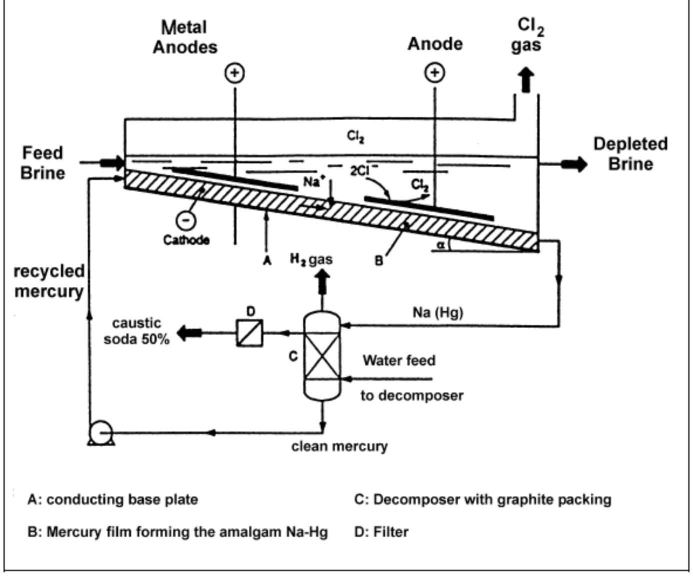
The depleted brine is recycled to the inlet of the cell after being enriched by the addition of NaCl crystals. Mercury amalgam formed by the reaction (NaHg) is pumped to the top of a vertical tank (called decomposer) filled with graphite impregnated with a transition metal (Fe or Ni) used to break it down into hydrogen, caustic soda at 50% and mercury by the addition of distilled water. The hydrogen formed is collected for use in other manufacturing processes.

$$2\ NaHg + 2\ H_20 \rightarrow 2\ NaOH + H_2\ (g) + 2\ Hg$$

The hot and wet chlorine gas produced in the cells is fed into a collecting pipe leading from the cell room to the primary chlorine processing, which comprises wet gas cooling and low-pressure compression. These tanks are directly in front of the cell room. Further chlorine processing takes place in an adjacent building.

The 110 kV voltage of the external electricity supplier is transformed to 10 kV in a substation near the site and then led to the 10 kV station of the site. The lower voltages required are produced in a series of step down transformers and are then distributed via several conduction rails. Vital aggregates for preventing hazards are connected to the emergency conduction rail. In case of voltage failure the stand by set is automatically started and switched to the emergency conduction rail.

Figure 1 shows the flow diagram of the mercury cell technology (excerpt from the “Chlor-Alkali” BREF, 2001)



THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident :

On 23 July 2009 a lightning strike caused a voltage dip in the external power. The chronology of the accident is shown in the following table :

01:12	Lightning in overhead line, voltage dip in internal power network (30ms -200 ms)
01:13	Control desk: rectifiers drop out, Potentiometers to zero
01:15	Attempt to start the chlorine absorption unit via a gas blower
01:30	Alarm activation
01:38	Arrival of the on call team “electrical workshop”
01:41	Loud bang, devastations in the low-pressure system of the chlorine processing
01:45 – 02:00	Electrical workshop team puts emergency power rail into operation, decouples intact and damaged units (chlorine low-pressure/ medium-pressure)
01:45	Sprinkler system in operation, arrival of fire brigade
02:00 – 03:00	Measurements of the fire brigade in the surrounding and at site. As a precaution, construction of a water shield
03:00 – 05.00	Removal of chlorine from the different parts via absorption unit, shut down of plant

Consequences of the accident :

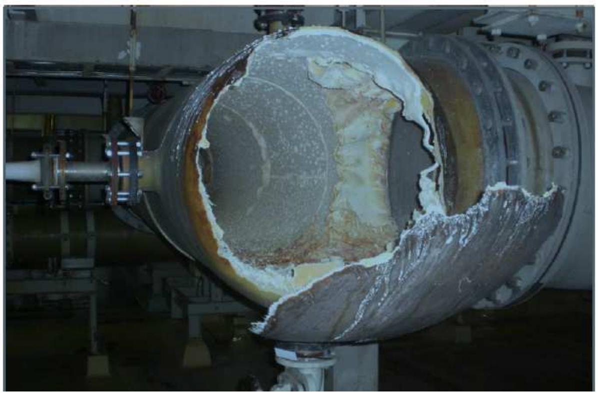
The whole low-pressure system of the chlorine processing was destroyed. The photos below show the damage to the chorine-collecting pipe below the cell room and to two cooling towers and a demister.

Up to 500 kg of chlorine gas were released in the course of the accident. A small portion was released due to the failure of the chlorine absorption unit after 1:12, but most of the gas was released after the explosion via the ruptured tanks.

The spread of the gas was hindered by the sprinkler system and the water shield.

Chlorine concentration measured by the fire brigade ranged between 0,1 and 1,5 ppm. The AEGL-1-Level for 30 minutes had been exceeded at two measuring locations; the AEGL-2-level for 30 minutes was not exceeded.

One member of the staff inhaled chlorine for a short time; one member was injured in the leg and hospitalised less than 24 h.



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 II*' directive on handling hazardous substances, and in light of the 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 amount of chlorine released was about 500 kg. The SEVESO threshold (upper tier) being equal to 25.000 kg, the amount released corresponds to 2 % of the threshold. The scale for the category “dangerous materials released” is 3.

The scale of the category “human and social consequences” is 1, because of two slightly injured employees.

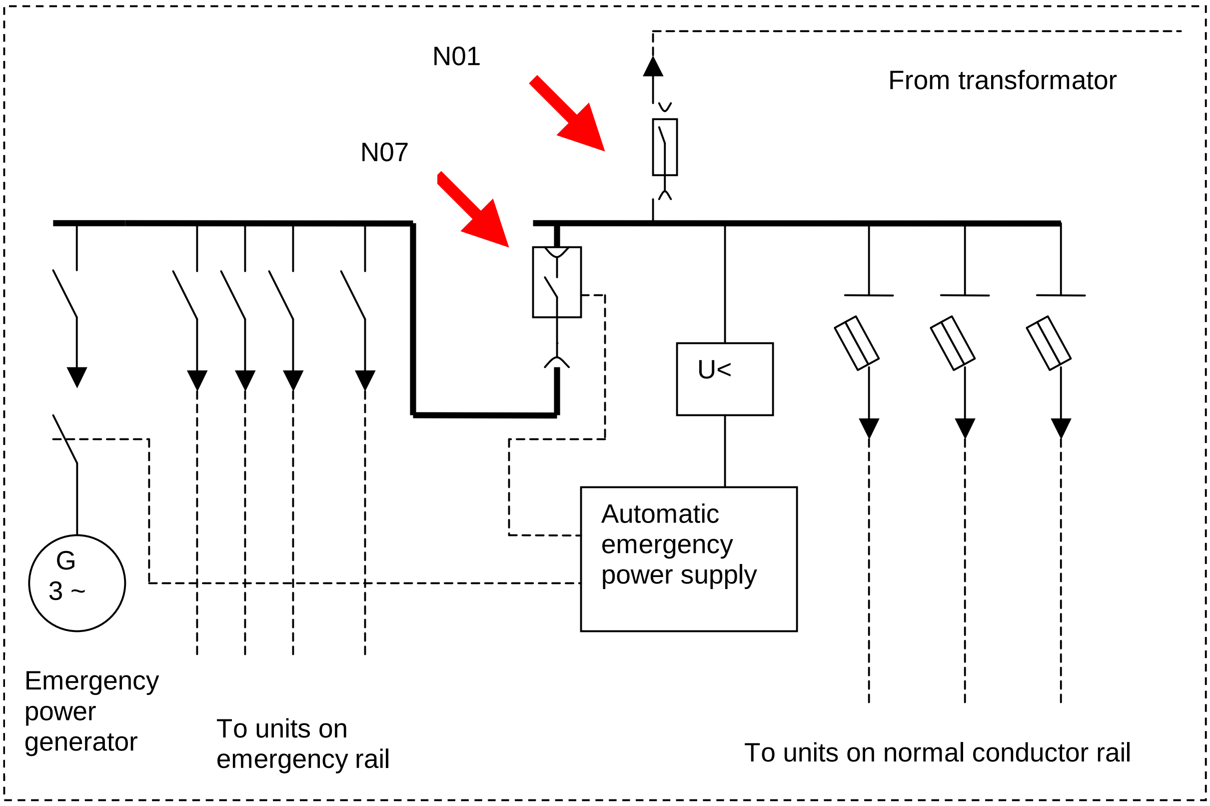
There were no environmental consequences according to the criteria of the European scale of industrial accidents.

The property damage resulting from the accident in the plant resulted to approximately 237.000 €. Production losses lasted for 5 weeks. The scale for the category economic consequences is estimated to 1.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

The major accident prevention policy with regard to power failure is based on the emergency power supply of the units necessary to prevent hazards. These units are especially the mercury pumps and the chlorine absorption unit. The electrolysers are expected to be out of operation during power failure.

The principle of the emergency power supply is shown in the following current network.



During normal operation the emergency conductor rail is supported by the internal power distribution, the switches N01 and N07 are closed. If the network monitoring registers a voltage dip and classifies the dip as failure, the N07 will open and the emergency power generator is started. On matching the connection conditions, the emergency power generator connects to the emergency conductor rail and supports the units with power.

After return of the power, there is an automatic synchronized changeover to the normal power supply. The automatic control synchronizes the emergency power supply with the internal net, closes N07 and switches off the generator.

This automation had worked for years, for example during a voltage failure on 21 July 2009.

On 23 July 2009, this happened: the voltage dip was registered by the network monitoring, the switch N07 was opened and the generator was started. But the emergency power generator was not connected to the emergency conductor rail, as the internal net had already returned. The opened switch N07 could not been closed, as the contradictory commands caused a blockade. The whole emergency conductor rail had no power, while the internal net was available.

The reaction of aggregates to voltage dips depend on different aspects as the size of the electric drive, discharge voltage, remanence and device specifications.

In this event, the medium-pressure compressor failed, while the low-pressure compressor remained operating.

Due to the failure of the medium-pressure compressor, the intensity for the electrolysis was automatically lowered to 6 kA.

The failure of the mercury pumps caused a break of the mercury surface covering the steel bottom of the cell, which is connected to the negative pole of the direct current. As a result, hydrogen was directly formed in the cell at the bare steel cathode. It was drawn together with the chlorine gas into the collecting pipe to the chlorine-processing unit, where it exploded in the low-pressure system of the chlorine processing.

The situation was complicated by the fact that some monitoring devices, which were not yet switched to uninterruptible power supply but were still connected to the emergency conductor rail, failed. These were measuring devices for hydrogen in the chlorine absorption unit, and for the Chlorine concentration after the absorption unit.

In addition, the 6 kA circuit was not monitored by the potentiometer. As a consequence, the operator could not get a complete and confirmed overview of the plant status. This is the reason, why a dangerous chlorine/hydrogen mixture could build up in the chlorine processing system for about 30 minutes. The probable sources of ignition were either an electrical sparking or electrical discharge in the cells or a spontaneous decomposition reaction due to the steam injector in the collecting pipe. After the first explosion in the collecting pipe, air was drawn in the low-pressure system by the compressor and caused subsequent deflagration and detonation.

A similar accident occurred in France in 1995 under comparable circumstances (electrical overload of a transformer, ARIA 22101). Other explosions due to an accumulation of hydrogen in the collection system of chlorine in Norway, Sweden, The Netherlands and France (ARIA 6442, 6443, 6444 and 10316) also highlight a lack of means for detecting hydrogen in the collected and processed chlorine (ARIA 14987).

ACTIONS TAKEN

An expert survey report was commissioned to clarify the facts leading to the accident and to derive the necessary actions to prevent such accidents in the future. This whole paper is based mainly on the expert survey report. The main recommendations were :

1. Optimisation of the control technology for the emergency supply in order to exclude blockades.
2. Design of the emergency power supply insuring a safety integrity level (SIL) 2 according to EN IEC 61508/61511.
    - Alternative 1: a redundant stand by set with a monitoring device in SIL 2 quality
    - Alternative 2: abandonment of emergency power supply in the safety policy

    Actions taken: the design of the emergency power supply in SIL 2 quality was not realizable. Instead, the redundant stand by set was implemented. Additionally the lack of emergency power supply is regularly regarded in the risk analysis.
3. Alarm of the failure of the emergency power supply and the mercury pumps in SIL 2, emergency shutdown in SIL 2
4. Visualization of the switching status of the power supply, completion of connecting control devices to uninterruptable power supply
5. Instructions for operating in exceptional situations

The implementation of the recommendations is surveyed by the competent authority.

LESSONS LEARNT

According to the expert, there may well be comparable power supply systems in other plants. He reckons the technical expertise concerning the power supply system drawn from this accident of general importance. The most important lesson we have learnt is that power failure should not be considered a binary event (voltage/ no voltage) in hazard and risk assessment studies. The consequences of very short voltage dips (30 ms – 200 ms) have to be considered likewise. When hazards due to power failure are possible, the emergency power supply should be designed in a quality ensuring a safety integrity level (SIL) 2 according to EN IEC 61508/61511. Alternatively the option of emergency power supply may be abandoned in the safety policy, requiring the appropriate risk analysis and plant design.

Action 4 gives evidence to the immanent problems when gradually improving existing plants. In this case, the switching cupboard for the monitoring devices had not yet shifted from the original emergency conductor rail to the uninterruptible power supply.

The recommendation 5 emphasizes the necessity of training operators for exceptional situations. To achieve this aim, two strategies were discussed. The expert recommended additional instructions. The company emphasizes on the training of detailed understanding with the argument, that no instruction could comprise all possible hazards.