Accidental spillage of a reaction mixture in a busy area

March 4, 2003

Clamecy – [Nièvre]

France

Projections
Chemistry
Reactor
Batch
Alkaline sulfone
Burst disk
Manufacturing tolerance
Fatigue at high temperatures

THE INSTALLATIONS IN QUESTION

The group:

A veritable "giant" in the chemical industry with annual turnover of 5.5 billion euros, the group employs 23,000 people throughout the world, enjoys a commercial presence in 150 countries and has a research and development budget of nearly 200 million euros.

The corporate body includes 9 different companies. The Clamecy site belongs to one of these companies which, with annual turnover of 620 million euros in 2003, is one of the world leaders in the detergent, cosmetics, agrochemical formulations markets and produces specialties for the industrial polymers and petrochemical industries.

The site:

The plant is located to the north of the Clamecy city centre, on the banks of the YONNE River and the Nivernais Canal. The establishment, classified as high-level SEVESO**,** is authorised with public easement (French regulations) for the storage and use of liquid toxic products (222 t).

The Clamecy site produces more than 400 fine chemistry specialty products. Its activity is divided between 2 hubs that meet the following needs:

- ✓ Organic chemistry: consolidation of soil, waterproofing, solvent, aerospatial-aeronautics, textile, hygiene, agriculture, petroleum products,
- ✓ Mineralogical chemistry: post-combustion catalyst, high-purity industry, colorants for plastic, cosmetics, and detergent.

The installation:

The accident involved the RAE 105 reactor of workshop F5 where the following products are manufactured:

- ✓ High temperature-resistant resins for the aerospace and aeronautical industries,
- ✓ Surface active agents for the detergent and cosmetic products industry,
- ✓ Dispersing agents for the agrochemical industry, and

Intermediate products for textiles.

On the day of the accident, the 12 m^3 reactor RAE105 was being used to produce GN base, which is used by the leather tanning industry. Manufacturing operations are discontinuous.

Operating principle:

Solubilisation of resol: Resol is rendered soluble in water through interaction with sodium bisulphite, soda lye and formaldehyde. The solubility obtained by fixation of the sulfonic methyl group CH_2SO_3Na also allows soluble alkaline crude sulfone to be obtained. It is then neutralized by sulfonic tetralene acid and formic acid, discoloured by a sodium bisulphite / formic acid mixture, then adjusted to the desired density.

Notably used in the manufacture of Bakelite, resol is a resinous substance obtained by sulfonation of phenol with sulphuric acid, neutralisation with soda lye and condensation with formaldehyde.

Operating procedure:

- ✓ Loading of reagents (soda lye 30%, sodium bisulphite and formaldehyde); the temperature of the environment after loading is approximately 60 °C,
- ✓ Heating (steam at 3 bar) up to 125 °C,
- ✓ Shut-down of the heating and increase in temperature up to 137 °C (+ or – 3 °C) by exothermy,
- ✓ The temperature is monitored by a local thermometer and the heating is restarted, as required,
- ✓ Salt content is monitored (target level: 50 to 52) by a sample being taken every 2 hours.

The complete phase takes place over a period of approximately 16 hours.

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

March 4, 2003 at 5.40 am: the burst diaphragm on reactor RAE105 burst and 5,000 litres of reaction mixture (soluble alkaline crude sulfone) was projected outside and spilled into 200 m^2 of storage space.

Workshop personnel, including the operator controlling the installation in question, informed the plant's monitoring station.

The firemen at Clamecy's main emergency response centre and the site spread neutralising products and absorbents. The substance solidifies at ambient temperature, thus enabling an external company to collect the residues and clean the ground soil.

The consequences:

The chemical substance expelled is not classified under the terms of the SEVESO directive and the accident had no sufficiently significant consequences to be rated on the European scale for industrial accidents.

However, personnel who could have been located in the zone of the burning and corrosive discharge could have been seriously injured in the accident. As luck would have it, the accident occurred very early in the morning when fewer employees were at the site. In addition, the storage area's retaining basin was able to contain the product, thus minimising the effects on the environment.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Circumstances:

March 3 at 2 pm: reactor loading operations (30% soda lye, sodium bisulphite, formaldehyde)

2.40 pm: start of heating - temperature increase to 125 °C (3 bar).

Once the heating was shut down, the exothermic reaction allows the temperature to rise to 137 °C. The operator monitors this temperature on a local thermometer and can turn the steam heating back on as required.

A sample is taken every 2 hours (salinity content) in order to monitor the reaction's progress. All measurements were in compliance with estimates until the next day at 4.30 am, i.e. 12 hours after the start of the solubilisation process.

March 4 at 4.15 am: upon arriving at his workstation, the operator noted a temperature reading of 140 °C and pressure between 2.4 and 2.6 bar.

4.30 am: the cure index measured had been constant for 2 hours.

5 am: the reactor was heated once again to maintain pressure at 2.5 bar.

5.30 **am**: the pressure was oscillating between 2.4 and 2.6 bar, the temperature was 139 °C.

5.40 am: the newly replaced graphite burst diaphragm, calibrated at 3 bar, ruptures; 5,000 litres of reaction mixture (soluble alkaline sulfone) was projected outward and spilled into the 200 m^2 storage zone protected by retaining catchpit.

Upper part of the reactor: mixer and burst disk discharge line (source: DRIRE Bourgogne)

Hypotheses:

- ✓ **Runaway reaction (increase in pressure): this hypothesis was very quickly dismissed** as the operator had just checked the pressure and temperature which were normal and the salinity index practically constant, which indicates that the reaction was nearly completed.

- ✓ **Incorrect installation of the burst diaphragm when replaced: this hypothesis was also dismissed** as the installation procedure was performed in accordance with the supplier's instructions (particularly the tightening torque); the diaphragm was installed in the proper direction. No trace of cracking or foreign bodies along the gasket plane, or other anomaly was reported.

- ✓ **Leak of the heating coil (steam): this hypothesis was dismissed;** no leak was detected during post-accident testing.

- ✓ **Failure of the steam regulator: This hypothesis was also dismissed** because the temperature was normal (139 °C) just a few minutes prior to the rupture an d the regulator was operating after the installation had been put back into service.

- ✓ **Insufficient burst diaphragm rupture pressure**: the recently replaced burst diaphragm came from the same batch as the previous one. It was installed in compliance with the supplier's installation recommendations. GN base production is the 1st operation performed in reactor RAE105 since the diaphragm was replaced within the framework of the installation's preventive maintenance program. **The manufacturing tolerances, as well as the drop in the material's efficiency due to fatigue and the operating temperature, were not taken into account when the diaphragm was dimensioned.** These elements confirm the hypothesis of a burst diaphragm calibrated at a burst pressure too close to the reactor's operating temperature.

As a result, the operator maintains that the probable cause of the accident was a burst diaphragm that was calibrated too close to the reaction's service pressure resulting in its rupture by fatigue.

ACTION TAKEN

2-tier action plan:

- ✓ **Placement of the reactor back into service**

The reactor's design pressure is 5 bar at 20 ℃. The experts deduced that its maximum service pressure must not exceed 4.8 bar at 140 ℃.

The installation was modified:

- High-pressure alarm with a threshold at 3 bar.
- Exhaust valve calibrated at 3.5 bar.
- Burst diaphragm calibrated at 4.8 bar maximum at 140 ℃.
- Discharge of the burst diaphragm's discharge conduit directed temporarily to a hermetic zone that is not frequently used.

Furthermore, the operating instructions were updated (T and P indicated on the existing log sheet).

- ✓ **Verification report of static safety devices**

During 2003-2004, a complete report on valves and burst diaphragms associated with the reactors and utilities was drawn up at the site. The study cost 50,000 euros. Nearly 250 devices were recorded and inspected, as well as the collection of their discharges. Their adequacy with the equipment and the processes was also checked. Analyses were conducted on the reactions implemented in order to determine the normal operating conditions and the possible deviations: runaway, overheating… To this end, the following conclusions were made:

- ✓ Only the manufacture of GN base is performed under pressure during normal operation at the site.
- ✓ Correct dimensioning (pressure and diameter) of the diaphragms and valves was determined. Some of these devices were changed.
- ✓ None of the burst diaphragms are connected to a collection network at the Clamecy site. The diaphragms of workshop F5 were equipped with a catch-tank retaining system. The other workshops, not presenting any particular risks in case of a diaphragm rupture, were not equipped in this manner.

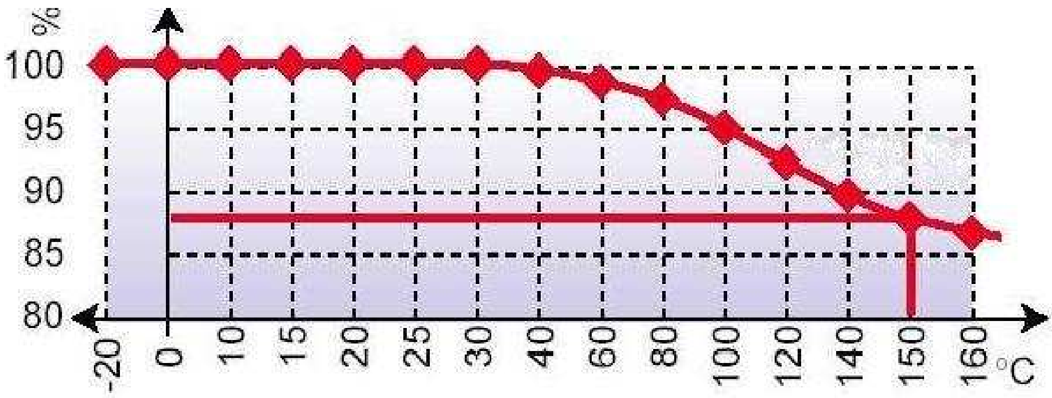
LESSONS LEARNED

The main lessons learned from this accident concern the following points:

- ✓ The importance of correctly installing the burst diaphragm: installation direction, number of screws, tightening torque…
- ✓ Releases from the burst diaphragm are to be collected in confined areas and without risk for personnel.
- ✓ During safety device design, accounting for not only the manufacturing tolerance, but also its loss of efficiency through fatigue and loss of efficiency under special conditions (in this case, the temperature).

In this case:

- ✓ **Temperature 140 °C**. According to a chart published by the diaphragm's manufacturer, the burst pressure at 140 °C is equal to 90% of the nominal pressure given for 20 °C.



- ✓ **Manufacturing tolerance +/- 10%:** this tolerance generally varies between 3 and 10% depending on the nature and the price of the diaphragm.
- ✓ **Fatigue coefficient 85% of the minimum bursting pressure.** On a batch process, a diaphragm is subjected to repetitive stresses that weaken it. The fatigue coefficient or service rate enables this phenomenon to be taken into account. It can vary from 70 to nearly 100% depending on the type of diaphragm.

Thus on the incriminated diaphragm, the **nominal burst pressure of 3 bar at 20 °C** is no more than 2.7 bar at 140 °C with a tolerance of +/- 10%. In the unfavourable case, the burst pressure of the new diaphragm is thus 2.43 bar. After being commissioned, however, and subject to fatigue, **the diaphragm may rupture beyond a pressure in the reactor equal to 2.07 bar**.