Toxic gas cloud emanating from a TiO_2 ore treatment plant

September 3rd and November 9th, 1999

Calais (Pas-de-Calais)
France

Electrical failure
Sulphur oxides
Organisation / deficient process controls
Check valve
Automated device
Washing tower
Self-sustaining reaction

THE FACILITIES INVOLVED

The site:

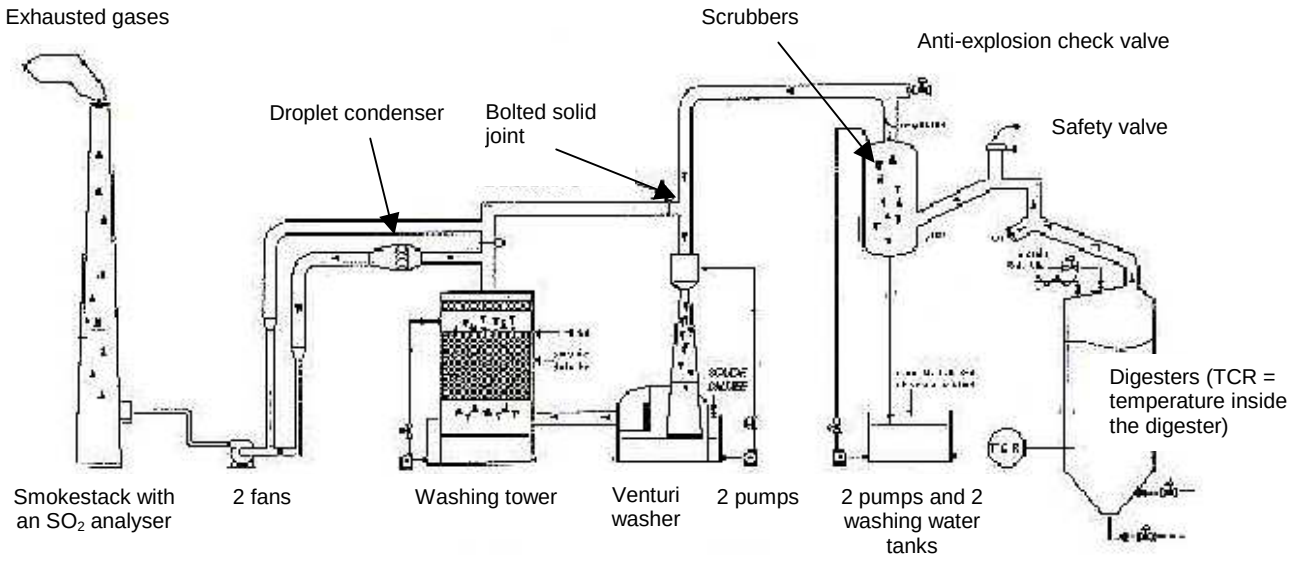
The company, with a workforce of 420, was manufacturing titanium dioxide pigments.

The plant was set up with two units, one dedicated to the actual production while the other came online in June 1993 to treat aqueous effluent generated at the site.

The unit involved:

The so-called "digestion" facilities responsible for both accidents were located inside the production unit.

This "digestion" process consists of exposing the titanium ore to a sulphuric acid (H_2SO_4) attack. The reactive gases formed (SO_2, SO_3 and droplets of H_2SO_4) are removed by means of a water wash (using scrubbers), followed by two soda washes (Venturi washer and tower).



Treatment of digestion gases (Source: site operator)

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The September 3rd accident:

Around 5:25 am, the automated device controlling the treatment of atmospheric discharges emanating from the digestion unit malfunctioned; this event triggered a shutdown of the gas treatment process for the entire operating unit. The untreated gases exited the building via a check valve installed on the roof, at which point the acid attack reaction, self-sustaining beyond a certain temperature (exothermicity), could not be halted.

The quantities of gas released were estimated at 600 kg and the discharge lasted 45 minutes. An unpleasant sulphur oxide cloud was noticed by a passer-by on Calais' eastern ring road. Once alerted, local fire-fighters showed up on the scene around 5:45 am.

The operator was unable to access the toll-free phone number set up for such purposes by the emergency response network.

The November 9th accident:

A power outage lasting from 8:47 to 9:27 am caused the gas suction and treatment system to stop operating. As was the case for the September 3rd incident, the untreated gases exited the building via the check valve. Gaseous discharges formed a thick cloud (containing approx. 600 kg of gas) that neighbours began noticing and reporting between 9 and 9:30 am. Children at a nearby school complained of breathing problems.

Consequences of these accidents:

Several individuals reported mild malaises during the November 9th incident.

On both dates, one gas digestion cycle load was lost (accounting for 600 kg on each occasion). Several million francs were expended to modify the installations accordingly.

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:

Accident on September 3rd, 1999

Accident on November 9th, 1999

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

A total 600 kg of gas (SO_2, SO_3) were released during each accident. Considering that the plume contained 100% sulphur trioxide, whose *SEVESO* threshold equals 75 tons, the Q1 parameter remained below 0.1% of the *SEVESO* threshold; consequently, the overall level of the "hazardous materials released" index reached 1 in each accident.

The "human and social consequences" index was scored a 0 for the September accident, as no injuries were reported, but climbed to a 2 for the November accident due to schoolchildren being incommoded by exposure to the cloud.

The "environmental consequences" index could not be rated due to a lack of sufficient information.

Likewise, the absence of information prevented rating the "economic consequences" index for both events.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

During the first accident, the automated control mechanism failed in the gas digestion and treatment plant unit, subsequent to a short circuit due to the poor state of repair of an electrical cabling system.

The second accident was triggered by a general power outage.

The gas treatment unit (equipped with extractor fans and pumps) shut down in both cases, raising digester pressure according to a reaction that could not be halted. The digester's safety valve was then opened, causing the discharge of untreated gases and acid droplets into the atmosphere.

ACTIONS TAKEN

In order to avoid recurrence of such events, the classified facilities inspection office requested that the company conduct a detailed analysis of the accident causes within a week, then within 2 months to have updated the site's safety report to take into account the electrical supply interruption, water supply distribution and piping, and the proposal for more suitable means of prevention (electric generating sets, washers, etc.), as well as to have installed high-efficiency detection systems even when the power supply shuts down.

LESSONS LEARNT

These two accidents highlight that the process implemented was inadequately controlled, with a glaring shortcoming on the part of the facility operator who had not introduced sufficient means to remedy the site's power supply defect. The safety report revealed a number of oversights. Also, the automated device malfunction had not been anticipated.

Several measures were adopted by the operator subsequent to these accidents:

- √ Backup power supply for the site via a 20 kV line operating in automatic mode
- √ Internal electrical supply backup units for a number of key installations (pumps, fans, automated device)
- √ Automated devices: different automation cards for secondary equipment (pumps, fans)
- √ SO_2 recording backup (as the main recorder was down during both accidents after just 20 min of operations).

Nonetheless, the problem of a widespread automated device malfunction had not been resolved a full 8 months after the accident.

In this same vein, the installation design had not been revised from an overall perspective. The reaction triggered was in fact self-sustaining following start-up and could not be easily stopped. When operating in degraded mode, reactive gas may be released once the safety valve protecting installations opens; the quantity of available emitted gas is known with precision (600 kg) since this amount is directly proportional to the constant mass of the reagents introduced. Additional mitigation measures should have been planned and detailed in order to better control and "treat" this accidental gas release: adding a second treatment column and the associated automated equipment, gas collection at the valve outlet for subsequent treatment or, by default direct discharge aboveground via the plant's smokestack to help disperse the cloud.