Uncontrolled emissions subsequent to a decomposition reaction inside a dryer

19 November 2011

Lanester (Morbihan)
France

Fine chemistry
Drying
Pressure surge
Toxic emissions
Temperature regulation
Risk analysis
Crisis management
Safety measures –automatism
Common defect mode

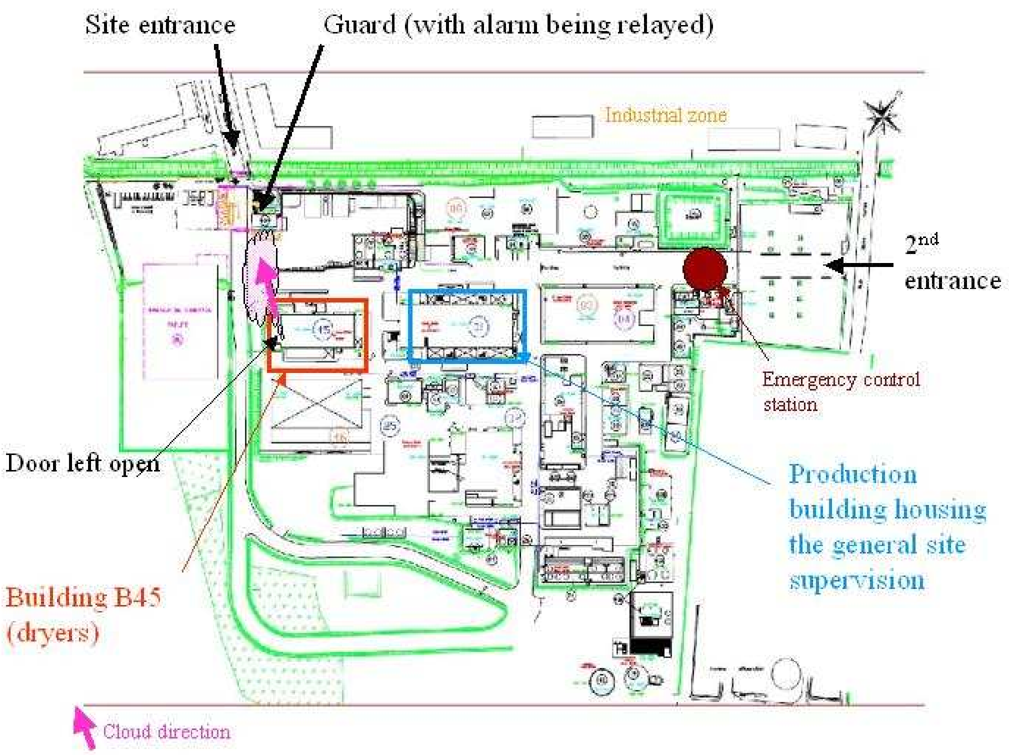
THE FACILITIES INVOLVED

The site:

This fine chemistry plant is situated in an industrial park within the Lorient metropolitan area; it is producing organic iodized products for pharmaceutical uses (medical imaging). This Upper-Tier Seveso site employs a workforce of approx. 220.

The closest dwellings are located about 150 metres from the building where this accident occurred.

Both the intermediate and final products involved are powdery. The batch-type (discontinuous) process includes drying steps for these various products. The B45 building, scene of this accident, is exclusively devoted to the drying of intermediate products.



The involved unit:

The B45 building housed five enamelled steel dryers with capacities ranging from 4 m³ to 6 m³: three so-called "rotary double cone" dryers (whereby rotational movement activates stirring); and two "screw" dryers (with stirring motion generated by rotation of an internal screw). The dryers were heated by circulating a heat transfer fluid inside their dual lining.

The drying operations were staged as follows:

- dryer loading with wet powder;
- vacuum pumping and gradual heating (temperature thresholds). A drying-cooling cycle could last more than 1 day (system managed by a programmable controller);
- cooling, followed by a gravity transfer.

Installed safety devices allowed halting the drying step and cooling the dryers upon detecting either a stirring malfunction, excessive temperature or a pressure surge. Cooling system availability was verified prior to initiating each drying operation. Both screw dryers had been equipped with a rupture disc, thus serving to channel discharge in the event of a pressure surge, as opposed to the 3 double cone dryers, none of which featured the same system.

The monitoring of drying operations had not been separately assigned to a full-time technician but instead was included among the tasks performed each shift by the production team, which conducted periodic verifications inside building B45. During periods with fewer onsite staff (nights, weekends, etc.), monitoring activity fell under general site supervision, centralised in the production building adjoining B45, and merely consisted of detecting an eventual triggering of an alarm or emergency shutdown. All alarms were relayed to the site's security office (Guard).

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

During the night of 19th to 20th November 2011, several dryers were running in building B45. The production of "DICOA" (an organic iodized substance with molecular formula $C_{16}H_{14}Cl_2I_3NO_5$) had been drying for a few hours in a rotary double cone type dryer with a capacity of 4 m³.

At 10:02 pm, a bursting sound rang out and an alarm was simultaneously activated in building B45, which was unstaffed at the time. This bursting was followed by the appearance of a pinkish cloud that spread outside the building via ventilation fans as well as a door that had been left open. The plume of smoke headed north and north-westerly, extending several tens of metres along the site's frontage road. According to witness accounts, this cloud was visible for around 30 min. The eventual DICOA decomposition gases were composed of diiode (I_2), hydrogen chloride (HCl), hydrogen iodide (HI), carbon oxides and nitrogen oxides. The cloud's pinkish colour was due to the presence of diiode.

The 18 employees operating the site at the time of this release were requested to assemble at the meeting point. The operator installed a water curtain in an attempt to attenuate emissions outside the plant.

The on-call manager arrived at the site by 10:20 pm. Fire-fighters, notified by neighbouring residents, showed up at 10:25. The decision to activate the external emergency plan was made at 10:58, at the behest of both first responders and the site operator.

Photograph of the cloud before its dispersion

Fire-fighter intervention wearing diving suits

Though it appeared at the outset that these emissions were due to product decomposition, a precise diagnostic of the accident (targeted installations, plus their possible evolution) was not immediately forthcoming since building access had been obstructed by the substances being released. Responders had to wear diving suits to survey the premises, during which they determined that the emissions had originated from a burst glass tube connected to the DICOA dryer, which was still being heated and whose contents had begun decomposing.

After an initial "blast" due to the burst tube, which was quite concentrated and visible, emissions were fed by further product degradation over the next three hours, i.e. the time required to identify the type of accident and organise emergency intervention with diving suits to shut down and cool the dryer. This mission was successfully completed near 1 am, and equipment cooling was periodically verified until 5 that morning. Around 5:30 am, the situation was deemed under control (i.e. emissions stopped, temperature in the dryer at 10°-12°C); the emergency plan was t hen lifted.

Airborne hydrochloric acid measurements at the site outlet did not reveal any abnormal concentration levels.

Consequences of the accident:

The initial mass of wet DICOA (solvent = water + ethanol) present in the dryer amounted to approx. 1.8 tonnes, i.e. on the order of 1.4 tonnes of dry DICOA. A portion of the decomposed product remained in the dryer (about one-third of the initial mass was found inside) and in building B45, whose walls, floors and ceilings had been covered by a pinkish deposit. The quantity released outside the site could not be accurately determined.

- Human consequences

No irreversible effect on human health was identified. Moreover, no personnel had been present inside the building when the accident occurred. The on-duty employee at the entrance and security office, located along the path of the plume, felt ill and was taken to hospital for medical clearance before resuming his shift.

Residents living within the emergency plan boundary were advised to remain indoors should the alarm be sounded; in reality, the alarm period lasted nearly seven hours.

Neighbours complained of eye and throat irritations. Foul odours were noticeable more than 1 km away.

Ioduria measurements taken among company personnel as part of an employee medical screening programme did not indicate the presence of any impact.

- Environmental consequences

At the facility site, the ground was contaminated (by iodine) over an area of approx. 250 m2 opposite the door left open. The contaminated soil was excavated and transported to an authorised dumpsite.

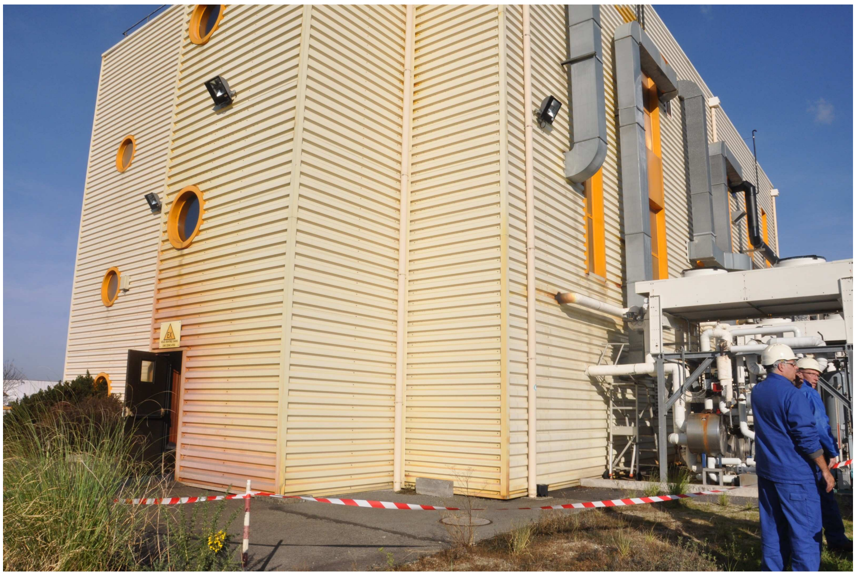
The soil analyses (for iodine and pH) conducted on 21st November beyond the site along the plume path suggested no presence of anomalies.

- Property damage

The effects of a pressure surge relative to the burst tube only caused localised damage: deformation of partition walls in the dryer room (positioned about 1 metre from the tube). The bursting pressure was assumed to equal 2 bar (i.e. the rated strength given by the supplier). The building cladding, just 3 metres from the burst tube, was not subjected to any damage, nor were any other parts of the building. The enamel on the affected dryer was however damaged.

A major clean-up effort was required inside building B45 due to the presence of deposits (see photo).

The dryers were restarted in December 2011 after verifying their structural integrity and a recertification procedure, with the exception of the defective dryer, which was not placed back in service until July 2012.



Traces of reddish deposit on building B45 - Source: DREAL Environmental Agency (Brittany)

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 quantity of substances escaping from the dryer was estimated at 1 tonne, of which more than half was iodine. As a result, the "Hazardous substances released" index reached level 1 or 2, depending on the form of iodine in the emissions (%HI vs. %I2).

The overall "Human and social consequences" index was scored a 2 by virtue of the advisory issued to neighbours to remain indoors in the event of emergency plan activation (some 150 single-family homes were included in the plan perimeter).

The "Environmental consequences" index did not reach level 1, given the limited surface area of polluted ground.

The total amount of property damage and production losses was not provided by the plant operator. Only the cost of direct damage (i.e. premises and machinery: replacement and/or repairs) was announced on the order of €800,000; hence, the "Economic consequences" index was at least equal to 2.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

This accident arose subsequent to a malfunction in the drying temperature control process:

Communication breakdown between a relay managing the drying process sensors and the programmable controller assigned to regulate temperature

⇩

The controller did not receive appropriate information regarding the temperature reached

⇩

The controller continued to order heating of the thermal fluid, which in turn heated the dryer

⇩

The temperature reached became excessive, causing the DICOA substance to decompose

⇩

Pressure surge inside the dryer, leading to bursting a glass tube connecting the dryer with the vacuum pump

⇩

Release of a portion of dryer contents inside building B45, and then to the outside

The a posteriori diagnostic carried out revealed a deficiency on an electronic component of the designated input/output head (manufacturer's defective equipment).

Given that the dryer security system for a high temperature or pressure reading had not been set up independently of the malfunctioning operating system (i.e. same relay and controller as for temperature regulation), the dryer system proved ineffective. Detectors likely sent information that a high level had been reached, but since this defect stemmed from the relay, the information was not transmitted and thus did not trigger the alarm or an emergency shutdown.

Moreover, the accident occurred on a Saturday during a period with fewer personnel on the job and with less intensive monitoring of drying operations, i.e. limited to (deactivated) alarm verification at the site's supervision desk. Such a malfunction might have been detected prior to the accident by controlling the temperature curves, which displayed an abnormal profile (temperature had remained blocked for the 4 hours leading up to the accident).

ACTIONS TAKEN

The local Prefect issued an emergency order on 22nd November making dryer restart contingent upon the plant operator's submission of an accident information report and implementation of remedial measures to avoid a repeat occurrence. This order also insisted upon the fact that certain priority actions that should have been applied immediately upon detection of an event capable of affecting a third party or evolving into such an event were in fact introduced belatedly, especially regarding the notification of rescue services, the activation of the emergency plan siren and insuring that the rest of the operating facilities stay in a safe mode…

The following measures, with a direct bearing on the accident, were adopted by the operator:

- revision of the safety report relative to dryers;
- installation, for each dryer, of a cabled safety switch for controlling the thermal fluid temperature that remained independent of the controller, hence reaching a high temperature level automatically shut down the heating;
- installation, for each DICOA dryer, of a second cabled safety switch to control powder temperature inside the dryer, in which case reaching a high temperature level also caused the heating to shut off;
- introduction, on each dryer input/output relay, of a continuous control to ensure open lines of communication with the controller (triggering of safe mode in the event communications were disrupted);
- modification of the monitoring procedure for drying operations;
- scheduling of a second assessment of the independence of safety systems throughout the entire site;
- organisational improvements in order to better respond to priority requests in the event of an accident, i.e. personnel evacuation, notification of the local population and emergency services, transition to safe operating mode;
- supply of Dräger tubes to determine airborne iodine concentration and thus facilitate management of an accidental event involving iodine;
- creation of a backup supervisory and control station in case access to the primary station has been blocked. A third station had also been planned;
- overlapping of essential functions performed in the entrance and security office (e.g. communications, inventory of protective gear, gate opening/closing), in the event this office has been rendered inaccessible;
- revised layout of emergency shutoff switches on the dryers and their function (e.g. turn off drying, but retain the stirring operation, ventilation cut-off, injection of coolant).

The operator had also anticipated process modifications in order to reduce risks at the source by means of eliminating DICOA drying (e.g. improved spinning efficiency, use of slightly wet DICOA).

Other measures, decided subsequent to the safety report revision, were either adopted or planned:

- for each dryer, installation of a second backup heating cut-off valve, dedicated to the cabled safety switch controlling the thermal fluid temperature;
- a 3-metre elevation of the rupture disc outlet on screw dryers, for the purpose of minimising ground concentrations
- modification of the heating sequence for DICOCl, another intermediate product, after analysis of this step's criticality;
- placement of a flooding device on each dryer: a fitting that made it possible to connect a water pipe so as to ensure rapid cooling (however with the need for human intervention).

At the Prefecture's urging and with Mayoral backing, the operator financed the installation of an alarm and phone information system to benefit neighbours, by offering the possibility to simultaneously send instructions to all local residents on the protocol to follow or information messages regarding the evolution of an accident.
.

LESSONS LEARNT

This accident has underscored the following points:

- The independence of process safety barriers is critical, especially with respect to events capable of causing the kind of accident these barriers are supposed to prevent or mitigate. In the present case, the system intending to place the dryer in safe mode when a high temperature is reached actually malfunctioned by being routed onto the transmission channel whose deficiency led to the accident in the first place (common defect mode);
- This accident offers a reminder of the care required to analyse risks and justify the hypotheses derived, as regards identifying the most feared events and selecting hazardous phenomena for input into the detailed risk analysis. The scenario involving a pressure surge and bursting inside a dryer had in fact not been listed in the safety report as potentially leading to effects offsite: this scenario had been rejected on the basis of a preliminary risk analysis. Moreover, such a decision could explain why the safety barriers installed around the dryers, specifically the high temperature level, had not received the same attention (i.e. an assessment of system independence) as those found to be correlated with a major accident;
- Special attention must be paid to periods when plants are operating with fewer staff members, to ensure that safety conditions remain at the same standard and moreover that the alarm and operational response to an accident are always quick and appropriate;
- Plant operators must be prepared and organised to relay an alarm very quickly to the appropriate rescue services and local population in the event of an accident displaying apparently uncontrolled effects or an incident that can evolve unfavourably due to rapid kinetics. Operators must therefore wisely integrate their responsibility to activate the emergency siren as circumstances dictate. The decision-making processes introduced within the scope of Internal Emergency Plans may prove too long in comparison with the kinetics of rapidly-developing hazardous phenomena. During this accident, the internal plan was not triggered before the external plan (1 hour after the event). The suitable training, drills and delegation of authority must also be provided by management to staff members designated to make fast decisions, e.g. during slack periods with fewer staff and when managers are absent from the site. One difficulty lies in the fact that since such incidents are (and fortunately so) most often of minor severity, both the organisation and practices have tended to focus on "removing doubt" rather than relaying an alarm quickly to the outside world;
- Whenever an accident occurring at a facility requires evacuating the entire workforce to the meeting point, questions arise over the safety conditions under which ongoing processes are conducted in the absence of onsite technicians. This issue must be anticipated (by deciding on the organisation to implement, identifying critical installations or operations to be rendered safe as a priority, i.e. even before leaving the workstation);
- The concern over maintaining installation control capacities in the event of an accident must also be anticipated, whether this entails intervening on the damaged installations or ensuring the safety of processes still ongoing. This emphasis could, for example, lead to protecting the premises housing the supervisor's station or adding a second station. During this accident, access to the supervisory posts (in building B45 itself and the adjoining main production building) had been obstructed by their location in an exclusionary zone, i.e. special gear (a diving suit) was required to obtain access. This situation may help explain the time delay before dryer cooling (3 hours);
- In addition to toxicological data, it is beneficial to be aware of odour thresholds for substances potentially released in case of accident, notably in order to facilitate the understanding and communication of health impacts. The lack of such impacts, despite odours perceived beyond 1 km from the site, must be justified;
- Administrative agencies also need to ensure the operational viability of their organisations in a crisis management context. Specifically, the external emergency plan called for informing the local population via the France Bleu Breizh Izel radio station: it turned out that this station was off the local airwaves certain times of day, including when this incident struck. For this reason, a phone-based information system was introduced as a follow-up measure;
- Risk prevention concerns need to be incorporated as of the installation design phase. Double cone dryers are not easily equipped with a device that allows channelling gases generated from an eventual pressure surge, whereby controlling discharge conditions allows reducing potential soil impacts. Furthermore, special attention must be paid to fragile components (glassware) in those devices capable of undergoing pressure surges.