Emission of dangerous substances in a surface treatment facility

March 20th, 2002

Issoire [Puy-de-Dôme]

France

Gazeous release
Metallurgy
Pickling
Fluoronitric acid
Aluminium
Exothermic reaction
Equipment breakdown
Periodic control
Evacuation

THE INSTALLATIONS IN QUESTION

The site

In 1939, the company is located on the outskirts of the city of Issoire, in the extreme northern part of the industrial estate, along the Paris - Nîmes rail line and the A75 motorway.

The company specialises in the die-forging of titanium and light aluminium alloy parts.

The site currently employs 350 individuals and produces approximately 2,000 tons of parts per year.

The plant primarily includes the following equipment:

- The forge: cutting of the metal, die-forging or forging of the products, heat treatments,
- Machining: pre-machining of the parts produced and die making,
- Inspection: final pickling and anodising (aluminium alloys), inspections and shipments.

The unit concerned

The accident took place on one of the two surface treatment lines, and more precisely on the control pickling line which is made up of 21 tanks made of stainless steel or composite material, each having a capacity of 6 m³ with a useful volume of 4.6 m³.

Photo DRIRE Auvergne

This line features specialized modules for:

- treating aluminium alloys: pickling parts after heat treatment (for the removal of the silica based product favouring this operation); the aluminium alloy parts undergo 3 successive pickling operations;
- treating titanium alloys: final pickling after heat treatment, one single pickling operation is foreseen for this type of part;
- the chrome anodising treatment for detecting faults (cracks) in aluminium alloy parts (entirely finished parts).

The treatment tanks are aligned and served by a travelling crane that transports the parts to be treated in baskets, for the small parts, or specific supports for the long parts. During the process, the treatment tanks are covered and connected to a single manifold connected to 4 stacks, each equipped with a 24,000 m³/h suction unit.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident

On March 20th, around 10:30 am, an operator was stripping aluminium aircraft fishplates (parts designed to connect the wing to the fuselage) in a cold aqueous solution of 15% pure nitric acid and 5% fluorohydric acid (by volume)[1]. The 4 parts, weighing 200kg each and measuring 2.50 m long, were placed on their special support and immersed into the treatment bath using the travelling crane. Upon attempting to remove the parts from the bath 10 minutes later, the operator noted that one of the two hoists did not operate. A maintenance technician intervened using a platform on the traveling crane's electrical control cabinet, located above. His action on the synchronization of the hoists did not repair the faulty equipment. The part support structure became unbalanced and the 4 fishplates became blocked in the bottom of the tank preventing the partly immersed load from being lifted out of the fluoronitric acid solution.

Photo DRIRE Auvergne

[1] *Bath volume 4,630 l, containing: 1,200 l of 60% HNO3, 580 l of 40% HF, and 2,850 l of water*

Under the responsibility of foremen, operators from the Control Department, equipped with appropriate protective gear (masks, overalls, gloves and boots), began transferring the bath to a mobile backup tank designed to hold spent solutions. The pumping speed turned out to be insufficient and, while only 1,600 l had been transferred, an exothermic reaction began between the treatment solution and the aluminium, generating a significant gaseous release into the workshop. The operators attempted to control the reaction by cooling the bath with a fire nozzle; this action proved inefficient.

At 11.00 am, the facilities were evacuated and the public emergency services were informed.

At 11.30 am, the evacuation procedure was expanded to all personnel at the establishment and an safety perimeter was set up at the request of the firemen.

Around 12 pm, a mobile chemical intervention unit arrived at the site.

Around 1 pm, the neighbouring plant (company restaurant, shops and services, involving approximately 450 people) located downwind was evacuated; traffic on the A 75 motorway was simultaneously restricted.

At roughly 3 pm, the firemen of the chemical unit donned hermetic suits in order to handle the incident. The temperature of the acid batch rose to 102° C. After diluting and lowering its temperature by adding water to the tank, the firemen continued the transfer operations started by the plant employees. The operation was completed at 4.30 pm.

Atmospheric pollution measurements conducted by the emergency services using Draegger equipment in the immediate area surrounding the shops and on the neighbouring plant site, then around 5.30 pm in the pickling shop were negative. The pickling line's air extractors remained operational, without creating dangerous fluoride or nitrous concentrations on the exterior on the facilities.

At 5.40 pm, the personnel of the neighbouring plant returned to their facilities and the A 75 was reopened.

At 9 pm, the establishment's stamping activity started up again, except for the Inspection Pickling shop.

The consequences

Three of the company's employees were affected and were admitted to the Issoire hospital; they were released around 8.00 pm.

From the environmental standpoint, all of the checks conducted by the firemen showed that there were no gaseous emissions harmful to the air quality of the surrounding area. Furthermore, the cooling of the treatment tank did not cause it to overflow and there was no consequence of the quality of the water released. The natural environments, fauna and flora were not effected by this incident.

In terms of equipment, the accident caused only minor damage. Only the treatment tank was damaged due to temperature increase. The fluoronitric solution transferred to the back-up tank was treated in the site's treatment plant. The operating losses of both the establishment and the partially evacuated facility next door were evaluated at approximately 305,000 €.

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, based on the information available.

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

The level 3 given to the human and social consequences is due to the evacuation of 450 individuals during 4h30 (parameter H7).

The losses of production for both companies are estimated at € 305 000, the indicator for the economic consequences is at least at level 1 without information about the financial cost apportionment between each one (parameters €16 and €17).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

At the request of the labour inspectorate, a verification of the travelling crane was conducted by an recognized organism, different from the one that habitually performs the operation. A brake failure on hoist No. 2 was diagnosed. This malfunction, followed by the blocking of the load of aluminium pieces in the acid treatment bath during intervention by the maintenance department, caused the subsequent exothermic reaction and gaseous emissions.

ACTIONS TAKEN

The day following the accident, the labour inspector and the CRAM engineer attended a meeting of the establishment's CHSCT (committee for hygiene, safety and working conditions).

The operator modified the specific load supports of the same type that were used when the incident occurred, by equipping them with axial stops preventing parts from shifting should the load become unbalanced.

The surface treatment line was authorised to continue operations on March 25th, following the repair of the travelling crane and the tank.

A Prefectoral order of June 27th required the manufacturer to update its danger study, particularly in terms of the following points:

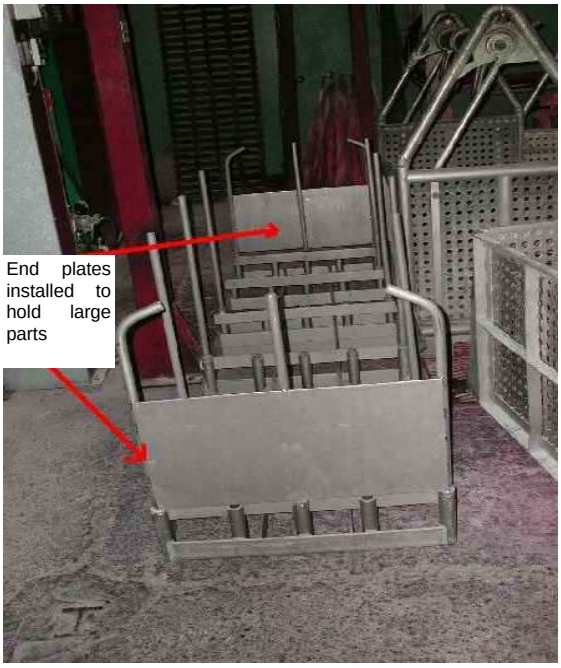


Photo DRIRE Auvergne

- the modifications made in the design of the units and in their operation since the initial authorisation,
- the physical and chemical characteristics of the products used or stored, while integrating the last known studies, particularly for hydrofluoric acid,
- the analysis of significant accidents involving this type of installation,
- the type and consequences of a possible accident on the units, with the definition of precise reference scenarios,
- specific measures to reduce the probability and the effects of accidents.

Measures to prevent and minimise the risks

Following this study, in addition to the modification of the baskets, the operator agreed to undertake the following actions:

- periodic verification of the hoists (internally and by an approved organisation),
- installation of a visual and audible alarm when the normal operating temperature is exceeded,
- installation of a system to ensure gravitational bath drainage of nitric and fluorornitric acids into an underground tank, thereby preventing a runaway,
- use of a trolley with telescopic forks and a rotating hook to mitigate possible failure of the basket handling hoists,

Furthermore, in terms of the part removal incidents, the operator defined a maximum intervention time beyond which the workshops are to be evacuated and the public emergency services are alerted.

Additional analysis

After the accident of March 2àth and the protective measures taken at the time – the evacuation of company employees and those of the neighbouring facility, stopping traffic on the A 75 motorway – the danger study, despite the safety features implemented, also evaluated the potential impact of this type of chemical accident on the surrounding area, without the intervention of the personnel (the subsequent impossibility to remove the parts from the acid bath or to drain the treatment tank).

In order to characterise the maximum danger potential, the most penalising scenario, that is the thermal decomposition of the bath's acid compounds (disregarding the quantities of acid used to attack the metal, side reactions with the air, oxidations or local reductions) were examined.

The exothermic reaction of the fluoronitric acid bath would lead to the emission of 345 Nm^3 (710 kg) of NO_2 and 307 Nm^3 (274 kg) of HF. The following characteristics of the releases taken into account:

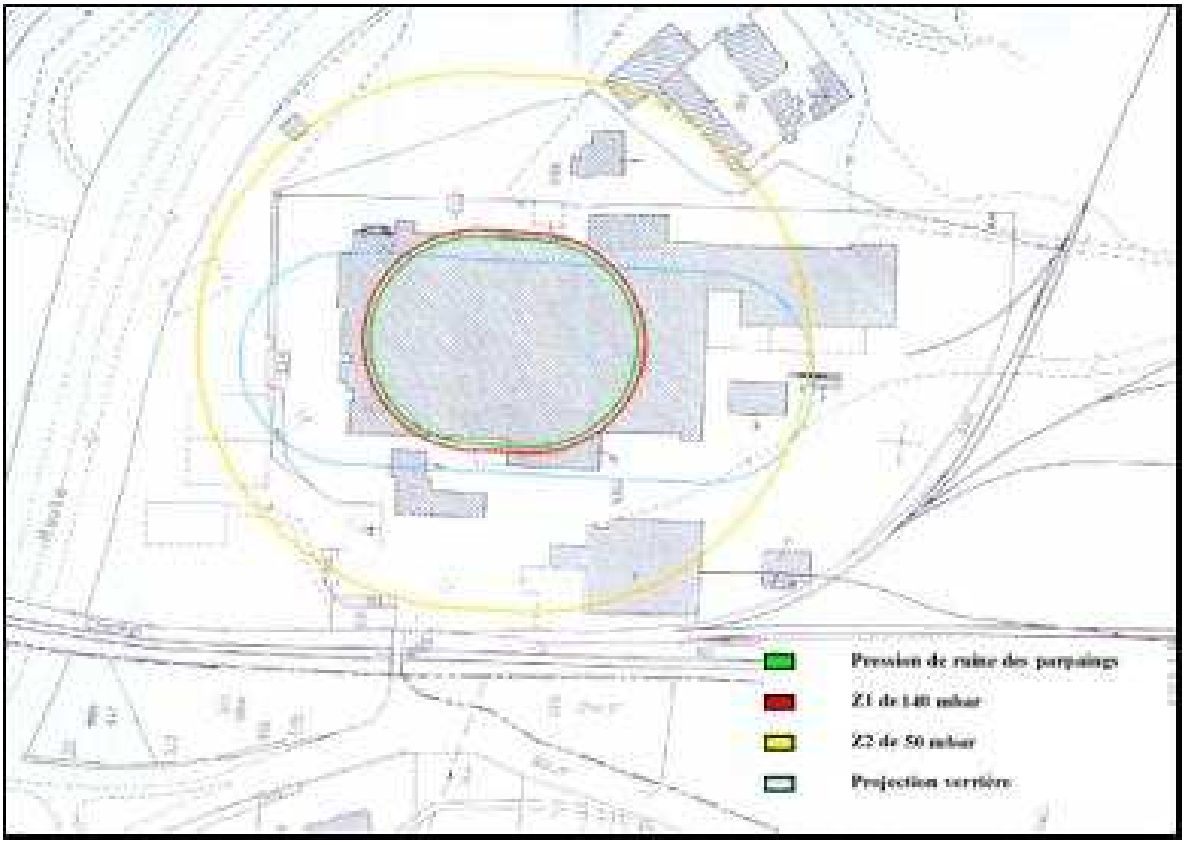
Pollutants	Total mass flow	Emission type
NO2	65.7 g/s (i.e. 16.42 g/s per stack)	Recording over 3 hours
HF	25.4 g/s (i.e. 6.35 g/s per stack)	Recording over 3 hours

The modelling of the atmospheric dispersion of these untreated effluents, which take the topography and the nature of the ground into account as well as the meteorological conditions that may be encountered on the site, has shown that the maximum concentrations, greater than 2 mg/Nm^3 for NO_2 and 1 mg/Nm^3 for HF, will be within a radius of approximately 250 meters around the stacks. The homes that are the closest to the site will thus be subjected to NO_2 concentration levels between 1 and 3 mg/m^3 and HF levels between 0.5 and 1 mg/m^3. *(See Appendices 1 and 2)*

In terms of toxicity, the reference threshold limit value (TLV) for nitrogen dioxide in the air of the occupational setting is 3 ppm (6 mg/m^3), that of hydrofluoric acid is 3 ppm (2.5 mg/m^3), for a period of 15 min. *(Refer to the INRS toxicological data sheets).*

According to the danger study, the threshold for irreversible effects for hydrofluoric acid, as it may be extrapolated (as per the Haber law) for a duration of 3 hours, is not reached both on the inside and on the outside of the stamping plant.

Beyond the chemical hazard potential, the study also estimated the risks presented by the explosion of the high pressure compressed air tanks (5 m^3 at 250 bar). The modelling particularly shows that nearly all of the manufacturing shops are within the overpressure zone (55 m) of 140 mbar (lethal effects) and that the 50 mbar zone extends up to 120 m from the source.



LESSONS LEARNT

In the metal surface treatment sector, a runaway reaction due to a part being in a bath for an extended period of time is not exceptional (fallen part, handling error, bath error…). Besides providing specific training to treatment line operators, the technical solutions proposed by the operator following the accident of March 20th must be able to be implemented on many units where the type of treatment bath and metals treated could lead to significant exothermic reactions and releases to the atmosphere.

It would appear essential that the operator evaluate the impact of releases resulting from a part being blocked in a treatment bath. The dispersion study conducted for the Issoire plant shows that the area immediately surrounding the unit in question (200 to 250 m) could be significantly effected in the case of violent thermal decomposition. *A posteriori*, the measures taken at the time of the accident, including the evacuation of plant employees and those of the company next door, and the shut-down of motorway traffic were a wise precaution in anticipation of a change toward this type of scenario.

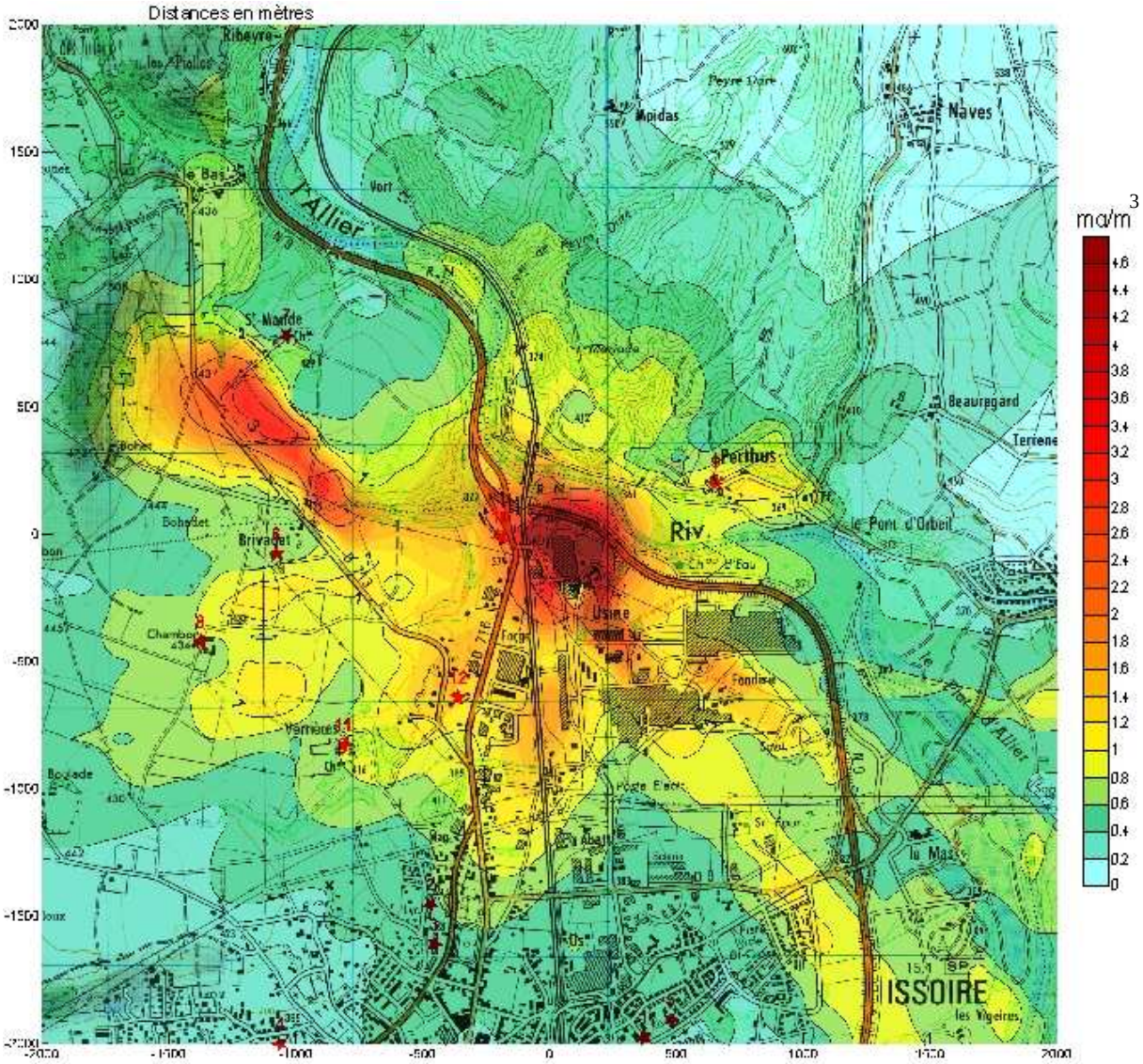
Furthermore, the danger study's evaluation of the effects of an explosion of the compressed air tank demonstrates the importance of not neglecting any scenario even those that concern equipment operating at regulated pressure.

Appendix 1:

Accident in a surface treatment facility
Issoire (63 - Puy-de-Dôme), France
March 20th, 2002

Simulation of the atmospheric dispersion of the accidental release of NO_2 vapours

Maximum NO_2 concentrations



Appendix 2:

Accident in a surface treatment facility
Issoire (63 - Puy-de-Dôme), France
March 20th, 2002

Simulation of the atmospheric dispersion of the accidental release of HF vapours

Maximum HF concentrations