

# Major Accident Occurrence in a Chemical Plant: Management and Technical Factors Emerging from the Inspection Activity

Romualdo Marrazzo<sup>a,\*</sup>, Paolo Bragatto<sup>b</sup>, Armando De Rosa<sup>c</sup>

<sup>a</sup>VAL-RTEC, ISPRA. Via V. Brancati n. 48 - 00144 Roma, Italia

<sup>b</sup>DIT, INAIL. Via Fontana Candida n. 1, 00078 Monteporzio Catone (RM), Italia

<sup>c</sup>DCPST, CNVVF. Largo S. Barbara n. 2, 00178 Roma, Italia

[romualdo.marrazzo@isprambiente.it](mailto:romualdo.marrazzo@isprambiente.it)

The presence of flammable gases and vapours in wastewater has been a well-known danger for decades, also due to the many accidents of the past, both in purification plants and in process plants. In hot work, in particular, it is essential to implement all the necessary measures (e.g. emptying, reclamation, insulation) to prevent sparks from igniting vapours and causing explosions and fires. Although these things are all well known, accidents of this type continue to happen even in the Seveso sites, moreover subject to strict controls. This article talks about a destructive accident occurred during hot work at a wastewater treatment plant in an upper-tier Seveso chemical plant. The paper highlights the lessons learned, in both organizational and plant terms, and the related return of experience for technical evaluation and control activities, starting from the consideration that the accident was originated during a relatively simple plant modification activity carried out by a third-party company.

## 1. Introduction

There are numerous experimental investigations in the scientific literature addressing ignition of vapour by sparks. In the presence of flammable vapours, a little spark is sufficient to trigger accidents with severe consequences for humans and assets. Even a little hot metal particle, originated by grinding, rubbing or friction is sufficient to ignite an atmosphere containing flammable vapours. The phenomenon has been known for decades and thousands of experiments was performed in the past with different metals and different vapour mixtures, aiming at understanding all details. A recent paper (van Wingerden, 2019) reviewed the most relevant experiments in this matter. The issue is well known and good practices and guidelines, including AICHE CCPS (2012), API (2002) and NFPA (2009), have been available for a long time, recommending the emptying, cleaning and insulation of tanks and pipes that may contain flammable mixtures, before to start maintenance interventions requiring the so called "hot works", which include cutting and welding. In the chemical and petrol industries in the last two decades, major accidents related vapour ignition by sparks are become less frequent in Europe. That is likely due to the European directives, including ATEX for the control of explosive atmosphere hazard, which addressed the improvement of technical measures in this field. A further improvement driver came from the Seveso Directive: for a couple of decades, the operators of major accident hazard establishments, driven by the Directives, have implemented systems of the "permits to work" PTW. An appropriate procedure to manage PTWs is essential to prevent accident maintenance interventions in process industries, but it has to be duly applied by contractors and operators and scrupulously verified by auditors. Hot works, in particular, must be addressed in appropriate way, in the framework of PTW system. According to a recent review (Yan et al. 2017), 27% of accident PTW related accidents involve hot works. The recorded accidents are due to the presence of the flammable and combustible materials in the item to be worked on or in surrounding atmosphere. Inappropriate organisation, communication and supervision are the root causes of these events. The lessons learned from the accidents contributed to the awareness of the operators, no less than the directives.

As discussed by Lambert and Woodward (2011), wastewater from chemical processes contain mixture of different materials, including flammables, and are a major threat, because, during cutting or welding intervention, vapours may be ignited by sparks. As discussed by Trávníček et al. (2022), these accidents are common in municipal sewer plants. In the US, the Chemical Safety Bureau CSB, investigated 13 hot work related major

accidents occurred, in the period 2001-2016 including municipal and industrial sites. CSB, in order to prevent these accidents, issued a Safety Bulletin, which provide operators an effective procedure to have safe hot works at tanks containing flammable materials (CSB 2010). In Europe, at Seveso sites these accidents are less frequent, but, albeit rarer, they continue to occur, despite regulations, guidelines and inspections. Thus, in the European database of accident at Seveso sites, there are at least two major accidents recorded in the decade 2010-20, triggered by hot works at wastewater tanks (ID=0911, ID=0958).

The paper discusses in the detail just the last event, happened in 2020 at a chemical site, upper tier according the Seveso classification. The method adopted to find the technical and organizational causes is discussed section 2. Section 3 presents the essential information on the accident. Section 4 shows the findings of the investigation. Section 5 provides the operators with a few practical suggestions. The last section tries to understand why the hazard related to hot works and flammable materials has been ignored, even though it has been for years present in regulations, guidelines and recommended practices.

## 2. Methods

In case of a major accident, the Legislative Decree 105/2015, the Italian implementation of Directive 2012/18/EU, imposes an inspection after the event. A commission is charged by Ministry of Ecological Transition (formerly Ministry of Environment), and it is made up by 3 members from: National Institute for Environmental Protection and Research (ISPRA - Istituto Superiore Protezione e Ricerca Ambientale); National Fire Brigades (CNPVF – Corpo Nazionale Vigili del Fuoco); National Workers' compensation Authority (INAIL – Istituto Nazionale Assicurazione Infortuni sul Lavoro). The inspection consists of collecting evidences through acquisition and verification of documentation, on-site visit and inspection on the state of the plants and equipment, interviews with workers representatives, occupational physician, internal staff and subcontractors. The commission investigates the dynamics of the event in order to learn lessons for preventing major accidents and mitigating their consequences, collecting information and data through the e-MARS (Major Accident Reporting System) database. The commission must prepare a final technical report, which states the analysis of the technical and organizational factors related to the accidental causes, the description of the dynamics and consequences of the event, with a focus on the corrective actions taken by the operator in reference to the Safety Management System (SMS) issues (Wood, M. 2018).

Reporting an event into e-MARS, on behalf of the European Commission, is compulsory for EU Member States when a Seveso establishment is involved and the event meets the criteria of a "major accident" as defined by Annex VI of the Seveso III Directive. The e-MARS database is a lessons learned database in accordance with the purpose stated in the Directive 2012/18/EU. The purpose of the e-MARS is to facilitate exchange of lessons learned from accidents and near misses involving dangerous substances in order to improve chemical accident prevention and mitigation of potential consequences (EU. 2020).

## 3. Site and Event description

The event consisted of an explosion of tank containing wastewater from batch production installation plant and subsequent fire in a chemical installation, located in a national chemical and petrochemical hub with a high concentration of major accident establishments.

These are the main characteristics of the accident: substances involved (greater than 5% of quantity in Column 3 of Annex 1 of the Directive 2012/18/EU (EU 2012); injury to persons (2 burned operators and 6 operators with hospitalizing injuries); management of emergency (evacuation, shelter-in-place, utility disruption and damage to real estate); immediate damage to the environment (according to Annex 6 of Directive 2012/18/EU); damage to property (on-site >2M euro; off-site > 0.5M euro).

### 3.1 Site and installation

The establishment is in an industrial area which is a national chemical and petrochemical hub with a high concentration of major accident establishments. There are vulnerable territorial/environmental elements within a two-kilometers radius of the site, consisting of: built-up areas, industrial/production activities, densely populated areas/buildings, services/utilities, transport, a rail network, an airport, port areas, vulnerable environmental elements (a protected lagoon), aquifers.

The establishment produces specialized chemicals used in the following sectors: cleaning, fine chemicals, paper, plastics, textiles, cosmetics, colourants. The establishment contains the following batch production plants: PM1 (inactive since 2003); PM3; PM4 and PM5; PM6.

Production installation PM6, where the event originated, can be used to synthesize the following, depending on market demand: iscotrizinol; palmeth-25 acrylate; PEG 1000 acrylic ester or (poly(ethylene glycol) diacrylate; methacryloyl ethyl trimethyl ammonium chloride homopolymer. Plant PM6 occupies a floor area of

approximately 90 m<sup>2</sup>. The apparatus is installed on a metal framework along with the apparatus belonging to plant PM4 and PM5.

As the event developed, systems and equipment pertaining to the other plants at the establishment became involved, including: a fiberglass atmospheric waste water storage tank (from which the event originated); products and chemicals on the establishment's forecourt stored in drums, intermediate bulk containers (IBCs) and tanks; pressurized (in line with the Pressure Equipment Directive) and non-pressurized (atmospheric) reaction vessels; tanker in the process of unloading (only the vehicle was affected, not the substance); installation process lines and piping.

### 3.2 Accident dynamic

The accident occurred in the morning (it was raining at the time the event occurred), when a fire broke out in the area of 2 tanks (TK 2.1 and TK 2.2), starting from an ignition of a flammable atmosphere during welding works, at a "batch" plant producing light stabilisers for the cosmetics market, which was in operation at the time of the event.

The accident occurred during modification works, carried out by an external firm (mechanical and electrical/instrumentation maintenance assistance), which was connecting tank TK 2.2, containing wastewater with flammable substances, to the wastewater network. For this work, a regular permit to work PTW and a hot work licence were issued, the latter having been issued following preliminary checks for the safe preparation of the area, in accordance with the applicable SMS procedure.

One hour before the event, the contracted workers had cut the pipe that was being worked on using an angle grinder and were preparing to place the new pipe, as planned, after having constructed the fitting where the pipe was to be attached. The event occurred when the previously cut pipe was being sealed, while an electric arc welder was in use. The external workers involved (two operators, with appropriate PPE) were on a work platform set up to ensure the safety of the activities in question, approximately 8-10 m above ground level. This work platform was approximately 5 m from the outer perimeter of tank TK 2.2.

The trigger gave rise to the explosion and catastrophic rupture of the atmospheric tank, resulting in the release of flammable vapours and the formation of a vast fire. In other words, an internal domino effect was generated, which subsequently affected all the units and plants of the establishment, in a succession of fires and explosions.

### 3.3 Involved substances

Based on past laboratory analyses, tank TK 2.2 was likely to have been holding wastewater containing the following hazardous substances: xylene, acetone, methyl acetate, ethanol, ethylbenzene, o-xylene and hexyl acid.

According to the notification form set out in Annex 5 Directive 2012/18/EU, the substance in question was present at the establishment under the following definition: WASTEWATER CONTAINING METHYL ALCOHOL, ETHYL ACRYLATE, WHITE SPIRIT, XYLENE. This substance has the following hazardous properties: P5c (hazard statement H226 - Flammable liquid and vapour); E2 (hazard statement H411 - Toxic to aquatic life with long-lasting effects). The amount directly involved in the event was approximately 130 tonnes, compared with a potential amount of approximately 144 tonnes (the tank's storage capacity).

At the time of the event, various types of dangerous substances were present at the establishment in the units affected (plants, units and storage on the forecourts), including: 2-ethylhexyl-4-aminobenzoate; Xylene; Acetone; Methanol; Ethyl acrylate; White spirit; Morpholine; bis-Aminopropyl ethylenediamine; tert-Butyl hydroperoxide; tert-Butylamine; Ammonia; Diisopropylamine; Xylenic mixture; waste EWC 160305 'Organic wastes containing hazardous substances'; wastes, decontaminants, washing mixtures.

## 4. Results

The technical and organizational factors related to the accidental causes, the consequences of the event, with a focus on the corrective actions in reference to the SMS issues, are described below, as they result from the application of the method referred to in section 2 of the paper.

### 4.1 Causes description

The accident occurred as a result of modification interventions that were being carried out by a third company, which was modifying a connection between the wastewater network and tank TK 2.2. The use of an electric arc welder when sealing the previously cut pipe caused the flammable mixture within the tank (wastewater vapour) to ignite. Furthermore, according to statements from the plant operators, the tank on which the line modification work was to be carried out (TK 2.2) was blanketed with nitrogen pumped in through the same pipe that was cut and then welded, at approx. 2.5 bar. It is possible that, precisely as a result of cutting the pipe, the inert nitrogen atmosphere was lost due to the broken connection.

In addition to the possible human cause linked to the error of operators, a series of elements concerning the organizational causes are examined.

They include design of plants/systems/equipment: the presence of hazardous substances stored on the forecourt were not adequately protected by fire prevention systems.

Another element that emerged relates to the process analysis, in fact there were no evidence of risk analyses having been done on the modification works carried out.

Therefore, a series of technical and management elements should be highlighted, which have contributed to inadequacy, lack of presence and/or lack of clarity, such as:

- isolation of equipment and systems: connection system between pipe and tank.
- maintenance/repair activities: activity not subject to the SMS management of change procedure).
- organizational procedures: aspects related to the implementation of the work permit, such as, for example, preliminary checks and/or during the execution of activities, and the management of changes, with specific attention to preliminary risk analysis.
- supervision and testing/inspections/records: control of on-site activities and related formalization.
- training/instructions: inadequate training of the operators of the third company on the major accident hazards related to the change.

#### **4.2 Consequences of the event**

Effects were recorded on human health.

Two employees of the third-party company sustained burns to 30-40% of their bodies. They were hospitalised for approx. 2 months. As far as the operator is aware, their injuries have not resulted in permanent incapacity.

Three employees visited in the emergency room and discharged on the same day: accident no. 4 days for first degree burns to the face and neck; accident n. 6 days by inhalation of toxic fumes; accident no. 7 days for multiple bruises.

People living in the industrial district within 1 km radius of the establishment were asked to stay at home with the windows closed until the emergency was over (from the start of the event until it ended at approx. 14.00).

As regards the effects on the environment resulting from the washout of the extinguishing water used during the event, no pollutants were detected in the protected lagoon nearby, while traces were found in the industrial canals of the site.

The fire affected all production areas, directly and by heat radiation, as well as part of the laboratory building, the control room adjacent to the production units and the cooling tower area. The assets were destroyed and are now no longer usable (apart from 15 metal tanks).

The costs amount to: EUR 35,000,000 (material losses, such as: raw materials; final and intermediate products; equipment, fixed and mobile tanks, machinery and installations; establishment management hardware and software; civil engineering structures and works; company vehicles); EUR 14,000,000 (response, clean-up, restoration costs, including the use of ships with anti-pollution equipment, with subsequent monitoring and replacement in the industrial canals).

#### **4.3 Corrective actions implemented**

The corrective actions implemented are explained in terms of emergency measures adopted immediately after the event and actions taken subsequently, by the Competent Authorities, and in terms of prevention and mitigation measures adopted following the event, by the site operator and management.

At the time of the event (approx. 10:20), the Internal Emergency Plan (IEP) was activated by the shift emergency coordinator (shift attendant) and external emergency services were alerted in the form of a call to the local station of the fire brigade. About on-site systems, automatic fire protection systems and fire-fighting equipment were activated, consisting in tank cooling towers and fixed water monitors serving the installations.

About 22 people, belonging to internal and third-party staff, who were present at the establishment on that day were evacuated.

The External Emergency Plan (EEP) was then activated by the Prefect's Office, following notification from the fire brigade. Following intervention by the off-site external emergency services, the fire was brought under control at approx. 14:00, and the emergency was declared over at approx. 17:00. Approximately 30 fire brigade vehicles attended with 90 firefighters, including from neighbouring stations.

In implementation of the EEP, as mentioned, people living in the industrial district within 1 km radius of the establishment were asked to stay at home with the windows closed until the emergency was over.

The fire brigade then checked the still-active pockets of fire and made the plants safe by: monitoring (using a thermal camera) and cooling one reactor; intervening on one tank on-off valve. The site operator, together with the fire brigade, then surveyed the site and the effects of the event in order to begin work to make the site safe,

which lasted for 1 month (until all the tanks containing hazardous substances present at the establishment were completely emptied).

After the event, the following emergency and environmental safety operations were carried out: a contract was concluded with a company specialising in making sites environmentally safe, resulting in a plan being issued; all tanks were completely emptied and the site was made safe by removing all hazardous substances present at the establishment; the environmental status was continuously monitored during decommissioning activities (hazardous substances possibly present in the air); cleaning of underground utilities, remediation and refurbishment of collection and sewage systems.

## 5. Discussion

The inspection activity conducted following the major accident, as well as the analysis carried out on the historical experience of events connected to plant modification activities carried out by third parties, highlighted some lessons learned and results of experience.

It is important to pay attention to the following elements:

- Always conduct a risk analysis on all types of modifications in accordance with the appropriate SMS procedure for management of changes (preliminary risks, risks during implementation and risks during operation), resulting in the identification of preventive and protective measures to be implemented, as well as the related training activities for the staff involved.
- Always keep systems subject to modification works under isolated and inert conditions to prevent the environmental conditions from changing, which could lead to the formation of potentially flammable and/or explosive atmospheres.
- The work permit process must always pay attention to: checks prior to and/or during the performance of the activities, supervision by the persons responsible and formalisation.
- Follow the procedures for the correct positioning of stores of hazardous substances and mixtures on the forecourt (e.g. tanks, drums, IBCs, etc.), including related fire protection systems and equipment, as a result of an appropriate risk analysis.

## 6. Conclusions

As discussed by Agnello et al (2012), at Seveso establishments, the complex documents underlying the SMS are managed by specialists, which are very far from daily operation. Major companies are usually committed to disseminate the content of the safety documents among employee and contractor workers, but at for small and medium sized enterprises, sometimes there is a "wall" between safety knowledge, contained in official guidelines and recommended practices, and real operation. This "wall" is a major obstacle for an adequate safety management and must be fought in any way. The lack or impoverishment of internal safety culture makes the organization impervious to external knowledge. In these organizations, everyone ends up following unwritten practices, as faster and simpler, and ignoring all the experiential and cognitive heritage, formed over decades. In the chemical specialties industry, are present many small and medium sized enterprises, featuring a poorer organization. As competition in this sector is higher, technical interventions are done under hurry pressure, and recognized practices for the management of the changes are possibly disregarded. Experience and knowledge are forgotten and, consequently, risks related to changes, particularly for temporary ones, are ignored or misunderstood at all.

It is important to open breaches in the above mentioned "wall" and assure that operation benefits always from all available knowledge. The company management should have as a priority the promotion of the safety culture internally, but where the internal organizations are poor, the associations have to carry out a capillary action to disseminate knowledge through their network. In order to implement such a dissemination, short webinars may be organized for on field operator, as well as simple bulletins, appropriate for workers.

In order to promote the safety culture, the experience gained from accidents, incidents and near-misses is valuable. Every relevant event, and not only the major ones, should be recorded, the detail described, the involved substances identified, the causes investigated, the emergency interventions and the corrective actions described. The incident and near-miss documents should be shared, throughout company and the industrial network, including contractors and allied companies. In chemical specialties industry, which is featuring a higher fragmentation, entrepreneurial associations should promote the sharing of incident and near-miss documents, as proposed already a dozen years ago by Gagliardi and Astarita (2008).

Regulatory authorities also have a big responsibility. In particular, the mandatory inspections, required by the Seveso Directive, can be an important opportunity to verify, in addition to the technical systems and procedures, the presence of a safety culture. In particular, in the chemical specialties sector, the inspectors have to pay attention to the management of changes, where recognized good practices may be forgotten, preferring treacherous and dangerous informal procedures, which are the root cause of accidents involving hot work and flammable substances. Sample interviews with personnel of all levels can be useful for inspectors to understand the level of awareness and knowledge of the personnel and possibly prescribe specific interventions for the promotion of the safety culture.

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