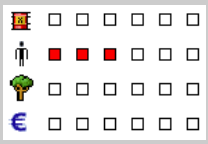
Risks deriving from the coexistence of automatic and manual systems

Toxic release following an uncontrolled chemical reaction

ARIA 40319 - 21/09/2010 - Germany - Heilbronn

20.5 – Chemical Manufacturing



An exothermic runaway chemical reaction abruptly occurred within a production facility when an operator initiated an automated sequence to add water inside a multi-purpose batch reactor. The reactor suddenly experienced a pressure build-up due to its foaming content, but the automated control system was not able to regulate it. The glass reflux condenser burst while the rupture disc remained unbroken, given that its bursting pressure had not been reached. The irritating HCl vapours released in the facility are evacuated outside by an employee through the ventilation system. These vapours intoxicated 7 people in the neighbourhood, 2 of whom would be kept in hospital overnight for observation.

The investigation conducted revealed that the sudden exothermic reaction followed a 30-litre spill of water into the reactor instead of the 3-litre quantity indicated in the procedure. The 32-litre water tank was connected to the reactor via a pipe fitted with 2 valves. The first valve, activated by the automated control system, normally delivers 3 litres of water, while the second manual valve is supposed to stay in the closed position at the beginning of this water addition sequence. During the accident however, the manual valve was left open, and this oversight led to quickly draining the 30 litres water content of the tank into the reactor. The exothermic reaction was triggered, and the sole control system designed to prevent chemical runaway was unable to function properly, since the system was designed to provide a control of the water added to the reactor through the closure of the second valve. Moreover, the manual valve, which was not equipped with an open/closed position indicator, could not be easily reached by the operator, making it difficult to control. This risk of exothermic reaction had been identified during the process safety study (i.e. the Hazard and Operability Study, or HAZOP), but at the time of the accident only a call for procedural improvements had been issued. The company limits the maximum volume of water which can be added at one time in the reactor and improves the automated control system. The safety studies (HAZOP) are updated for all exothermic reactions carried out on in this apparatus. A particular attention is paid to consequences of operating failures and a balance is found between risk control measures and the potential severity of the consequences.

Risks deriving from the coexistence of automatic and manual systems

Production constraints and technological breakthroughs have promoted the development of automated production systems in the industry since the beginning of the 1980's. In some instances, these modern systems still coexist with older manual devices kept in order to accommodate degraded mode operations (malfunction, maintenance, unit shutdown or start-up). Accident data suggest however that this coexistence entails its share of risks.

A key circumstance during the accident sequence is the malfunction or unavailability of the automated system. When installations are controlled in manual mode, the operator's role becomes critical to ensure effective continuation of the process, or its restart or transfer into safety mode. With little practice in this type of control procedure, which is often more taxing on personnel than the automated mode, operators are prone to commit errors that eventually lead to accidents. One of the most common scenarios is failing to control whether the valve is open or closed (ARIA 8138, 23074 and 31023) or shutting off a vital piece of equipment like a pump (ARIA 7176 and 8231), yet situations in this category might also entail confusion (ARIA 35821) or the late detection of instrument malfunction (ARIA 14619 and 30920).

The analysis of these accidents shows that apparent human errors tend to hide organisational deficiencies [1]. Despite the existence of operating procedures (sometimes nothing more than simple verbal instructions), the operator may suddenly have to handle a manual operating mode that has not yet been mastered due to a lack of training and/or regular practice. Under such conditions, fatigue and stress can appear (ARIA 38418), along with difficulties in correctly ascertaining the physical and chemical state of the process [2]. The operator might thus be placed in a position of acting too hastily or slowly, leading to the accident in spite of being convinced of having acted appropriately and completed all necessary steps (ARIA 6327, 8138, 24665, 3536 and 30920).

Automated systems lie at the heart of process control systems, for the primary purpose of handling hazardous substance. They are also used as part of associated safety equipments. Operators may choose to bypass these equipments, especially during restart phases or transient phases when such equipments might not be well adapted to exceptional operating conditions. Production constraints can also create temptations of bypassing an automated system which is limiting the process performance [2] due to limitations imposed by an automated sequence or an unstable operating regime (ARIA 6537 and 38148). The smallest control error in manual mode operation can easily trigger an accident in the absence of an automatic mechanism able to detect, and eventually correct the misguided course (accumulation of explosive product: ARIA 164 and 6537; toxic leak: ARIA 19295 and 32484; chemical runaway: ARIA 212). The accidental aspect is more evident when an automated safety system is bypassed; because such systems may be considered to be of little use, as their activation are rare while any malfunction will significantly disturb the process operation: false alarms, untimely emergency shutdowns (ARIA 2900, 11107, 21466 and 36496). Safety systems are also responsible for setting process operating threshold conditions that may be tempting to bypass or violate in order to increase the production (ARIA 17531 and 38674). The incentive to bypass automatic systems may be even stronger if this bypass is short, giving the false impression that it has no consequences, such as equipment testing (ARIA 32484).

Even under normal operating conditions, the Heilbronn accident (ARIA 40319) shows that maintaining a manual system on a process, whose control has since been automated, creates an "accident-prone" environment when the results of the risk analysis are not completely applied. "Edge effects" from the old manual system on the new automated system are also possible, such as the unwanted activation of an equipment responding to both types of control systems (ARIA 1690 and 3212). This kind of environments becomes even more "accident prone" when the automated system only partially replaces its manual counterpart (ARIA 184, 11181 and 21136), as the operating speed of automated equipment can surprise the operator in charge of conducting the manual phase of the process (ARIA 38431). Shifting from automatic to manual mode during production also leads operators to commit errors, due to a lack of adequate training/practice on this more demanding and less often used mode (ARIA 31630 and 35432).

For over 30 years, the automation of production and safety systems has undeniably made it possible to reduce industrial accident risks, especially with regard to processes that use or manufacture materials with a high hazard potential (pressure, temperature, flammability, toxicity, etc.). However, this streamlined approach to executing routine control and monitoring tasks has paradoxically compromised operators' capabilities to face unusual situations. In this kind of situations, a reliance on manual controls systems is often unavoidable and shall be taken into accounts in accident scenarios analysis, equipment ergonomics, maintenance strategies, design of operating procedures and operators training.

Bibliography :

[1] LORY M. and MONTMAYEUL R., The accident and the organisation - Collection Synthèse, Editions *Préventique*, 176 p., 2010, ISBN: 978-2-911221-47-8.

[2] BARPI - Human and organisational factors as part of the accidental mechanisms in fine chemistry, September 2007, available on : *http://www.aria.developpement-durable.gouv.fr/ressources/in070139maj26_09_07.pdf*

Additional references (detailed accident reports):

- ARIA 3536: Explosion and fire of a hydrogen peroxide unit
- ARIA 8231: Accidental release of solvents
- ARIA 30920: Ethylene release into the atmosphere

Accidents whose ARIA number has not been underlined are described on the Website :

www.aria.developpement-durable.gouv.fr

ARIA 164 - 27/04/1989 - 39 - TAVAUX

20.13 - Manufacturing of other basic inorganic chemical products

Inside a chemical plant, an electrostatic filter for removing dust, containing 696 plates sized 17.5 m x 7.5 m x 18 m on a 116-MW coal-fired boiler, exploded. The accident occurred during a restart procedure after a two-week shutdown for maintenance ; it resulted from the accumulation of 440 m³ of gas inside the boiler following failure to close the backup burner feed line (300 m³/hr), which had been opened 1 hour and 20 minutes before the accident and which was discovered 90 minutes after the accident. One manual valve and two automatic gate valves stayed open (no visual control of valve position, automated shutoff of gate valves while continuing to inject compressed air, warning message ignored). The explosion caused 1 death and 8 injuries among the technician staff. Shattered window panes and projectiles were observed up to 250 m away. Total property damage was estimated at 20 MF.

ARIA 212 – 19/07/1990 - UNITED STATES - CINCINNATI

20.12 - Manufacturing of dyes and pigments

A rupture disc broke on a reactor used in the manufacturing of acrylic resin during pumping at the bottom of a device containing a hot mix of cleaning solvents. The reactor had been heated under manual control without following procedures or employing automated control mechanisms ; the installation's residual temperature had risen too high. The resulting vapour cloud exploded; 2 technicians were killed, 60 other employees were hurt and 30 individuals outside the facility were physically affected. At least 1,000 neighbours and 80 subcontracting personnel had to be evacuated. Property damage was extensive and losses were evaluated at 120 MF ($23 M).

ARIA 3212 - 08/04/1991 - 71 - LE CREUSOT

25.30 – Manufacturing of steam vapour generators

Fitted with an automated regulation system and continuously operated without supervision since 8 February 1991, an overheated water boiler (19.2 MW, 160°C, 11 bar) exploded during a manual control phase upon attempting to transition to a boiler with less capacity. The accident was caused by gas accumulation inside the firebox following the untimely opening of 2 solenoid valves in series, responsible for controlling the burner feed line. An electrical short tied to a previous cabling configuration, retained unexpectedly when installing the automated control system, wound up triggering a control relay switch common to both valves. No victims were reported; property damage, though significant, remained confined to the unit in question.

ARIA 3536 – 22/04/1992 - 38 - JARRIE

20.13 - Manufacturing of other basic inorganic chemical products

An explosion, noticed tens of km away, and a fire destroyed 1,000 of the 4,000 m² contained in a hydrogen peroxide (H_2O_2) unit located in the vicinity of hydrogen and chlorine tanks. The fire spread into the sewers, and a nauseating odour was perceptible. A safety perimeter was set up. One employee died and 2 others were injured; property damage was assessed at 483 MF. In escaping from an insufficiently-sized retention basin, 1,000 m³ of fire extinction water containing solvent polluted the DRAC River.

This accident stemmed from a deficient electric power card within one of the unit's digital control system cabinets. Several elements then entered into play, worsening the situation : analytical obstacles ; ill-advised human intervention on the automated device ; partial automation of the unit's emergency shutdown sequence ; non-independent control/safety protocols acting on the same instruments ; inadequate controls in place for ensuring the successful execution of installation safety procedures combined with several manual operations not completed by technicians when facilitating the unit shutdown sequence ; a lack of specific safety recommendations on installations ; and confusion written into the recommendations and existing procedures.

Due to defective seals on the safety shutoff devices (pump discharge valves, automatic regulation valves), backflow of hydrogen peroxide from the extraction column towards the oxidiser made it possible to gradually increase concentrations in the reactive mass of powerful and destabilising H_2O_2-metal agents, whose exothermic decomposition was initiated and then accelerated. The resulting oxygen caused installation pressure to rise along with a burst in the connecting pipe, which had never been fitted with a safety valve or equivalent device. The reactive mass, partially drained from the production machinery, ignited at a hotspot. Organisational deficiencies in terms of safety training would provide the grounds for a legal suit filed 3 years hence against several senior plant managers.

Many technical and organisational improvements were undertaken following this accident : installation of impermeable safety shutoff equipment, protection of pipe sections prone to pressure increases during H_2O_2 decomposition, command/control system upgrade (with a safety system dedicated to emergency shutdown independent of the process control system, a new control room, enhanced workstation comfort and ergonomics), increased installation retention capacities and sewer protection, redefinition of subcontractor tasks and greater focus on information/training, issuance of appropriate safety recommendations, completion of safety reports relative to H_2O_2 manufacturing, transfer and storage procedures.

ARIA 6327 – 27/03/1986 - 69 - DECINES-CHARPIEU

71.12 - Engineering activities

Within a research centre, a study was conducted to improve output of the phenol oxidation reaction using hydrogen peroxide. During cleaning of the piston reactor with water at the end of the first test, an explosion caused projectiles to be released. One of the technicians positioned adjacent to the pilot installation was seriously injured (temporary deafness due to the explosion). Property damage was minimal (partial destruction of the micro pilot). The accident was caused by a mechanical malfunction on the phenol line as well as by shutdown of the hydrogen peroxide pump. This shutoff sequence was poorly interpreted by the technician, who manually reactivated the pump. Excess peroxide in the reactor led to a runaway reaction and the eventual explosion.

ARIA 7176 – 26/06/1995 - 56 - LANESTER

21.10 - Manufacturing of basic pharmaceutical products

A security officer smelled solvent near an underground cistern containing 30 m³ of dimethylacetamide (DMAC). The tank, built without a retention basin, was placed onto a simple concrete slab and closed on 3 sides. When a technician forgot to stop a pump in degraded mode (manual operations, without servo control), solvent continued to be distributed. Since the flow control valve was closed (for an unknown reason), pressure in the circuit rose and a leak occurred on a PVC flange. The DMAC dissolved this flange, and 3 m³ of product spilled into the stormwater collection network, then into the PLESSIS River and LORIENT harbour; 100 m³ of water were required to dilute the product. All PVC flanges were subsequently replaced by stainless steel parts.

ARIA 11181 – 25/04/1997 - 62 - CALAIS

20.14 - Manufacturing of other basic organic chemical products

An exothermic reaction involving diethanolamine and thionyl chloride in solvent phase, initiated 16 hours earlier, yielded chlorhydrate and a gaseous effluent neutralised in a washer after exposure in a glass column. Following a whistling noise, the column burst at 9 am. A toxic cloud (composed of HCl/SO_2) drifted onto a street adjacent to the plant, where residents had to be evacuated. The internal emergency plan was activated: 13 people suffered from intoxication and were hospitalised 15 min later. The unit had been automated for a year. The flow/reagent/agitation servo control mechanism, planned at the outset, had never been installed. One of the 4 technicians well versed in plant operations acknowledged an (agitation) alarm at the beginning of the reaction. The stirrer had remained turned off. The accident occurred upon manually restarting agitation after an electrical outage in the workshop.

ARIA 14619 – 30/09/1998 - 44 - INDRE

20.15 - Manufacturing of nitrogenous products and fertilisers

At a fertiliser plant, a dense and whitish cloud was released into the atmosphere during a 30-minute period subsequent to a pH disorder on the gas washing device set up in the granulation workshop. Technicians did not respond quickly enough to this operational drift given that the installation was running in manual mode since the regulation system had been disassembled the same day for maintenance. The site operator modified the alarm sound signal to make it perceptible beyond just the control room. The automatic regulation system for neutralising washing juices was improved.

ARIA 17531 – 7/09/1999 - 91 - GRIGNY

46.71 - Wholesale of fuels and ancillary products

Around 11:30 pm, a strong smell of hydrocarbons was indicated by residents living near a petroleum depot located along the banks of the Seine River immediately after the pipeline delivery of 2,640 m³ of unleaded gasoline. Arriving onsite at midnight, fire-fighters halted all rail and river traffic in the depot vicinity, yet were not allowed inside the facility since the local manager of the operating company had refused assistance from external responders. When the Prefecture cabinet director showed up at the scene around 3 am, fire-fighters were ultimately authorised to intervene and observed the overflow of a gasoline tank. The associated retention basin, which had received several m³ of the gasoline collected, was covered by a foam blanket. This operation was complicated by an insufficient flow rate and pressure on the premixing network, as well as by the removal offline of a portion of the fire protection network following a valve rupture.

Despite the absence of any serious consequences, this accident still would have generated a major risk in the event of ignition.

The classified facilities inspectorate issued the following observations :

- The tank that overflowed was not being directly fed, but instead fed via several intermediate tanks positioned higher and filled by the pipeline beyond their "upper" and "very high" limits, with these levels being balanced thanks to gravity ;
- For this purpose, the upper and very high level alarms were bypassed, thus depriving the site of a line of defence, given that the signal retransmission necessary for the pipeline operating company to halt delivery upon alarm signal detection was no longer available ;
- Subsequent to a modification in the internal electrical network at the depot from a few months prior, the operator was unable to restart the facility's fire pumps from the backup power supply (electric generating set) ;
- The fire water network had not been entirely functional: due to a leak on a network tap, the operator had blocked a portion of the premixing network, thus creating the difficulties encountered by fire-fighters during the night ;
- Onsite safety organisation was clearly flawed, leading the operator to ignore the deficiencies inherent in his own depot.

A prefectural order imposed a number of emergency measures : shutting off pipeline supply to the depot while waiting for service to restart, reading tank level probes, and producing an accident report. The operator received an official injunction to restore the fire water network to full capacity within 24 hours.

Feedback had not been taken into account by the site operator, who had already undergone at least 6 incidents involving depots over the previous 8 years.

ARIA 21466 – 12/09/2000 - 30 - ARAMON

21.10 - Manufacturing of basic pharmaceutical products

A leak of over-pressurised and overheated glycol water occurred at a chemical plant after the rupture of a pipe joint. At 2 am, a technician recorded a drop in coolant temperature (150°C), preventing vacuum drying operations from continuing. On-call staff diagnosed a loss of communication link between the utility automation feature and the plant's digital control system. A specialist in such systems confirmed the defect of a card on the utilities automation, whose replacement had been postponed until the next morning. Once the specialist left the premises confident of his diagnosis, the on-call technician decided to restart the unit. He short-circuited all of the safety mechanisms for hot fluid, as noted by the supervisor, and replicated the corresponding settings in manual mode. Called by another workshop an hour later, the technician abandoned the post for 30 min. Upon his return, the hot fluid had exceeded 180°C, and a noise resembling a detonation shook the plant. After joint rupture, the glycol water vaporised on the premises, which were closed immediately thereafter. The only consequence of this incident was a production loss. A plant working group suggested several remedial measures: revise access to the various system levels; reduce the number of staff members certified to take part in the programme and prioritise access ; train subcontracted personnel depending on their access authorisation; install cabled safety systems ; improve decision-making system reliability at night or outside of the normal schedule.

ARIA 23074 – 6/04/1979 - FRANCE

19.20 - Oil refining

Inside a refinery's catalytic cracking unit, an explosion occurred on a layer of gas at ground level. Following a level drop in the decoupling drum of the gas washing process, the manual valve for allowing water to enter opened. The water level rose in the drum due to a deficiency in the drum's regulation control chain before the manual valve could be closed. To accelerate drainage, the drum's regulation valve bypass towards the flare was opened even though the bleed valve of this same drum had remained open without supervision. The butane contained in the reflux drum then freely entered the flare decoupling drum and ultimately reached the sewer, forming a layer of gas at ground level. A flash was quickly triggered and the technician, caught in the explosion, was killed. The accident led to a temporary shutdown of refinery installations. The origin of this flash may have been the lamp used by the technician, given that the accident happened at night. The shock of the valve square driver on a piece of machinery or ignition of the gas cloud on the slurry reboiler (reputed as the catalytic cracking unit's heaviest liquid effluent) at 325°C, adjacent to the drum and sewer, are two other possible causes. The C4 distillate cut had contained a high concentration of trans-butene-2, whose self-ignition temperature lies below 320°C.

ARIA 24665 – 26/05/2003 - 13 - PORT-DE-BOUC

20.14 - Manufacturing of other basic organic chemical products

At a facility specialised in manufacturing basic plastics, a biphasic leak occurred on the safety valve of a bromation reactor containing 2 tonnes of dichloroethane with 5% bromine chloride (BrCl). Spreading of the mix remained confined to the production plant, as well as within the released cloud of hydrogen chloride. The facility's internal emergency plan was activated. Internal responders used a "water blanket" to limit both evaporation and the risk of inflammation, in addition to cleaning the premises ; all liquid wastes were transferred to an impermeable tank. Rail traffic on a nearby line was halted as a precautionary measure. The emergency plan was lifted 2 hours after the accident, with no injuries reported. Excessive reagent (BrCl) flow was the cause of pressure rise inside the reactor and safety valve operations: the intake control valve had been temporarily replaced by a manual valve as part of a maintenance operation. During the days prior to the incident, repeated clogging had led to changing the recommended position of the manual valve. To avoid such an accident from recurring, various remedial actions were implemented: design of the reagent loading line to ensure the flow rate always lies below the effective vent discharge rate ; improved tracking of temporary modification requests ; installation of a filter on the reagent loading line to prevent the risk of clogging; a study of the safety valve network in order to minimise the risk of vent clogging via a biphasic drive.

ARIA 31630 – 14/03/2006 - 45 - SEMOY

20.59 - Manufacturing of other chemical products (not otherwise classified)

At a chemical plant, 3 kg of methyl ethyl ketone (MEK) were discharged through the safety valve on a reactor following a pressure rise (to 50 mbar) inside the reactor. Solvent vapours escaped via the vents and spread both in the unit and outdoors on site premises. Upon noticing the odour, technicians checked all reactors in the zone and remarked that the temperature of one of them had reached 91℃, far surpassing the recommended 50℃. The heating circuit was closed and the cooling system activated. The accident occurred after loading raw material (MEK and 1,4-dioxane) at the time of setting heating conditions : the position of the temperature regulation loop in manual mode while the regulation valve remained open caused the excessive heating. Noncompliance with control instructions when beginning to heat the reactor was specifically cited. Moreover, the very high temperature alarm threshold had been set at 150℃ and temperature readings were not being recorded. The measures adopted subsequent to this accident focused on: introducing controls and monitoring procedures for batch reactor heating, improving the modification tracking procedure used in safety reviews (regarding alarm thresholds) ; accepting completed works; and verifying alarm thresholds during temperature indicator calibration.

ARIA 32484 – 8/11/2006 - 77 - GRANDPUITS-BAILLY-CARROIS

20.15 - Manufacturing of nitrogenous products and fertilisers

In a chemical plant producing fertilisers, an ammonia release at the level of the hot ammonium nitrate solution station intoxicated 4 employees, 2 of whom were working for a subcontractor. The installation was placed in safety mode and local fire-fighters were notified. The 4 injured personnel were all hospitalised for exams and cleared to leave 5 hours later.

The accident occurred even though the unit in question had been operating since the previous evening. Regulation of the nitric acid (HNO_3) flow rate, which is usually an automated process, was switched to manual mode when encountering difficulties in stabilising the reaction medium pH. A maintenance service call had been scheduled at 9 am on the day of the accident.

During this service call, the low flow and high flow safety mechanisms were inhibited for the time it took to complete testing. After manipulating the nitric acid intake valve, the flow of HNO_3 stopped suddenly, causing an excess build-up of ammonia in the reactor. The technician unsuccessfully attempted to reactivate the flow safety mechanisms, before deliberately tripping the reactor. Basic vapours were then discharged via the facility's vents and by the degassing of non-recycled condensates discharged into the gutters crossing the unit.

A defective nitric acid valve caused this accident : a broken pin was found inside the station at the time of its disassembly. This equipment problem could not be detected before disassembly, and the control room relay did not indicate any defect.

The lack of a unit-wide alarm, compounded by an inadequate risk analysis prior to maintenance work, was also cited.

As for feedback from this accident, personnel training improvements were envisaged, especially aimed at temporary safety device downtime and the installation of ammonia detectors connected to an alarm.

ARIA 38418 – 28/08/2008 - UNITED STATES - INSTITUTE

20.20 - Manufacturing of pesticides and other agrochemical products

At a pesticides plant with 520 employees, a 17-m^3 tank used to treat methomyl residue in a particular solvent (methyl isobutyl ketone, MTBK) suddenly rose in pressure at 10:20 pm and exploded 15 minutes later. The explosion severely damaged the production unit, ripped pipes and caused a fire fuelled by the 8 m^3 of product present in the tank. Onsite teams responded, with assistance from external fire-fighters, in accordance with a mutual emergency response protocol.

The site is adjacent to a major university and a river. Police closed the nearby motorway. The operator's failure to inform authorities, specifically regarding potential toxic releases, slowed the coordination of emergency measures; authorities ultimately decided to confine 40,000 local residents to their homes for 3 hours. The fire was extinguished at 2:45 am.

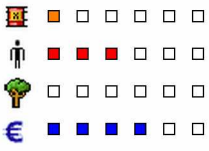
Two employees, dispatched to verify the cause of a tripped pressure alarm on the tank, were killed (1 instantly, the other 41 days later as a result of extensive burns). 6 fire-fighters and 2 employees of a rail company present onsite were intoxicated; 1 required a full day of hospitalisation. Damage (mainly shattered windows) on buildings and vehicles was reported up to 10 km away in areas located downwind, though the majority of losses were within a 2.5-km radius. The extent of damage outside the site amounted to $37,000 (€25,000).

A tank 25 m away, protected by an anti-projection shield and containing 6 tonnes of methyl isocyanate (MIC), was hit by debris yet did not leak, thus preventing spreading of this highly toxic product (the same that caused the Bhopal disaster (ARIA 7022)).

The U.S. Chemical Safety Board conducted a survey that found the accident to be primarily caused by organisational flaws: lack of sufficient oversight during the start-up phase with a new computerised control system; inadequate training of technicians in use of this new system; noncompliance with written start-up procedures (in need of updating), including the circumvention of measures aimed at controlling critical risks. Other exacerbating factors were also cited: cursory safety study prior to restart, equipment in poor working order, insufficient communication during shift changes, employee fatigue caused by working conditions at the time of restart (overtime hours, stress) Moreover, the operator deliberately sought to withhold information, particularly as regards the facility's MIC storage, behind the excuse of anti-terrorism laws.

The residue treatment tank as well as the unit's entire control system had been revamped during a long summer down period. Production started back up prematurely due to a strong demand for the product.

A series of problems on the production chain upstream of residue treatment absorbed technicians' full attention and led to concentrations of methomyl in residues, exceeding 20% despite an authorised maximum of just 1%. Under normal operations, residues would decompose in the tank; gasses were treated and the solvent was used to fuel other parts of the plant.
Since a safety bypass had been circumvented, the treatment tank could not be filled ahead of time with "clean" solvent or preheated; moreover, the liquid level remained very high (due to an automated governor forced to operate in manual mode), producing excessive residue concentration and leading to a runaway reaction and the eventual treatment tank explosion.

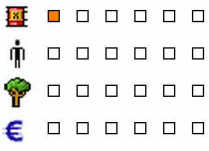


ARIA 36496 – 15/07/2009 - 57 - SAINT-AVOLD

20.14 - Manufacturing of other basic organic chemical products

Superheater "A" on vapour cracking unit no. 1 at a petrochemical platform exploded around 3 pm. Of the 8 personnel present at the time, 2 were killed and the other 6 injured. Projectiles, composed mainly of refractory material, were sent distances on the order of 100 metres and some pieces close to 50 cm in size fell in the immediate vicinity of the superheater; a dust cloud was visible directly above the site.
The Internal Emergency Plan was activated : the plant was evacuated and 70 fire-fighters arrived at the scene. Of the 6 injuries, all requiring hospitalisation (including 2 subcontracted employees working onsite), 5 were released the same evening. No damage or other impact was recorded offsite, outside of the sound of the blast. Cylindrical in shape with a 5-m diameter and some 20 meters high, this water vapour superheater, tied to a chimney of the same height via a connecting cone, did not contain any toxic product. The explosion was not followed by a fire outbreak. Subsequent to violent atmospheric storms during the night of July 13th to 14th and with water infiltration entering a utility room disturbing the digital control system, vapour cracking line 1 had been shut down and placed in safety mode. This line's restart procedure was launched in the morning on the day prior to the accident. This procedure was long to carry out, since the start-up routine had to be performed section by section. On 15 July, superheater A was reset around 3 pm with the intention of a manual ignition. A technician had shown up with an adjustable pole to light the pilots when the superheater exploded. The bodies of this technician and a second employee were found underneath rubble from collapse of the superheater floor.
According to the site operator, this accident resulted from various causes, namely :

- an accumulation of flammable gas, still below the flammability limit : investigations conducted forwarded the hypothesis of a gas flow towards a burner during both the start-up phase and ignition step ;
- ignition of the dust cloud by the lighting pole or by a hotspot inside the superheater convection zone. Other ignition sources could be hypothesised as well (e.g. electric spark, static electricity), although the two identified above appear to be the most plausible. A number of circumstances facilitated the occurrence of this accident, whose severe consequences were due to the presence of personnel in the vicinity at the time of powering up the facility ;
- failure to proceed with a vapour cleaning of the superheater prior to restart, in violation of operating protocol ;
- gas intake through a burner in the absence of a flame on the corresponding pilot ;
- the technical safety barrier, according to which it is prohibited to supply burners without a visible flame on the pilot, was not operational. This barrier was composed of an automated mechanism that closes gas feed valves if the flame detector is not signalling the presence of a flame 10 seconds after valve opening. Following a number of erratic detection alerts shortly after installation, this automated detector mechanism was deactivated due to the limited number of shutdowns/restarts planned for the unit over its operating cycle.



ARIA 38431 – 10/05/2010 - 26 - PIERRELATTE

20.13 - Manufacturing of other basic inorganic chemical products

At a plant specialised in transforming material containing uranium in addition to fluorine products, a leak estimated at 3 kg of fluorine (F_2) occurred on one of the two stations for filling bottles with a gas mix composed of fluorine (at 10% and 20%) and pressurised nitrogen (N_2).
Around 10:30 am, a technician began the packing of 4 racks simultaneously, 2 on station "A" and 2 on station "B". These racks were already pressurised internally at 50 bar and needed to reach 105 bar. The technician had previously prepared the installation (with the appropriate F_2/N_2 ratio) by introducing compression on backup station "C", which had since risen to a pressure of 70 bar. Around noon, he stopped the simultaneous filling of both stations, with the pressure inside all 4 racks on the order of 90 bar. Only the filling of station "A" was continued. At 12:11 pm, the pressure of station "A" racks equalled 105 bar. Since their filling cycle had been completed, the automatic switch took place, to allow filling station "B" racks, whose pressure had remained at 90 bar. The technician removed the station "A" racks to replace them and then continued with the production schedule, which entailed opening the gate that had served to confine the packing installation. At 12:21 pm, station "B" racks reached their 105 bar target, at which point the automated mechanism transferred the compressed F_2/N_2 mix back onto station "A". The technician however had not had sufficient time to replace the station "A" racks, and the F_2/N_2 mix was discharged to the outside at a pressure of 10 bar via the packing clips. At 12:30, in-house safety teams shut off the compressor, which in turn stopped the discharge. After examination by the plant's medical staff, 3 employees who had experienced slight discomfort were allowed to return to work a few hours later yet remained under 24-hour medical observation as a precautionary measure.
This incident was caused by the technician's erroneous judgment of the set-up, assuming an internal pressure of station "B" racks at 50 bar instead of 90 bar. This faulty assessment stemmed from the simultaneous filling of stations "A" and "B", given that such an operation had not been prohibited by the installation control system. The installation was shut down, and the Hazard and Operability Study (HAZOP) had to be revised so as to redefine safe operating conditions for the site.