

Explosion and fire on an acrylic acid tank at a chemical plant

29th September 2012

Himeji

Japan

Chemical industry
 Acrylic acid
 Thermal runaway
 BLEVE
 Management of change
 Instrumentation
 Internal emergency plan
 Organization

THE FACILITIES INVOLVED

The site:

The plant has been producing basic chemical products (acrylic acid and acrylic esters) and specialty products (super-absorbent polymers, resins, catalysts) since 1973. The facility occupies a 900,000 m² site in an industrial park located at Japan's Himeji Port (Fig. 1).



Fig. 1: Location and view of the plant in its industrial zone at the port (Source: Google Maps)

The facility comprises various storage and production units (Fig. 2), four of which are devoted to the production of acrylic acid, a raw material used in manufacturing the site's flagship product: super-absorbent polymers. As the Group's main plant, this Himeji site on its own accounts for 20% of worldwide production of super-absorbent polymers (320,000 tonnes/year), most of which are inputs for the production of disposable diapers. The chemical group that owns the facility is the world's 3rd largest manufacturer of acrylic acid, the Himeji plant accounting for 46 of the 62 tonnes produced annually by the group.

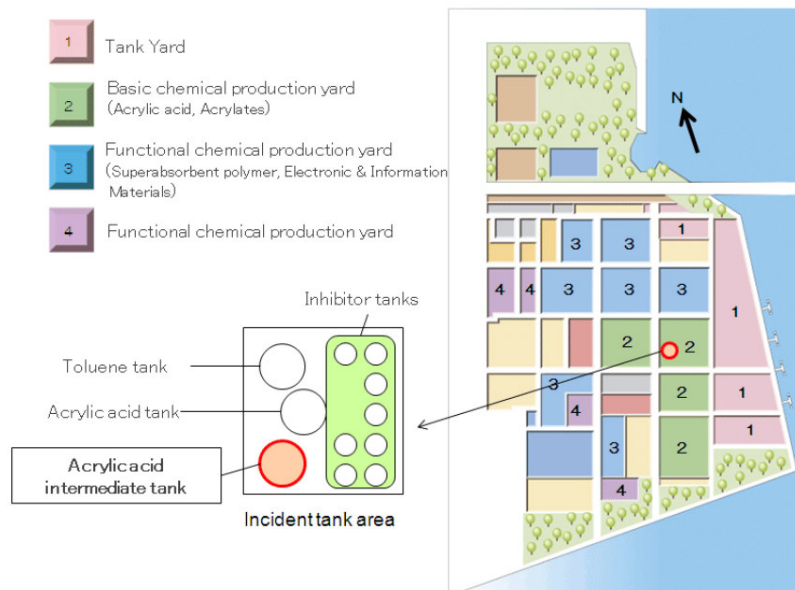
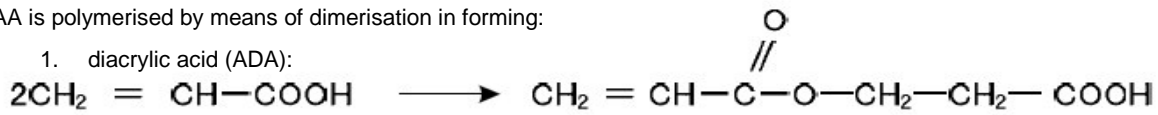


Fig. 2: Location of the various units within the plant layout (Source: plant operator)

The unit involved in the accident:

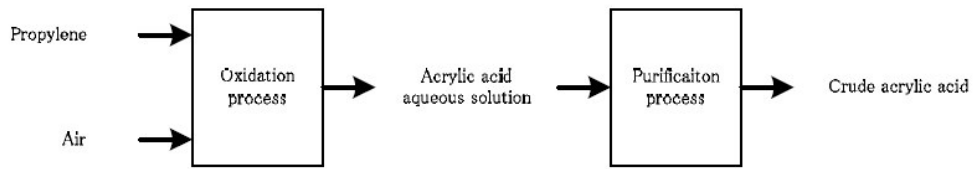
The damaged unit was one of the four dedicated to the acrylic acid batch synthesis and purification. Acrylic acid (AA) is a flammable, organic and irritant product that in its natural state is highly unstable due to a conjugated double bond and that polymerises easily via exothermic reactions catalysed by light, heat and oxidising products. To prevent such polymerisation from occurring, the acid is stored away from direct light in atmospheres where oxygen content can be closely controlled (at around 5%) and stabilised by polymerisation inhibitors. Temperature control is also essential since AA can solidify from 14°C and evaporate from 140°C.

AA is polymerised by means of dimerisation in forming:



AA is synthesised according to a 2-stage process (Fig. 3): its production, in the strictest sense; followed by purification of the distillation columns. Several iterations are required to eliminate impurities at the bottom of the columns and thus obtain the desired purity (99%).

【Crude acrylic acid production process】



【Glacial acrylic acid production process】

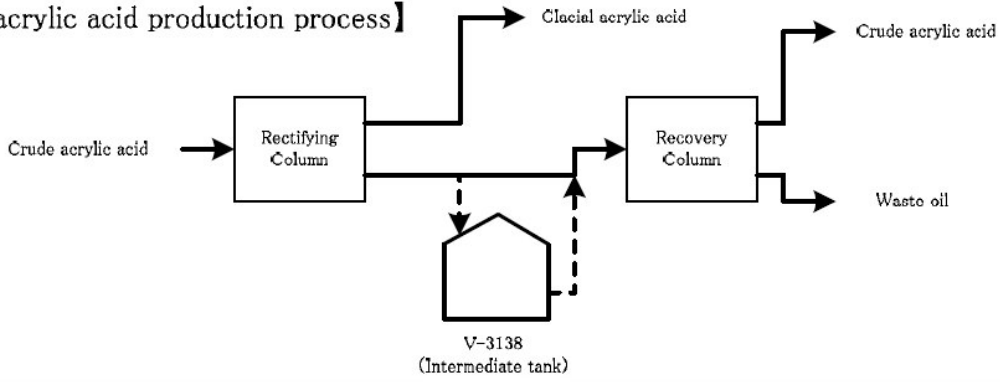


Fig. 3: Synthesis process for glacial acrylic acid (Source: operator)

Between its installation in 1985 and 2000, a 70 m³ intermediate storage tank served to store the mix remaining at the bottom of two rectification columns during a 2-day maintenance period. Under normal operations, the bottom of a single rectification column supplies a recovery column either directly or by routing via the intermediate tank: the volume stored in the tank had been limited to 25 m³, and the cooling loop installed on the lower part of the tank had been sufficient to cool the mix (Fig. 4).

During column drainage for maintenance, the tank was full and a bottom-to-top tank recirculation system made it possible to cool the mix evenly (Fig. 4). The tank expansion space was depleted of its oxygen (7% oxygen, 93% nitrogen) in order to eliminate ignition risks. Moreover, the tank was heat insulated to prevent excessive cooling of the stored mix.

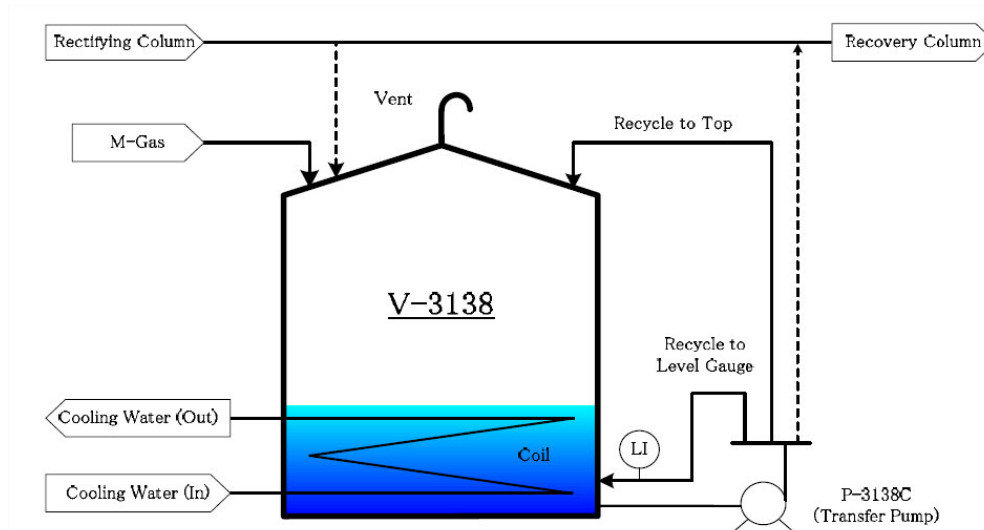


Fig. 4: Operating principle of the intermediate storage tank (Source: operator)

This mode of operations was modified in 2000: the mix at the column bottom was systematically routed via the intermediate tank in order to regulate supply of the recovery column. However, since the tank was being more frequently used, a precipitation phenomenon on the tank bottom appeared as the mix cooled, interfering with the level measurement and regularly clogging the racking pump strainer. To overcome this problem, a new recirculation line was installed between the tank bottom and the upper wall where the level probe had been placed. Since this step failed to resolve the problem, a new operating procedure was ultimately introduced in January 2010: during normal operations, the mix at the column bottom directly fed the recovery column, without being routed via the intermediate tank. This revised procedure proved to be efficient in significantly reducing cleaning frequency (Fig. 5), but at this point the tank was only being used when the rectification column was turned off. According to this configuration, upward recirculation could only be activated once the recovery column had been shut down, given that the accumulated mix volume then exceeded the 25 m³ corresponding to the cooling loop design criterion.

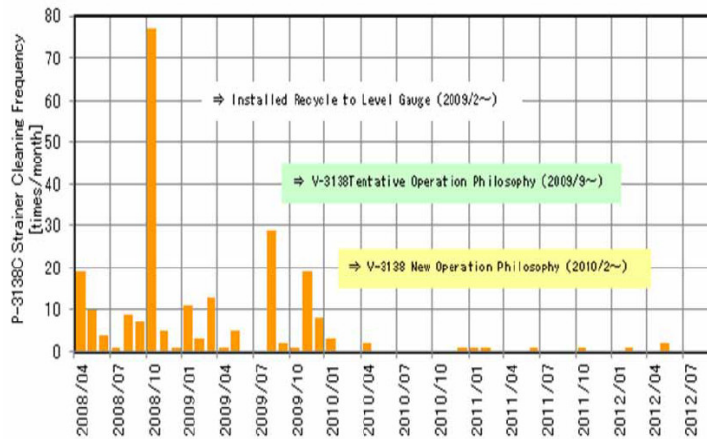


Fig. 5: Evolution in tank cleaning frequency vs. time and enforced operating procedures (Source: operator)

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

Accident chronology:

- 1st phase, start-up (21st through 25th September): Following a maintenance shutdown period, the unit was gradually brought back online. The tank's cooling loop was initiated; inerting of the expansion space got underway and the recirculation loop near the probe was activated. Beginning on the 24th, the recovery column received inflow of the mix from the column bottom via the tank, at a volume stabilising around 10 m³. The transfer pipe between the bottom of the rectification column and the tank was steam traced to prevent clogging due to product precipitation (Fig. 6).

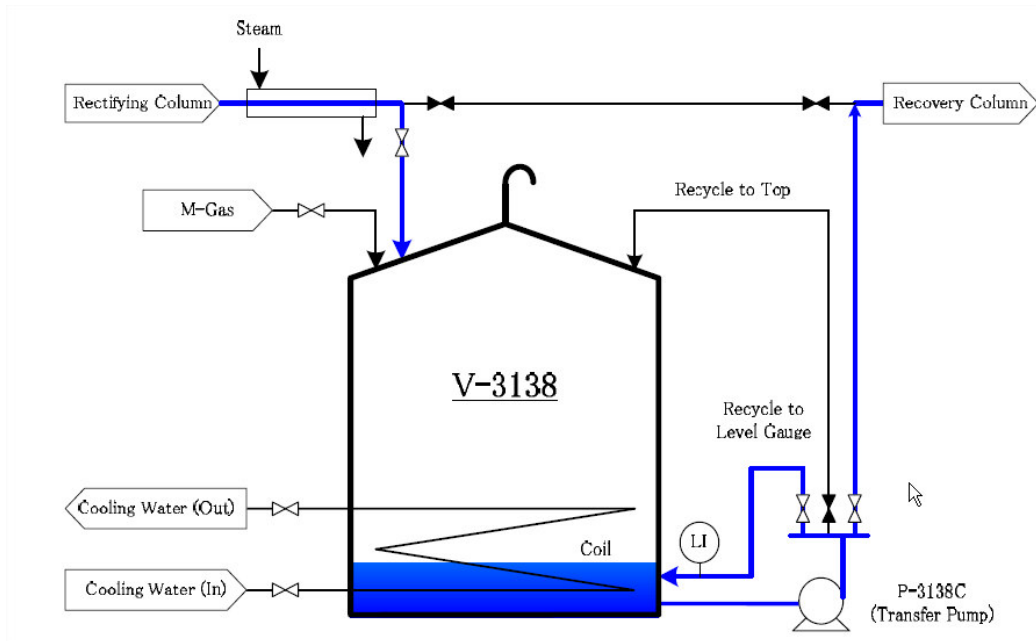


Fig. 6: State of intermediate storage tank during unit start-up (Source: operator)

- 2nd phase, filling (25th through 28th September): At 9:30 am on the 25th, the recovery column supply from the tank was shut down in order to test that column's capacity, while the tank continued to be fed with mix from the rectification column bottom. The maximum tank operating volume (60 m³) was reached on the 28th at 2 pm, i.e. after 77 hours of filling. Since the upward recirculation loop had not been activated, the layer of mix above the cooling loop had not been cooled (Fig. 7). The exothermic dimerisation of AA was initiated, causing a sharp increase in average temperature of the stored mix (from 40°C to 60°C).

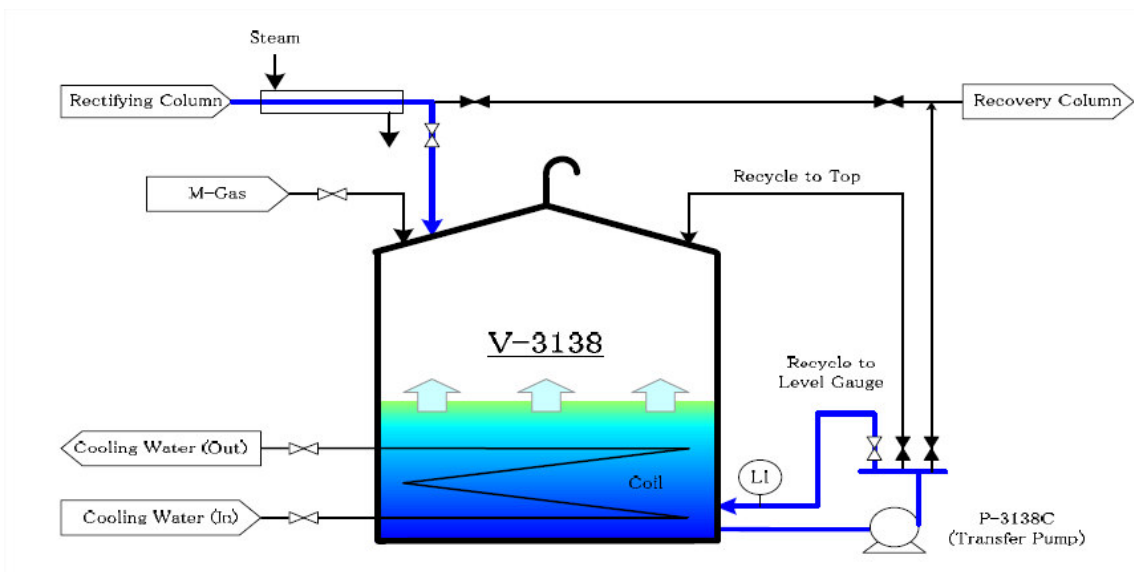


Fig. 7: State of the intermediate storage tank during filling (Source: operator)

- 3rd phase, thermal runaway reaction (28th until the morning of 29th September): On the 28th between 2:00 and 2:10 pm, tank filling was completed and the recovery column was restarted, yet at this point it was being directly fed from the bottom of the rectification column without routing via the tank. The mix layers above the cooling loop were not being cooled since the upward recirculation loop had still not been activated (Fig. 8). The mix temperature thus kept rising due to the effect of AA dimerisation and climbed to 87°C in the upper layers at 2:10 pm. On the morning of the 29th, exothermic dimerisation continued until the mix had reached proportions of 40% of AA and 60% ADA, increasing its average temperature by roughly another 40 degrees.

The remaining AA then began to homopolymerise. The corresponding chemical reaction, which was even more exothermic than the previous one, raised the stored mix to 160°C by 1:20 pm; at this temperature, the remaining AA evaporated (boiling point: 141°C) and the liquid fraction of the mix exceeded the upper level

measurement limit set for 85 m³. White vapours began escaping by the vents, an event that enabled a technician to detect the runaway reaction and sound the internal alarm. With help from fellow technicians, he set up a sprinkling system at 1:30 pm by drawing from 6 fire hydrants in order to cool the tank and hose down the escaping vapours. Around 1:50 pm, the plant's fire-fighters provided backup and sprinkled the tank using a water cannon supplied by a tanker lorry. This response represented the only available means of extinction (as the addition of inhibitors or water in the tank had become impossible), though it turned out to be ineffective given that the tank was heat insulated. The operator then notified the municipal fire department; arriving on site at 2:05 pm with 3 fire trucks and a brigade of approx. 30 men, the municipal crew resumed the tank sprinkling operation.

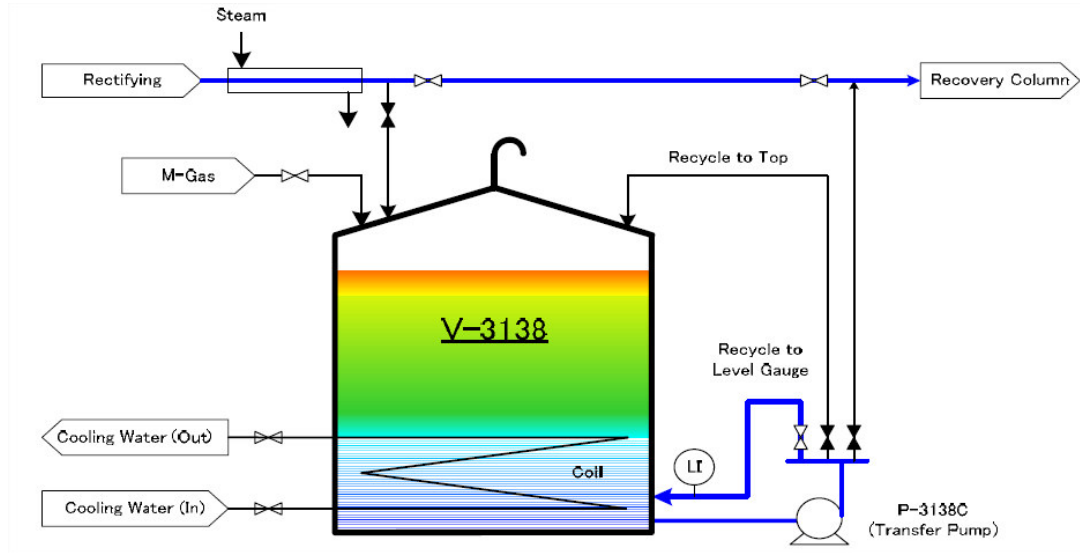


Fig. 8: State of the intermediate storage tank during the thermal runaway reaction (Source: operator)

- o 4th phase, the accident (afternoon of 29th September): Pressure inside the tank suddenly began to increase at 2 pm, as the vapour flow rate had greatly surpassed vent discharge capacity (Fig. 10). The tank shell started to crack around 2:20 pm given that the internal pressure reached 2.5 bar and the mix temperature hit 240 °C.



Fig. 9: View of the damaged unit after the BLEVE-type explosion (Source: Japanese television report)

Leaks formed due to cracking, which lowered the internal pressure; however, this sudden pressure drop caused the mix to boil and at 2:35 pm a BLEVE explosion (internal pressure = 6 bar, explosive force = 3 kg TNT equivalent) burst the tank, ejecting its boiling contents within the immediate vicinity. The mix ignited on a hotspot (damaged electrical cable or sparks created by metal debris), initiating a fire around the tank that would not be brought under control until 10:36 pm (Fig. 9).

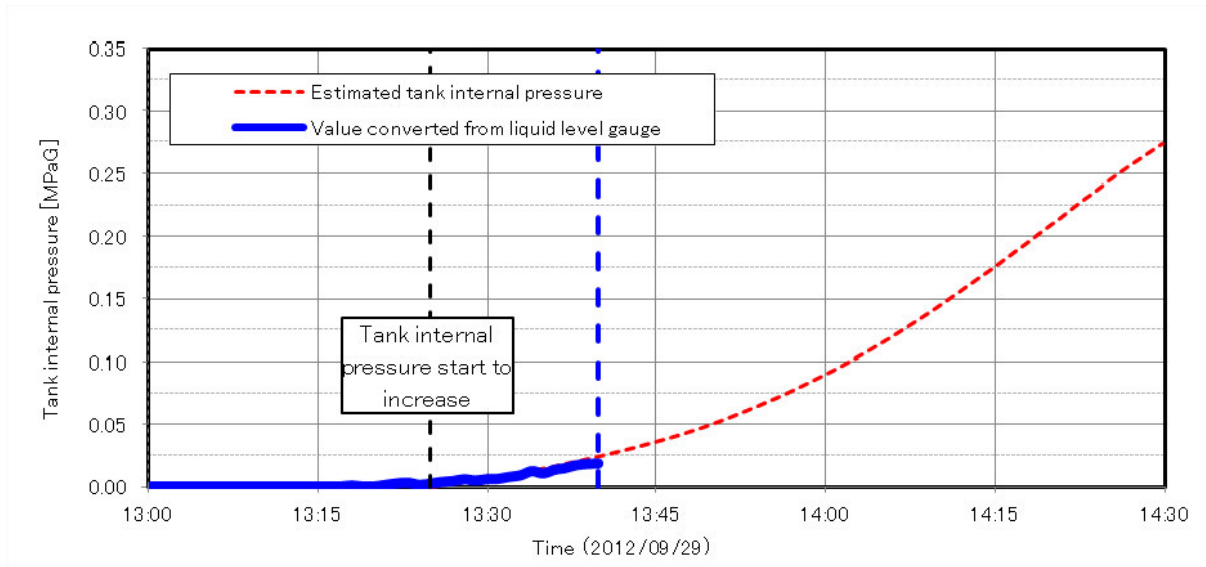


Fig. 10: Evolution of internal tank pressure on 29th September between 1 and 2:30 pm (Source: operator)

Consequences of this accident:

Blasted a distance of over 100 m, more than 80 pieces of debris damaged 6 of the 10 other nearby tanks located within the same retention basin (Figs. 11 and 14). In all, 67 m³ of lost AA and 28 m³ of lost toluene fuelled the fire from inside the basin; the blaze then spread southward to: an electrical transformer station, surrounding cables, and 2 fire trucks in service (Fig. 12). Pumps and pipe racks were also destroyed.



Fig. 11: View of damage after the BLEVE explosion (Source: operator)



Fig. 12: View of fire trucks ablaze after the BLEVE explosion (Source: Japanese television report)



The accident accounted for 37 victims:

- 1 municipal fire-fighter was killed while connecting a hose to supply a truck parked 20 m from the tank,
- 2 municipal fire-fighters and 3 internal fire-fighters sustained serious burns,
- 22 municipal fire-fighters, 7 internal fire-fighters and 2 police officers were slightly injured.

These injuries stemmed either from splashes of mix striking the body (Fig. 13), or from thermal effects produced by the fireball following the BLEVE explosion, or from thermal effects radiated by the ignited basin.

Property damage amounted to €15 million while production losses, caused by the 9-month plant shutdown (first total, then partial), rose to €450 million.

Fig. 13: View of splashes striking an employee involved in fighting the fire (Source: operator)

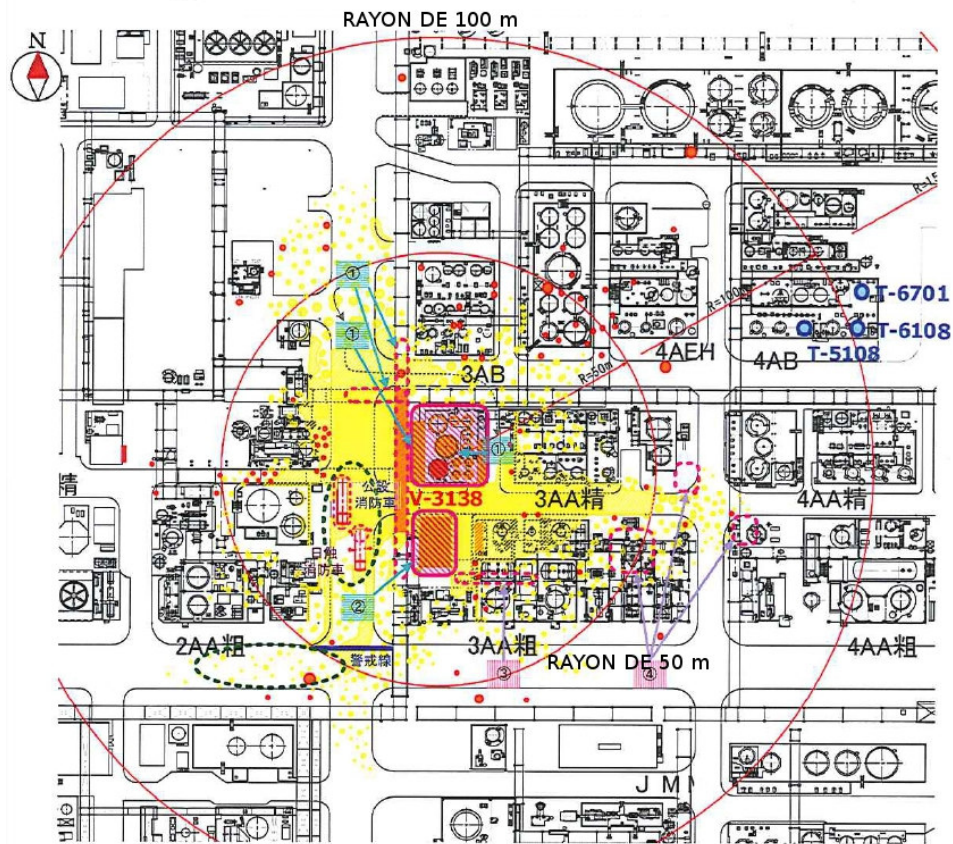


Fig. 14: Thermal effect zones (shown in yellow) and debris projections (red points) (Source: operator)

The European scale of industrial accidents:

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the "SEVESO" Directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

Dangerous materials released		<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>
Human and social consequences		<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>
Environmental consequences		<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>
Economic consequences		<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>

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

The "hazardous substances released" index was scored a "4", due to the 68 m³ of AA lost during the accident.

The "human and social consequences" index was rated a "3", owing to the 37 victims, including one death among the municipal fire-fighting crew.

The "environmental consequences" index could not be determined given the absence of environmental impacts.

The "economic consequences" index was scored a "6", as a result of the opportunity cost of production losses generated by the total plant shutdown for 1 month and the 9-month shutdown of the damaged unit (i.e. €450 million).

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The trigger point of this accidental sequence can be traced to human error. Even though the recirculation loop opening had been incorporated into the new tank operating procedure established in January 2010, the technician failed to activate this step on 21st September when placing the intermediate tank back into service. The upper layer of the mix thus remained stagnant and had not cooled since the beginning of the filling operation on 25th September, thus allowing for onset of the exothermic reactions of dimerisation and polymerisation, followed by a runaway reaction once the tank was full.

Technicians failed to notice the warming mix in the tank before 29th September at 1:20 pm, when white vapours wafted through the vents. By this time, the reaction had become impossible to contain, and the resources typically implemented to control the initiation of polymerisation (i.e. adding an inhibitor or water) were no longer feasible.

Moreover, 3 factors served to exacerbate this accident:

- The mix exited the column bottom at 65°C, though in order to avoid clogging of the pipe feeding the tank from the column during the product's natural cooling, a portion of this pipe was steam traced with a temperature regulation loop set at 90°C so as to prevent polymerisation through excessive heating. The mechanical instruments associated with this regulation often seized (due to rust), and the entire set-up had to be disassembled during unofficial maintenance work between December 2009 and the end of the long shutdown period, at which point the mix was arriving in the tank at over 100°C instead of the 60°C initially intended.
- The selected fire-fighting strategy (sprinkling with water) was inefficient due to heat insulation inside the tank.
- The plant operator's delay in notifying municipal fire-fighters, combined with the absence of coordination and preliminary information, overexposed the municipal response team during the fire fight, thus leading to a particularly heavy human toll in their ranks: 1 death, 3 seriously injured, and 22 slightly injured.

Beyond these direct causes, the accident analysis points to several deep-rooted organisational issues as well:

- **The tank operating manual was not up to date.** When the new tank operating procedure was written in 2009-10 by engineering teams after installation of the recirculation circuit around the level probe, the updated version of this manual was not made available to unit technicians. The previous manual did not mention the need to activate the recirculation circuit in the upward direction when the stored volume exceeded 25 m³. Just one sign posted above the valve on this circuit read: "*Closed during normal operations, only open if volume exceeds 25 m³*", but this message was placed 15 m from the column drainage control zone where the technician was stationed and out of the technician's line of sight.
- **Inadequate training for technicians working in nonstandard operating modes.** Since January 2010, the tank had only been used when rectification columns were down and with limited volume (i.e. < 25 m³). Taking the recovery column offline was the first time the mix could accumulate in the tank and surpass 25 m³, for which the cooling loop had been initially designed. Out of practice with using the intermediate tank on a regular basis and even less familiar with the complete filling procedure, the technicians were not aware of the importance of upper recirculation under these conditions.
- **An insufficient risk analysis** prevented the operator from recognising the importance of an accurate and continuous mix temperature control both in the tank and at the outlet of the traced pipe section. Such controls appeared to be essential for primary equipment (e.g. columns) but not for this ancillary tank, which therefore was not fitted with any instrumentation. The continuous temperature control criteria for production machinery had not been standardised across this international chemical group but instead were being defined plant by plant. Moreover, the inhibitors and inerted atmosphere basically failed to prevent the formation of ADA, while the role of temperature as a determinant factor was not readily known to plant personnel.
- **The absence of internal and external experience feedback mechanisms both inside the plant and throughout the Group.** In April 1994, polymerisation was initiated on another of the plant's intermediate AA

tanks. The incident analysis led to installing continuous temperature probes on all intermediate tanks receiving mixes from the column bottom at temperatures above 80°C. Since the damaged tank was receiving an incoming mix at 60°C, it had not been equipped and the incident was never reported either internally or to the Group's other sites. Moreover, the Group had not set up a system for recording and analysing accidents occurring in similar facilities affiliated with other companies elsewhere in the world.

- **Poor oversight of plant modifications.** The risk of cooling failure in the tank had not been taken into consideration by project teams during the unit extension works in 1994. Team members considered that saturating the mix at the column bottom with inhibitor was sufficient to eliminate this risk. Furthermore, installation of the steam tracing temperature regulation device seemed appropriate on its own to remove any risk of overheating at this stage of the process. Consequently, the capacity of the tank cooling loop had not been upgraded. The efficiency of the new operating procedure introduced in January 2010 had eliminated the need for recirculation around the level probe (fewer deposits and less frequent tank use => accurate level measurement) and should have led to cooling loop removal since its function overlapped with the tank's original upward recirculation.
- **Inadequate supervision of maintenance operations.** Removal of the tracing temperature regulation system had not been recorded in the log.
- **Lack of emergency situation drills.** The internal operations plan had not incorporated a scenario in which the means for controlling polymerisation proved ineffective, or else a detailed scenario regarding intervention in the case of an AA thermal runaway reaction in a tank. The only instructions given for this type of accident had merely consisted of a diagram indicating how to cool the tank by sprinkling it with water. The responsibilities to notify municipal fire-fighters were not clearly laid out, and the Group had not issued a guide to assist the various plants draft a comprehensive plan well-adapted to potential accident scenarios. Moreover, no efficient means were available to contain an accident involving an advanced state of polymerisation.

ACTIONS TAKEN

Immediately following the accident, Japanese administrative authorities ordered closure of the plant for the amount of time required to conduct the post-accident expert appraisal in the explosion zone. The other plant units were allowed to restart operations a month later, but the damaged unit, even after being rebuilt, was not granted its operating permit until completion of the technical investigation carried out over 9 months by a commission of internal and external experts.

The operator implemented the following remedial measures:

- Reassessment of operating conditions for all reagents used in the plant, with emphasis on:
 - defining ranges of acceptable values for common operational settings,
 - identifying the critical parameters to be continuously monitored throughout the processes,
 - installation of instrumentation on devices to allow for such continuous monitoring;
- Application of the modification management procedure for non-routine work and minor process-related modifications;
- The internal operations plan was updated: mitigation methods adapted to each scenario were clearly explained; an on-call system was introduced; timelines for notifying the municipal fire department and the type of information relayed in this context were established;
- Improvement of technician training and drills: training course methods and content were revised; an awareness campaign focused on potential hazards presented by the various substances used in the plant; warning signs were updated at all site units;
- Enhanced controls: inspections were performed by external bodies, and the routine inspection protocol was revised;
- A system for handling experience feedback on incidents and accidents arising both internally and outside the facility was set up.

LESSONS LEARNT

An analysis of this accident provided perspective on the following technical and organisational lessons:

- The updating of operational documentation must strictly correspond to all process changes;
- A technical or procedural modification to a process, even minor in nature, can fundamentally alter the initial risk analysis and, with it, the design of safety barriers;
- Technician training and drills must also focus on infrequent and extraordinary phases, such as equipment testing;
- For each product displaying risks of ignition, decomposition or runaway reaction, the control parameters deemed critical, e.g. the outcome of a HAZOP analysis, must be subject to continuous monitoring by technical staff throughout all process stages;
- Regular communication with follow-up is necessary between the design, maintenance and operations teams.



Fig. 15: Media repercussions of the accident in both the French and international press

Note: The information presented in this document has been extracted from the detailed report filed by the Official Investigation Commission and published in March 2013; an English-language translation may be downloaded at the following Web address (link operable in September 2013):

http://www.shokubai.co.jp/en/news/file.cgi?file=file2_0070.pdf