

## Safety practice

# Runaway reactions, case studies, lessons learned

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Runaway reactions are a major source of industrial accidents. They can occur in a wide array of sectors, including chemicals, petrochemicals, food processing, plastics and rubber manufacturing, and metalworking and are primarily caused by a loss of process control. The processes involved are quite diverse, encompassing chemical reaction, polymerisation and distillation, among others. The loss of process control is related with various factors that are examined in this article. Several accidents that occurred in France and recorded in the ARIA<sup>1</sup> database are used as examples.

### Causes

#### Instrumentation malfunction

Many products are manufactured according to very precise processes, and the proper functioning of these processes requires strict specification of temperature, pressure, respective quantities of each reagent, stirring speed, etc. Any drift in any one of these parameters could trigger a loss of process control. The ARIA database describes several accidents directly linked to instrumentation malfunctions that resulted in runaway reactions, among which erroneous settings or down pumps leading to poorly calibrated flow rates (hence non-compliance with reagent quantity specifications), broken stirrers, failure of the pH or temperature regulation, and control system deficiencies. These instrumentation malfunctions are capable of causing shutdown of a site's utility lines.

#### Aria 44071: Runaway chemical reaction inside a pharmaceutical plant following an electrical power outage

A transformer caught on fire at 7:45 pm on a production building's basement floor at a Seveso lower tier-rated pharmaceutical plant. The building's electrical power was cut, causing shutdown of the reactors' stirring and cooling mechanisms. An exothermic reaction that was taking place at the time became uncontrollable. The reactor's rupture disc, calibrated at 4 bar, broke, and the explosion vent opened to protect the structural integrity of the reactor. A quantity of the reaction mix at 70°C, composed of several hazardous products, projected onto one employee and six fire-fighters in the vicinity and formed a 60-m<sup>2</sup> puddle on the floor.

The plant operator activated the internal emergency plan and the facility was evacuated. The safety report conducted on-site had not identified any comparable scenario. No backup source had been allocated to ensure the continued

operations of critical equipment. Activities assigned to the damaged building and associated solvent storage zone were suspended until the safety systems (fire detection control, both post and automatic extinction) were once again operational. A diagnostic assessment of all site electrical installations was performed, along with a study, on the backup power supply for critical equipment, dedicated to exothermic reactions, i.e.: cooling, stirring, temperature and pressure probes.

#### Human error

This category contributes a significant source of loss of control incidents. The accidents catalogued in the ARIA database reveal that human error is regularly highlighted as a cause — for example, a valve left open; a wrong reagent injection; failure to complete an intermediate step during product manufacturing; hastily or excessively introducing one of the reagents; improvised initiatives such as repeating the addition of a catalyst to initiate a reaction that is slow to start.

#### Aria 40496: Explosion of a chemical reactor column

In one of the workshops at a plant producing intermediate organic synthesis compounds, a runaway reaction coupled with an explosion (approx. 1 kg of TNT equivalent) took place in the 3.5-m high glass column overlooking a 3,000-litre reactor. The explosion triggered a fire outbreak inside the unit. A 110-kg cloud of hydrochloric acid (HCl) hovered over the site before dispersing after a few minutes due to a favourable wind. The noise alerted the technical staff, who promptly placed the installation in safe operating mode and launched the internal emergency plan. The staff began to fight the fire using the resources at hand, and were then joined by fire-fighters who brought the blaze under control within twenty minutes.

One employee sustained loss of hearing due to the explosion and property damage amounted to €700,000.

On the day of the accident, a batch production had been underway involving the addition of 1,000 kg of a cold liquid ethylene compound along with 750 kg of a highly flammable and volatile silyl (hydrosilane). The homogeneous mix was then supposed to be poured into a 2nd reactor at 100°C in the presence of a catalyst to form the final product. The hydrosilylation reaction was maintained under control by

gradually introducing the mix. However, in this incident, a sudden rise in mix temperature caused a pressure surge and a pneumatic burst of the column. The hydrosilane was hydrolyzed into HCl upon coming into contact with humid air and then decomposed into the hydrogen that triggered this fire.

The investigation revealed that in order to compensate for the loss of catalyst activity (this was the seventh consecutive batch), which would have necessitated an extended batch time, a technician took the initiative to insert around 10g of new catalyst into the reactor at the same time as the raw materials. Data studies and laboratory tests actually indicated that the reaction could not have started in the low temperature reactor (5–20°C), since deviation from the temperature required for synthesis (at 90°C) appears to safeguard the reaction safety of this modification, i.e. now deemed to be minor. Nonetheless, the tests conducted by the operator following the accident revealed that at these temperatures, an exothermic hydrosilylation reaction could arise following an induction period lasting several hours in the presence of trace alcohol amounts. Since the catalyst had been placed in solution with a ketone, an infinitesimal quantity of ketone (in the order of 0.01%) was found in the mix inside the reactor and subsequently reduced to alcohol by the hydrosilane. Despite an extensive process of analysing reaction risks plus the synthesis of 36 batches without an accident in six years, the accident occurred on the only batch for which the process had been slightly modified. The operator reminded plant technicians that:

1. this modification should have been rated as significant and undergone an in-depth, collective analysis prior to implementation; and
2. any modification to a process must be justified and accompanied by compensatory safety measures.



### *The presence of residues, deposits and accidental additives*

Many accidents are caused by poorly cleaned reactors, tanks, pipelines or distillation columns containing impurities, residues that accumulate, or accidental additions of undesired substances. These residues, impurities or other products are all capable of reacting with the reagents being introduced, hence leading to an uncontrolled reaction.

### **Aria 7069\*: Explosion in a batch unit / SO<sub>2</sub> discharge**

A reactor exploded in a fine chemicals plant during the chlorination of an alcohol by thionyl chloride (SOCl<sub>2</sub>). The relatively non-exothermic reaction took place in a solvent medium (1,2 dichloroethane or DCE), under a slightly lower pressure and a temperature of 70°C maintained by means of steam injection. The reactor initially contained the SOCl<sub>2</sub> in solution in the DCE, with the alcohol being added under close monitoring for 30 hours. At the time of the accident, the reactor was being fed for three hours by successive 200-litre loads of alcohol, with the first injection still incomplete. Monitoring performed by two technicians, one of whom was a trainee, included an hourly reading of both the temperature and pressure drop; no anomaly had been observed until that point.

Upon hearing a noise accompanied by a break to the protective disc on the glass column connected to the reactor and noticing smoke around the disc joints, the technician turned the feeder control box selector switch to the "off" position. As he closed the alcohol feed valve and was making his way to the valve used to shut down steam injection, he spotted that leaking on the column was becoming more persistent. He immediately left the unit, requesting that a co-worker follow him out — at which point the explosion happened.

A rupture disc calibrated at 0.3 bar and the glass fixtures on top of the device burst. The explosion or toxic gases emitted once the equipment had broken killed the trainee technician, who did not exit the premises quickly enough.

The feeder was equipped with two valves. The upper one (loading side) was found in the closed position while the lower valve (reactor side) was open with a reversal of the pneumatic control hoses. These recordings supported the hypothesis of an accidental addition of water into the reaction medium via the feeder. The laboratory simulation of such an addition found that the SOCl<sub>2</sub> hydrolysis with the formation of SO<sub>2</sub> and HCl led to a sudden pressure rise.

The accident was due to a combination of several factors, including reversal of the feeder's lower valve control hoses, causing a position inconsistent with the logic of the local programmable controller; non-lockout of the feeder used during a prior synthesis, thus leading to an accidental introduction of water; and an untimely intervention on the feeder control box.

The plant operator modified the feeders in order to prevent hose reversal and created block diagrams of valve positioning along with a mechanical lockout system. He replaced the glass equipment by fired steel machinery for those reactors capable of generating gases and set up systematic recording of process settings. A series of general measures were also adopted or improved, i.e. the monitoring, certification or reconfiguration, if needed, of equipment prior to any new batch launch, implementation of a unit-specific anomaly logbook, systematic and periodic audits of the various units/processes, plus an assessment of the installation configuration and environment with respect to the production documentation, mandatory wearing of the leak mask.

In addition to equipment malfunctions, human error and the presence of residues, organisational deficiencies are often observed — for example, lacking or inadequate controls; procedures that are either missing, inappropriate or not followed; insufficient technician training; substandard new or modified processes; poorly identified risks; and ineffective risk analysis.

The risks associated with the ensuing reaction are in fact not always appropriately evaluated, especially when scaling up a process from laboratory to industrial scale. Once conditions have been defined and the risk analysis validated, technicians must

be trained in the specific process and all the hazards related to both the process and substances involved. These basic steps are sometimes neglected due to urgent production needs or cost-saving measures. Plant personnel may be pressured into handling a large number of operations in a short period of time, resulting sometimes in a failure to properly monitor potentially hazardous reactions. Adequate staff training, coupled with regular reminders, also serves to avoid a common operational drift — the same manual sequence is repeated without asking why, improvisations are made, to the point of skipping a step due to a lapse in concentration.

### Aria 7135\*: Atmospheric discharge of a reaction mix from a polymerisation reaction containing formo-phenolic resins

At a chemical plant, the rupture disc calibrated at 1.5 bar on a 15.2-m<sup>3</sup> reactor broke inside a formo-phenolic resins workshop. The batch production extended over a ten hour period. The formol and phenol were loaded into the heated reactor then the soda used as a catalyst was gradually introduced into the device, which was maintained in a vacuum.

On the day of the accident, the three reagents were introduced into the reactor. The reaction accelerated with a rise in temperature / pressure of the enclosure and ultimately resulted in the rupture of the calibrated disc. Six tonnes of reaction medium (formol at 11.5%, phenol at 0.6%, soda and resin) were expelled through the roof and subsequently fell both inside and outside the plant over a radius of 400m. Vegetable gardens and several vehicles were covered in residue fallout.

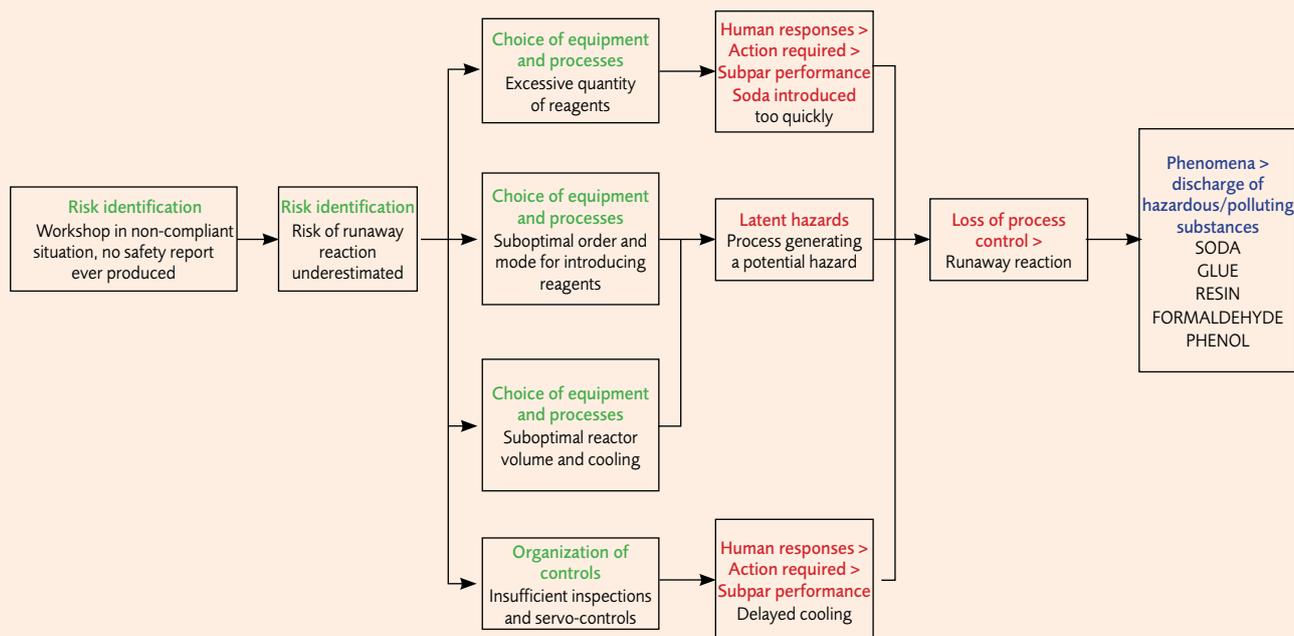
The plant operator cleaned the site. Soil and vegetable analysis revealed the presence of phenol (from 0.02 to 4.08 mg/kg). Some of the garden-grown vegetables were harvested for destruction, and a wheat field which received some chemical substances fallout was mowed. All damages were reimbursed.

Following an overly rapid soda flow, exacerbated by a

major reactor loading, cooling of the reactor began too late (12 min after the temperature rise, judging by the log). The product quantities involved were very high despite complying (according to the operator) with the operating protocol (approx. 15,500 kg for a 15.2-m<sup>3</sup> reactor). The reaction accelerated while the cooling systems on the reactor, which had reached 127°C, were no longer operational.

The high reactor loading level, the inadequate cooling capacities available and the inappropriate lockout temperatures all contributed to loss of control of the reaction process. Moreover, the loading of the main reagents at the beginning of the cycle, in breach of professional best practices, triggered this runaway reaction. The workshop was not in possession of the regulatory authorisations required to manufacture this new type of resin; no process or installation safety reports had been drafted previously.

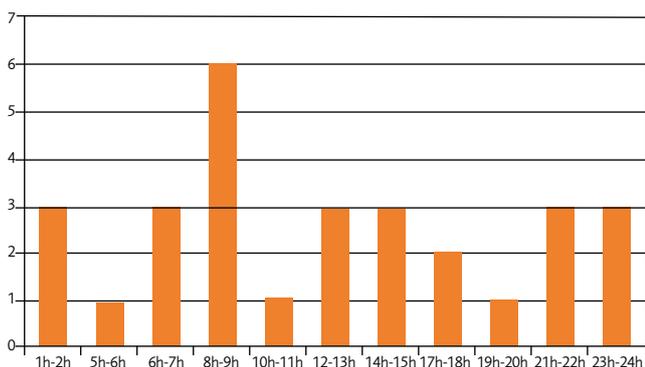
The operator altered the plant's process in favour of continuous formol injection in order to improve heat release control. The reagent quantities were reduced, and tracking of both the reactor's operating settings and chemical reaction sequence was upgraded.



Modelling of the accident (tool developed in the ARIA database)

## Circumstances

Start-up and shutdown phases make up a significant portion of the circumstances leading to the loss of process control. There are however others, such as substance transfers, pumping and demolition which can also lead to the loss of process control and upset maintenance periods. Nonetheless, nearly half of all accidents recorded for purposes of our study occurred during operations. Closer examination of the time of accident occurrence (when known) reveals that the most frequent period covers the morning hours of 6 to 9 am (start-up / shift change), followed by midday, i.e. noon to 2:30 (fewer personnel / shift change) and the period from 9 pm to 2 am (also fewer staff on duty and a shift change).



Number of accidents at different times of the day

### Aria 161: Explosion and fire inside a chemical plant

A novice technician was left without supervision. He was assigned to handle a process being implemented for just the second time, whose operating procedure did not specify the order in which reagents were to be introduced.



## Consequences

The loss of process control often provokes a violent chemical reaction with a range of potential consequences:

- Explosion or fire involving equipment (reactor, tank, distillation column, etc.) or released substances, if they are either flammable or explosive;
- Injuries of varying severity, or even death, from intoxication due to toxic substances escaping into the air, fire smoke or from falling equipment or other property damage;
- Pollution of the natural environment following the dispersion of hazardous substances being released or generated;
- Property damage, encompassing equipment deformation, broken devices, even destruction of the production building and its surroundings.

### Aria 7956\*: Explosion / fire in a synthesis workshop at a chemical plant

An explosion and fire occurred at night in a workshop set up to synthesise toluene diamine (TDA), by means of hydrogenating dinitrotoluene (DNT) in the presence of Raney nickel, during a scheduled maintenance downtime. In-house fire-fighters brought the fire under control within 35 min; in the meantime, four employees required hospitalisation. One of them, who was handling the valves to wash the hydrogenation reactors with isopropanol, sustained burns over 40%-50% of his body and died 15 days later. The workshop was completely destroyed. The reactor burst; the bunker housing the workshop was deformed due to the combined action of the blast wave and sprayed fragments; the reinforced concrete wall was ripped open, with rebar twisted; and the control room was heavily damaged. Glass panes were broken over a 50- to 100-m radius, while the distillation unit juxtaposing the bunker was damaged and allowed isopropanol and TDA to escape, adding fuel to the fire. Buildings belonging to the neighbouring industrial facility located 150 m away suffered deformations to their lightweight structures. Wind dispersed the gaseous pollutants released ( $\text{CO}_2$ , CO, NO<sub>x</sub> and unburnt organic matter). The environmental impact remained limited.

According to the investigation conducted, this explosion resulted from injecting pure DNT into one of the reactors washed by the circuit used at the time of production start-up. Two valves connected in series equipping this DNT feed line were found partially opened (at 10°) after the accident, most likely allowing 500 to 700 kg/h of product to flow into the reactor. The heat release upon hydrogenation of a small quantity of DNT probably triggered the sudden decomposition of the remaining DNT, while abruptly reheating the reaction medium.

Corrective measures were adopted to prevent routing pure dinitrotoluene into the reactor. These were elimination of the DNT intake line on the injection tank, addition of two automatic on-off valves on the mixing tank's DNT feed line, closure of the link (by an automatic on-off valve) between the mixing tank and the injection tank during the reactor washing

phase, modification of the washing procedure (transition from discontinuous to continuous washing), and arrangement of all reactors in a way that limits the time personnel spend in the bunker.



Control room



Workshop

## Lessons learned

The various accidents presented in this paper, along with those from the study sample, reveal that inadequate risk management and identification are often to blame. When preparing a process, questions regarding reagent stability and/or toxicity must always be raised, as well as the reactivity of substances among themselves. This requires perfect knowledge of chemical reaction characteristics (temperature, pressure, kinetics, etc.) prior to designing the unit, plus, if applicable, the other reactions capable of occurring (especially in the event that the process breaks down). Optimal reaction conditions must be determined by a study conducted ahead of time, with special focus on the following questions:

- what would happen when deviating from these conditions, what margin is available with respect to reactor temperature and pressure?
- what volumes (reactor/reagents) and what cooling systems should be foreseen in the case of an exothermic reaction, in order to maintain control over the process?
- what safety devices should be planned and where should they be placed in order to ensure their efficiency in the

event the process is no longer under control?

- what control devices should be specified (e.g. temperature and pressure probes, sensors adapted to the reaction kinetics and/or the kinetics of any potential process breakdown) and what servo-controls will verify and ensure that the process runs smoothly?
- has consideration been given to managing those instances when sensors and safety devices are out of commission (backups, shared operating systems, etc.)?
- what materials are to be used for the reactor and ancillary equipment (e.g. refrain from using glass equipment in case of reactions accompanied by a gaseous release; avoid container-content incompatibilities)?
- for batch processes, in which order should the reagents be introduced, and at what speed?
- have the specific risks related to transfer operations (introduction of reagents, washing solutions into the reactor starting from a large tank, drainage, etc.) undergone analysis?
- are any chemical substances in the vicinity capable of entering into contact with those already involved in the process and then interact?

To conduct a relevant risk analysis, existing methods like LOPA (Layer of Protection Analysis) quantify the level of risk reduction by assessing contributions from the various layers encompassing all barriers encountered, from process design through to emergency measures activated in case of an accident. Implementation of a Safety Instrumented System (SIS) serves to prevent a degraded operating situation from deteriorating to the point of causing an accident (installation of sensors measuring reaction parameters, analysis of the ultimate deviation with respect to defined conditions and, if necessary, process switch into safe operating mode).

Once the process has been established, site personnel must be properly trained and advised about the risks incurred should it deviate from conditions defined in the set of specifications.

Both employee training and the drafting of instructions and procedures prove to be critical in avoiding unfortunate changes and initiatives undertaken by the technical staff. Any modification, even one deemed minor, must only proceed after a full evaluation of all potential consequences regarding the process; moreover, the final decision must entail coordination. Signage, relative to both the process (valves, pipeline, tanks, etc.) and emergency services (extinguishers, fire protection systems), must not be neglected. Insofar as possible, process automation must be implemented in order to reduce staff involvement, thus limiting human error, provided that the safety and control devices can guarantee appropriate process operations. In the case of particularly risky operations, a dual control by two technicians is advisable. Moreover, several accidents have indeed caused the unit to lose its utility lines. It is important therefore to make use of backup feed lines on critical equipment undergoing exothermic reactions.

1. *ARIA: Database of technological accidents accessible via [www.aria.developpement-durable.gouv.fr](http://www.aria.developpement-durable.gouv.fr)*
2. *\*Accidents described in detail on data sheets available for consultation on the ARIA site*