Release of toxic gases in a pesticide plant

Night from 2 to 3 December 1984

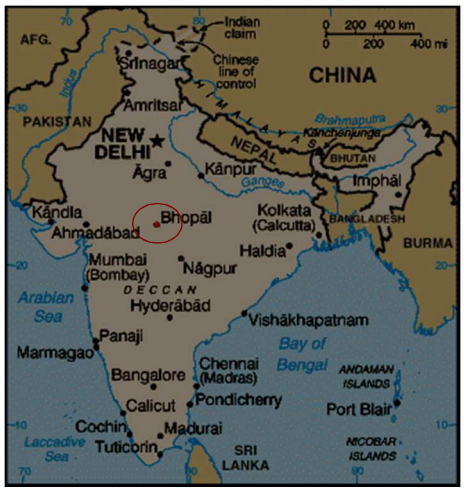
Bhopal

India

Methyl isocyanate (MIC)
Pesticide
Automation
Human and organisational failures
Maintenance

THE FACILITIES INVOLVED

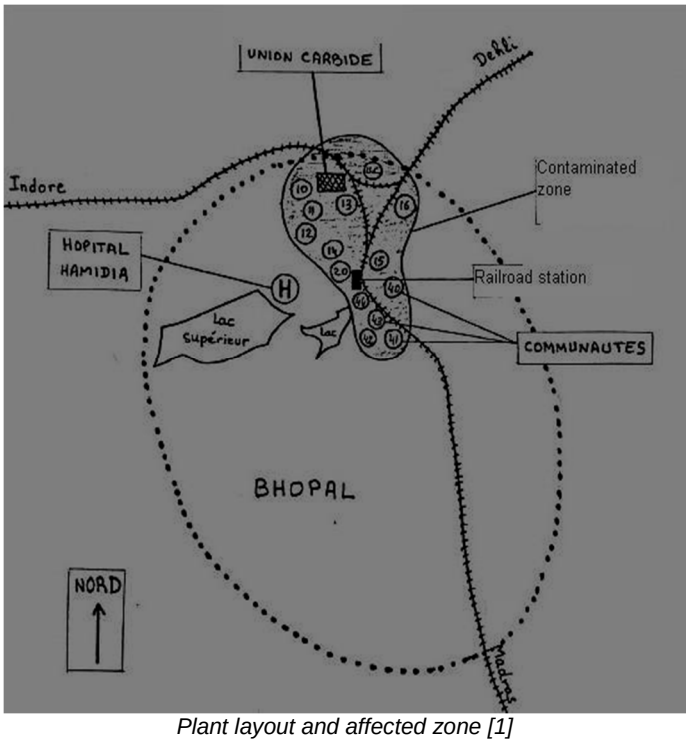
The site:



In 1969, the American company Union Carbide (UC) installed in Bhopal, capital of central India's Madhya Pradesh State, a manufacturing plant dedicated to the product Sevin, a powerful insecticide from the carbamate family derived by reacting methyl isocyanate (MIC), whose chemical formula is CH3-NCO, with α-naphthol.

Ten years later, 2 production units were built specifically to synthesise on-site the raw materials used in this reaction, as an alternative to transporting synthesised materials by lorry or rail. The MIC manufacturing unit, involving the reaction of phosgene (also produced on-site) with monoethylamine in the presence of chloroform (solvent), was launched in 1980.

The chemical facility, administered through the subsidiary Union Carbide India Limited (UCIL), was located less than 2 km from the Bhopal train station and encompassed over 6.8 ha. At the height of its activity, nearly 1,000 employees, most of whom unskilled and only speaking Hindi, were working at the site.



Plant layout and affected zone [1]

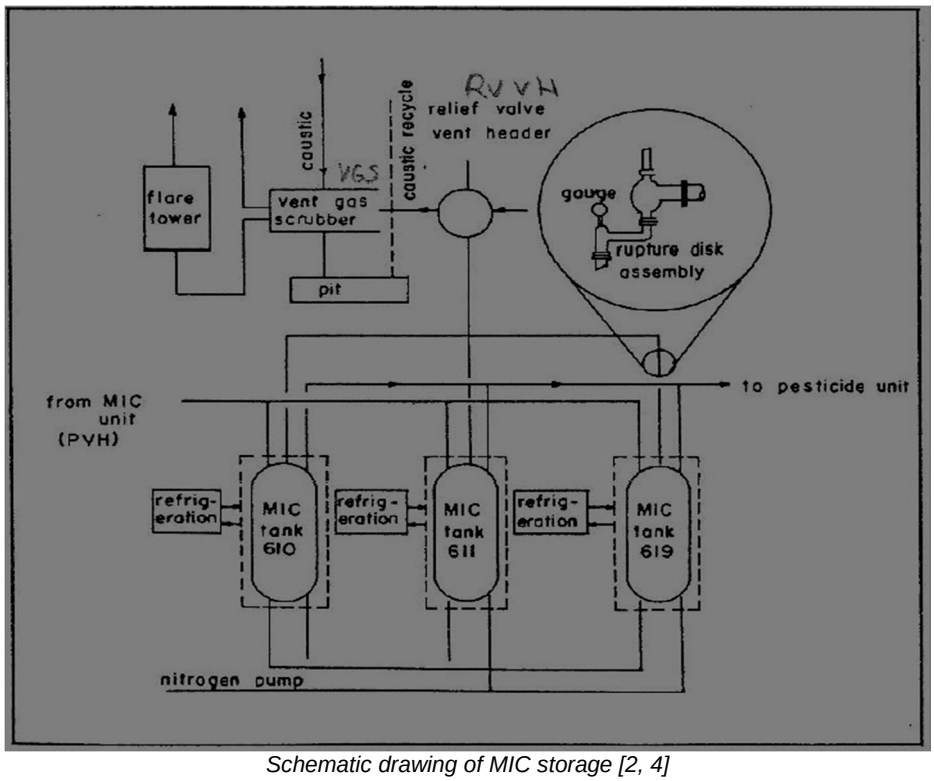
Shantytowns bordering the site [12]

Once the plant was operational, many shantytowns sprang up nearby, in particular to house plant personnel and their families. In 1984, a large number of makeshift residences were literally standing adjacent to the site.

The involved unit:

The methyl isocyanate (MIC) storage facility contained 3 tanks with a 60-m3 (50-tonne) capacity each (MIC tanks 610, 611 and 619 shown on the diagram), with the third one (no. 619) purposely kept empty to serve as a backup should problems arise on the other 2, which were to be filled at no more than half their capacity.

These tanks were horizontal and cylindrical (diameter: 2 m, length: 13 m), made of stainless steel and partially buried in concrete casings. They were nitrogen pressurised (0.35-0.69 bar) and refrigerated (0°C) in order to maintain the MIC in a liquid state, limit its evaporation and polycondensation (so-called "trimerisation"), and minimise the penetration of impurities capable of triggering reactions.



Schematic drawing of MIC storage [2, 4]

The tanks were connected to one another as well as to the MIC and pesticide production reactors via a dense network of pipes fitted with taps and valves.

Should pressure rise in one of the tanks, a safety valve tared at 2.76 bar ("RVVH" on the above diagram) channelled the gas to a neutralising tower ("VGS" on the diagram) running on soda (NaOH) in order to neutralise the toxic gas. Upon exiting the washer, these gases were to be burned with a flare positioned 40 m high.

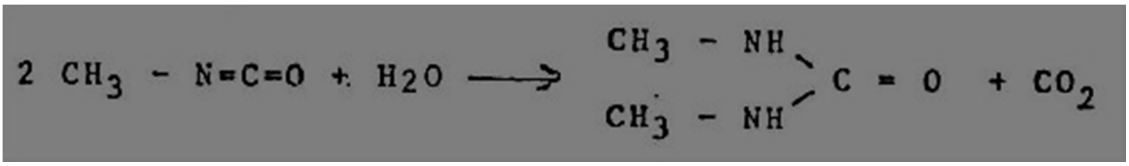
A rupture disc provided a sealed joint between the safety valve and the contents of each individual tank. A pressure gauge was placed slightly upstream of the disc (circled system on the diagram).

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

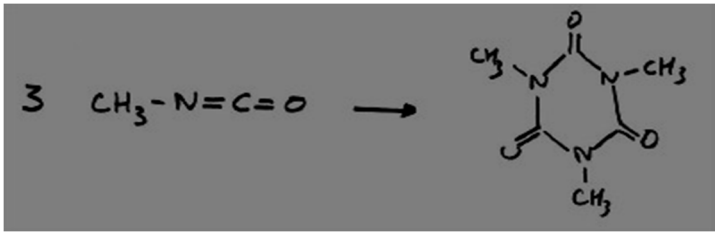
During the evening of 2nd December 1984, 500 litres of water were accidentally introduced into tank 610, which at the time contained 42 tonnes of MIC.

The MIC strongly reacted with the water, as follows:



MIC hydrolysis (exothermic reaction) [5]

The analysis of residuals left in the tank revealed that an MIC trimerisation (polycondensation) reaction had taken place as well, initiated by the heat released by the hydrolysis reaction and catalysed by iron, whose presence was also identified in the residue (iron salts stemming from the corrosion of cistern metal due to chloride ions, most likely resulting from the abnormally high chloroform content (12-16% instead of 0.5%) upon completion of the last distillation run between 18th and 22nd October).



MIC polycondensation forming 1-3-5 trimethyl isocyanurate (highly exothermic) [5]

A runaway reaction occurred, self-accelerated by the presence of contaminants and increased temperature (up to 200°C). The heat generated by the trimerisation reaction had been sufficient to vaporize the remaining MIC and initiate other chemical reactions yielding the various products found in the tank residue [2,5,7,9].

The pressure rapidly rose from 0.14 to 3.8 bar: the rupture disc broke, then the safety valve opened. A small proportion of the gases were treated in the neutralising tower (the little amount of soda present reacted), which quickly became saturated given the ineffective circulation of soda and subsequently allowed toxic gases to pass directly to the flare. Since the flare was inoperable, these gases were therefore being released untreated outside the plant.

The gas cloud and toxic aerosols primarily contained MIC, but potentially some of the other substances initially present or produced through "parasitic" reactions, including: phosgene, hydrogen cyanide, carbon monoxide, hydrochloric acid, and monoethylamine [7,10]. The exact composition of the released gas remains unknown. Given the night-time weather (an inversion layer), the cloud, which was heavier than air, drifted at ground level and was thrust by a weak wind towards the nearby shantytowns southeast of the site.

At 00:30 am, the plant alarm sounded. 120 workers were present at the facility, most of whom respected the evacuation order and fled in the direction opposite the wind (although a flight across the wind would have limited the exposure), despite difficulties imposed by the 2.5-m high enclosure wall topped with barbed wire and by the fact that the majority of emergency exits had been obstructed.

Around 1 am, fire nozzles along with water curtains were deployed in the aim of diluting the toxic emanations and cooling the cistern; however, these water curtains were limited to 10 m and thus had no effect on the gas cloud that was released at a height of 40 m.

Around 2 am, local police recorded the first phone calls regarding the accident.

Around 2:30 am, the siren alerting the population was activated, even though about 40 tonnes of MIC had already been released into the atmosphere. The cloud gradually extended more than 3 km covering a land area estimated at between 20 and 50 km², again according to sources.

The release of MIC stopped around 2:30 am after closing the valve, with pressure falling back below the tare limit of 2.76 bar.

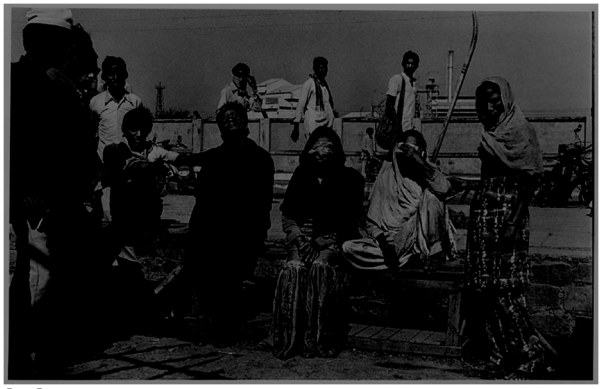
Consequences of the accident:

The exact number of victims will never be known with certainty; first estimated at 1,700 deaths and 170,000 intoxications, the toll has worsened over the years. According to sources, figures now stand at between 5,000 and 25,000 deaths and 200,000 to 800,000 injured. The latest official statistics, confirmed by the Madhya Pradesh State government, report the total number dead at 3,787 (2,259 of whom died "immediately") and over 500,000 intoxications.

Many victims perished in their homes, while sleeping or trying to escape. More than 4,000 animals (cattle, pets) lost their lives and vegetation was burned over a vast zone.

[12]

The injured streamed into the city's hospitals just after daybreak. These establishments, underequipped and not prepared for such a surge of victims, were quickly saturated, requiring makeshift installations to be assembled. Due to the company's lack of communication and a denial regarding the potential presence of hydrogen cyanide in the discharge, physicians facing extreme symptoms (acute oedema in the lungs, respiratory distress, persistent coughing, ocular lesions, etc.) were very hard pressed to identify a suitable treatment.



[12]

This disaster was also the cause of many serious long-term health-related consequences for the exposed population, including: respiratory disease, persistent coughing, early cataracts, depression, neurological disorders, cancer, tuberculosis, joint pain, gynaecological disorders, early menopause, spontaneous abortions, and leukaemia. Infant mortality spiked by 300%, and the rates of uterine cancer are the highest in all of India. Any long-term tracking of the population has been complicated however due to changes in oversight organisations and moreover because a majority of the exposed population being monitored have gradually been "lost", with most moving elsewhere.

The sudden shutdown of site operations following the accident exacerbated the disastrous environmental consequences: thousands of tonnes of toxic wastes were being stored under unsafe conditions, thus contaminating the public water supply

network. Some sources noted the presence of 25,000 tonnes of solid waste. A journalist asserted observing the presence of mercury in basins, bins filled with toxic substances and bags containing highly hazardous chemical products in a number of site hangars. This journalist also indicated that during the monsoon, infiltrating rainwater became charged with toxic compounds and polluted wells used for drinking water.

Also recorded was a major contamination of soils and groundwater, which nonetheless was not tied to the gas discharge but rather to a pre-existing chronic site pollution due to plant effluents containing high concentrations of both heavy metals and toxic substances. In 1999, the soil still contained significant quantities of mercury, chromium, copper, nickel and lead. As of 2003, the rates of mercury were exceeding current standards by a factor of six million. Chloroform, carbon tetrachloride and benzene were all detected in the water of wells located south and southeast of the plant. The vegetables and fruits grown in the immediate vicinity displayed these same toxic compounds in large quantities. Such an exacerbated chronic pollution would affect local populations for a long period of time [12].

Derelict site [12]

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 II*' directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

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

The 40 tonnes of MIC discharged represent 26,700% of the corresponding Seveso threshold (0.15 t - MIC), which brings the "hazardous substances released" index to a "6" score according to parameter Q1 (Q1 > 10 times higher than the threshold).

Three parameters are considered when determining the rating level of the "human and social consequences" index: H3, H4 and H5.

- Parameter H3 is assigned a "6" rating, given a number of deaths above 50.
- Parameter H4 is also assigned a "6", as the number of seriously injured topped 200.
- Parameter H5 receives a "6" as well, with the number of minor injuries in excess of 1,000.

As a result, the "human and social consequences" index is scored a "6".

To determine the "environmental consequences" index score, the only "known" parameter is Env13, rated a "4", as 5,000 tonnes of toxic wastes were being stored on the plant's 35-ha area.

Lastly, the overall "economic consequences" index was scored a "6" by virtue of exceeding criterion €18, given that the elimination of 5,000 tonnes of toxic wastes was estimated at $500 million (> €20 M).

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

Circumstances:

The Indian “green revolution” in the 1960’s had required a massive increase in the indigenous production of chemical fertilisers and pesticides. This was the context in which Union Carbide Corporation was permitted to set up the Serin manufacturing plant at Bhopal. [13] However, in the following decades, UC had to withstand the competition created by the arrival on the market of other insecticides (pyrethroids) and initially decided to close this financially troubled facility (budget deficit: $4 million a year). After negotiations with the Indian government, which sought to maintain employment in this impoverished region, **it was decided to keep the site open, although a drastic cost-cutting program was implemented to streamline activities. This culminated in the 1983 Operation Improvement Program, which imposed layoffs, less maintenance and a lower frequency of controlling parameters and inspecting equipment.** [13]

As a result, on the day of the accident, **the following technical safety measures were no longer effective:**

- storage had no longer been refrigerated for at least six months without any compensatory action ever being implemented, thus increasing the risk of MIC reaction;
- since 21st October, storage had no longer been nitrogen pressurised, increasing the risk that outside contaminants enter the reservoir;
- soda titration and circulation in the washing tower were no longer being controlled as of 23rd October 1984, causing a serious decline in efficiency (the survey would show that such steps would have been insufficient in any event given the tower's undersized design relative to the quantities being processed);
- the flare had been disassembled a few days prior for maintenance, though without adopting any compensatory measures;
- the MIC temperature, pressure and storage level indicators were all defective, and moreover the high-temperature sound alarms had been disconnected since they were permanently ringing (given that refrigeration had been stopped);
- "backup" tank 619 had been partially filled (1 tonne);
- subsequent to modifications that had not given rise to a risk analysis and were not being "tracked", a portion of the installations (valves) would have been replaced with simple steel instead of stainless steel, as specified in the initial design (thereby accelerating corrosion). Also, some lines would still have been connected to one another.

Moreover, the most recent MIC production run dated from 18th October and tank contents had not been analysed since then. The analyses carried out after the accident (in a small intermediate buffer tank used during transfers) revealed that the stored MIC held an abnormal quantity of chloroform. The steel walls of some valves would thus have corroded, thereby releasing ferrous ions, which in turn catalysed the MIC trimerisation reaction that took place at the time of the accident.

It is also important to mention that MIC being neither a raw material nor a product but a reaction intermediate, it should not have been stored in such quantities. Besides, there is an alternative way of making Serin from the same raw materials, merely reacting them in a different sequence and producing a less toxic intermediate than MIC. However, this lower hazard alternative implies higher manufacturing costs. [13]

Causes :

The origin of the water added to the MIC tank has generated multiple hypotheses and a good number of legal and political confrontations, in diminishing the weight of a precise factual analysis aimed at providing feedback. As a case in point, the Indian government has prevented external investigators (including the operator’s) from gaining access to the accident site and from interviewing some of the key actors (e.g. on-duty technicians). Just a few interviews were conducted over a year after the event, making their contents harder to use since the human mind has a natural tendency to "rewrite history" (psychological protection or self-defence mechanisms: refusal to admit error, omissions, simplifications, etc.), especially given the emotional impact this event produced.

The primary hypothesis widely disseminated in the media focused on an operational error that occurred while washing partially obstructed pipes: a sliding plug, introduced as a physical barrier and intended to prevent liquid from flowing past, would not have been installed and this oversight allowed water to enter a tank that nonetheless was located over 120 m away [2,3,6,7,8,10,12].

Experts retained by the site operator refuted this theory that they considered too "simplistic", given the distance involved and the height differential between the cleaning zone and the tank: this explanation implied that an entire series of valves normally closed had leaks or were left open (even though some of the valves tested more than a year later were found to be perfectly sealed) and moreover that a very large quantity of water under high pressure had been injected, which seemed implausible [9]. UC claimed that the water had been introduced directly at the level of the pressure gauge located upstream

of the tank rupture disc (see 1st diagram on p. 3) either as an act of sabotage or as a result of technician error, since a worker could have mistaken a connection during a product transfer (scheduled that evening) and hooked up the water intake on the inlet designated for nitrogen injection used for "expelling" MIC [2,6,8,9,10].

Regardless of the error resulting in the introduction of water, all reports agree in emphasising the widespread organisational negligence tied to the highly degraded operating conditions inside the plant (defective or bypassed technical barriers, a lack of personnel and insufficient training, etc.) as well as to poor preparedness on the part of both the company and local authorities in dealing with an accident (no adoption of an emergency / evacuation plan, no urban development controls, lack of information disseminated by all actors regarding product toxicity) [3,4,5,6,7,8,10,11].

These conditions were further compounded by an **inadequate reliance on feedback** from previous accidents or incidents and the **failure to acknowledge alarm triggers**. In fact, as of May 1982, American engineers at the Technical Centre of the UC Group's Chemical Products and Plastics Division in South Charleston accused, in their safety audit report, the plant of failing to comply with operating and safety rules, as well as numerous instances of negligence (corroded circuitry, absence of automatic extinguishers in hazardous zones, deformation of equipment parts, insufficient number of pressure indicators, leaks of MIC, phosgene and chloroform, burst pipes, inadequately certified personnel). However, this audit did not oppose the shutdown, already planned in January 1982, of the refrigeration unit. Plant employees and journalists had also attempted in vain to expose dysfunctions at the site, in addition to substandard working and safety conditions, in particular following a string of accidents: 2 injured during a fire on 24th December 1978; 1 death during a phosgene leak on 26th December 1981; intoxication of some 20 employees by an MIC leak on 10th January 1982; intoxication of 25 employees by a phosgene leak on 10th February 1982; 1 technician burned over 30% of his body due to contact with MIC in August 1982; 4 victims reported on 5th October 1982 (release of toxic vapours subsequent to the bursting of a flange connected to several pipes at the level of the MIC production unit); 3 workers and several neighbours intoxicated in October 1982; 2 victims in 1983; and 1 death by inhalation of toxic gases in January 1984 [3,8,10,11].

A graphical model of the underlying defects and deep-rooted causes is proposed in the Appendix (last page of this information sheet).

ACTIONS TAKEN

The Faith operation, conducted under the supervision of authorities, began on 16th December 1984 in order to eliminate the MIC still present after the accident in tanks 611 and 619. The Sevin production workshop was temporarily restarted for the purpose of removing MIC from storage. All precautions were taken: protection of tanks from pollutant intake, widespread sampling aimed at product verification, public information dissemination regarding the operation, availability of gas masks, installation of a safety perimeter, ambulances at the ready, on-site presence of squads of fire-fighters and police officers [7].

Since the Madhya Pradesh State government had refused to renew the plant's operating permit, the facility's closure announced in July 1985 meant the loss of some 700 jobs; the site was left derelict.

On 24th June 2004, the Indian government approved the judicial proceedings underway in the United States seeking to require the American company that purchased UC to clean the Bhopal site. The cost of eliminating the nearly 5,000 tonnes of toxic wastes spread over the plant's 35-ha and neighbouring parcels was estimated at $500 million.

Derelict site [12]

According to an agreement reached between UC and the Indian government, the compensation paid amounted to €378 million ($470 million). This sum remitted on 24th February 1989 by UC and UCIL, processed by the Indian Central Bank, was partially frozen in an account. In 1989, as a means of compensating all victims, Indian authorities distributed the minimum to each party: €1,750 per death, and €450 per injured victim, which is very meagre even by Indian standards. Both the Indian government and UC were indeed accused of collusion in the matter of compensation. In July 2004, the Indian Supreme Court finally ordered the Central Bank to immediately release the remainder of UC's 1989 settlement and distribute it to victims. It was announced that these payments would commence on 15th November 2004.

In May 2004, India's regional government announced that healthcare would be offered free of charge to all victims and not just the poorest among them.

Derelict site [12]

Initiated in 1987, the judicial hearing underwent several twists and turns. Charged at first with homicide, the 8 defendants (7 Indians and the American company president) benefited from a 1996 decision by the Indian Supreme Court. As the nation's final judicial arbiter, the Supreme Court proceeded by recasting the case as homicide by negligence, a misdemeanour charge punishable by a maximum 2-year prison term.

On 7th June 2010, the Bhopal Criminal Court sentenced the 7 individuals deemed responsible for the disaster (the eight person being dead in the meantime) to a 2-year prison term and a fine of 100,000 rupees (€1,751). They were given leave to appeal and immediately released on bail. [13] A $10,000 (€8,354) fine was imposed on Union Carbide India for negligence. The company's Managing Director at the time, cited as "on the run" by the court, was not specifically named in the verdict.

On 12nd November 2014, the parent company that had acquired in 2001 the subsidiary which owned the plant received a summons to appear before an Indian jurisdiction but did not answer the notification. A new audience is planned on 14th March 2015. [12]

LESSONS LEARNT

This disaster, the worst ever in the history of the chemical industry, underscores **the importance of maintaining efficient technical and organisational safety barriers over the long run**. During the period of economic difficulty experienced at this site, many trade-offs were implemented that sacrificed safety and with no proper risk management practiced by any of the actors led to tragic consequences and the tremendous toll paid by the neighbouring population.

In addition, this accident recalls the importance of **facility layout (risk analysis, etc.) and safety system design**. The hypothesis of a runaway reaction due to water intake into the MIC storage had not been taken into account in the risk analysis and when designing the dispersion column (the quantity of soda contained would have enabled neutralising no more than 3.5 tonnes of the 40 actually released), and moreover it was not certain that the flare, even had it been operable, could have absorbed a flow rate of 15 to 20 tonnes/h.

The Bhopal accident also underscores the **pivotal role of effectively managing modifications**. While the unit was rather well designed at the outset aside from its insufficient instrumentation (and perhaps overdesigned storage volume for highly toxic substances [11]), still the modifications introduced without a detailed risk analysis and without compensatory measures at the time of bypassing basic barriers for managing safety constituted a latent hazard that merely required an erroneous manoeuvre for disaster to strike [4,5].

Lastly, this accident highlights the importance and complementarity of risk management measures implemented across the world subsequent to the disaster: **reduction of risk at the source, controls over urban development near installations, emergency plans, and public information dissemination. Today, one estimate that a simple wet cloth over mouth and nose might have been enough to save many lives. Likewise if inhabitants and employees had had the reflex to flee across the wind instead of down-wind.**

Remains of the Bhopal installations today [12]

It is undeniable that the Bhopal accident caused a shift in the way that the industry views process safety and contributed to a move towards safer design, reduced inventory of toxic chemicals, a focus on human factors, employee engagement and emergency planning.

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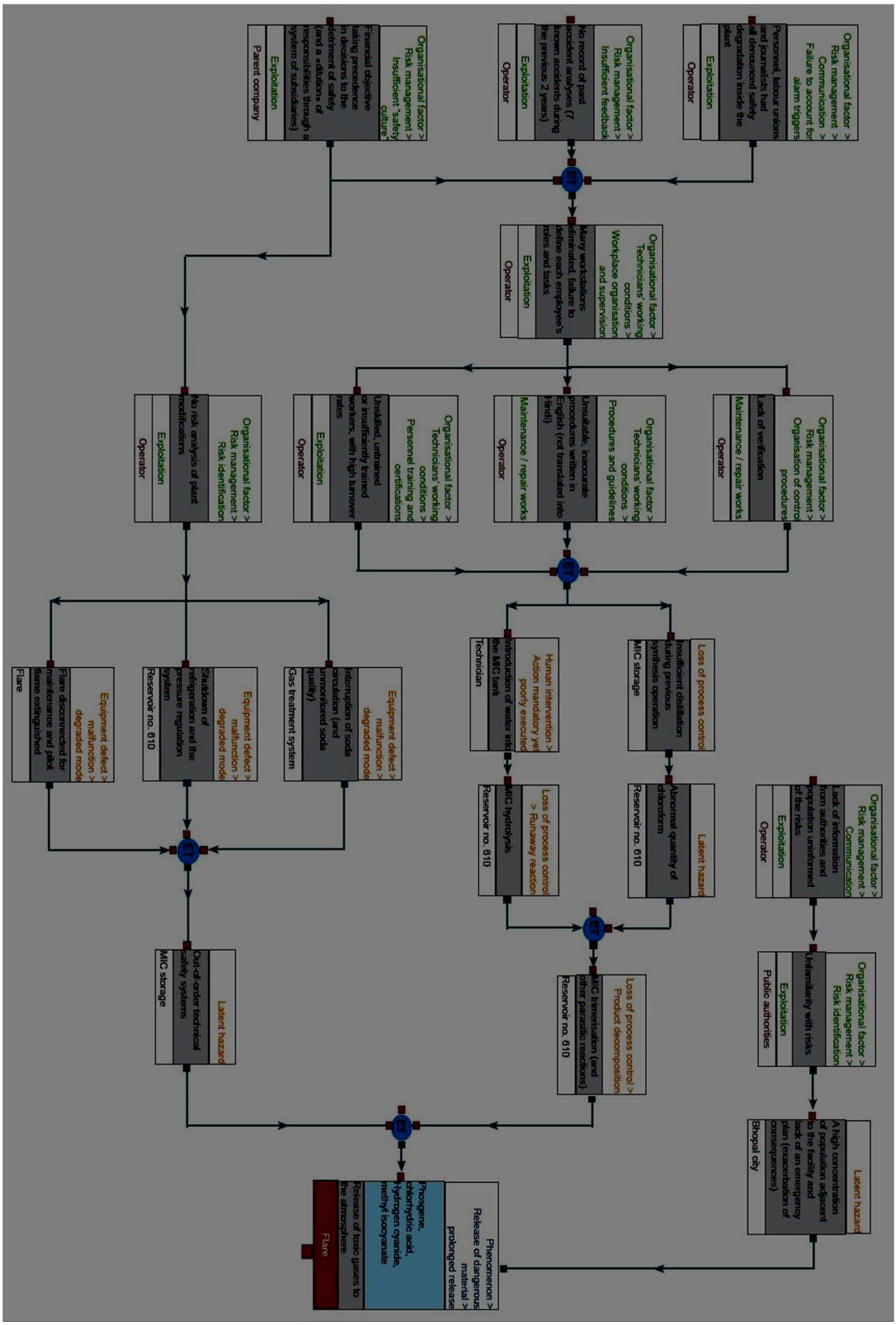
GRAPHICAL MODEL


Organisational factor > Risk management > Communication > Failure to account for alarm triggers
Exploitation
Operator
Personnel, labour unions and journalists had all denounced safety degradation inside the plant
Organisational factor > Risk management > Insufficient feedback
Exploitation
Operator
No record of past accident analyses (7 known accidents during the previous 2 years)
Organisational factor > Risk management > Insufficient 'safety culture'
Exploitation
Parent company
Financial objective taking precedence in decisions to the detriment of safety (and a dilutions of responsibilities through a system of subsidiaries)
Organisational factor > Technicians' working conditions > Workplace organisation and supervision
Exploitation
Operator
Many workstations eliminated, failure to define each employee's roles and tasks
Organisational factor > Risk management > Organisation of control procedures
Exploitation
Maintenance / repair works
Operator
Lack of verification
Organisational factor > Technicians' working conditions > Procedures and guidelines
Maintenance / repair works
Operator
Unsuitable, inaccurate procedures written in English (not translated into Hindi)
Organisational factor > Technicians' working conditions > Personnel training and certifications
Exploitation
Operator
Unskilled, untrained or insufficiently trained workers, with high turnover rates
Organisational factor > Risk management > Risk identification
Exploitation
Operator
No risk analysis of plant modifications
ET
ET
ET
ET
Organisational factor > Risk management > Communication
Exploitation
Operator
Lack of information from authorities and population uninformed of the risks
Organisational factor > Risk management > Risk identification
Exploitation
Public authorities
Unfamiliarity with risks
Latent hazard
Bhopal city
A high concentration of population adjacent to the facility and lack of an emergency plan (exacerbation of consequences)
Latent hazard
Loss of process control
Insufficient distillation during previous synthesis operation
MIC storage
Abnormal quantity of chloroform
Reservoir no. 610
Loss of process control > Product decomposition
MIC trimerisation (and other parasitic reactions)
Reservoir no. 610
Loss of process control > Runaway reaction
MIC hydrolysis
Reservoir no. 610
Human intervention > Action mandatory yet poorly executed
Introduction of water into the MIC tank
Technician
Equipment defect > malfunction > degraded mode
Interruption of soda circulation (and unmonitored soda quality)
Gas treatment system
Equipment defect > malfunction > degraded mode
Shutdown of refrigeration and the pressure regulation system
Reservoir no. 610
Equipment defect > malfunction > degraded mode
Flare disconnected for maintenance and pilot flame extinguished
Flare
Latent hazard
Out-of-order technical safety systems
MIC storage
Phenomenon > Release of dangerous material > prolonged release
Phosgene, chlorhydric acid, hydrogen cyanide, methyl isocyanate
Release of toxic gases to the atmosphere
Flare