Incident

Bhopal – The company's report

based on the Union Carbide Corporation's report – March 1985

Introduction

Speculation has led to the many conflicting reports that have been produced over the months since the leak of Methyl Isocyanate at Bhopal in December last year. Only recently have the facts come to light and soon reports by all concerned parties should have been published. In March 1985 Union Carbide Corporation, Danbury, Connecticut, published its report based on records and examination of the Bhopal plant after the incident. The features of the process and the events leading up to the incident are explained in this article though no attempt is made to question the actions of those concerned. It is hoped that following the publication of the Indian Government's report, a follow up article will be produced.

The reaction

The manufacture of Methyl Isocyanate (MIC) in Bhopal can be represented by two reactions.

1) Reaction of raw materials, phosgene and monomethylamine to form methylcarbamoyl chloride (MCC)

$$\underset{\text{phosgene}}{COCl_2} + \underset{\text{monomethylamine}}{CH_3NH_2} \rightarrow \underset{\text{methylcarbamoyl chloride}}{CH_3NHCOCl} + \underset{\text{hydrogen chloride}}{HCl}$$

2) Pyrolysis of methylcarbamoyl chloride to form MIC

$$\underset{\text{MCC}}{CH_3NHCOCl} \rightarrow \underset{\text{MIC}}{CH_3NCO} + \underset{\text{hydrogen chloride}}{HCl}$$

The process

Carbon monoxide produced on site was reacted with chlorine, brought in by tank truck, to form phosqene. This phosgene was then reacted in excess with monomethylamine (MMA), also brought in by truck, the reaction taking place in the vapour phase. Chloroform was used to quench the reaction products before they were fed to the phosgene stripping still (PSS) to separate unreacted phosgene for recycle. The bottoms from the PSS were then passed through the pyrolyser to separate HCl from the crude MIC, and onto the MIC refining still (MRS) where MIC was distilled and the bottoms, consisting of MCC, chloroform, residues and some MIC were returned to the process.

The refined MIC was stored in underground tanks before being transfered to the Derivatives Unit.

A simplified flow chart for the process is given in Figure 1.1.

The plant

The items of plant of particular relevance to the incident are the MIC refining still (MRS), the MIC storage system, the vent gas scrubber (VGS) and the flare tower.

MIC refining still (MRS)

A 45-tray column was used for the final separation of MIC from chloroform, MCC and residues from the process. The separation conditions were particularly critical with a high reflux ratio of 20:1 required to ensure the desired product specification was maintained. (The product specification required the chloroform content to be less than 0.5%.)

Full instrumentation was provided to maintain other operating conditions.

MIC storage system

MIC was stored in two of three 57 m^3 tanks. The third tank was used for emergencies and for temporarily storing off-specification product. The tanks were constructed from type 304 stainless steel resistant to corrosion from the stored on-specification product, and were mounded and covered with a concrete deck for protection and insulation.

The MIC was normally kept at around 0°C by circulation through heat exchangers cooled by a 30-ton refrigeration plant, using a non-aqueous coolant. Water was not used in order to avoid the possibility of contamination following a leak.

The tanks were designed for full vacuum to 3.8 bar (54.5 lbf/in^2) at 121°C and were hydrostatically tested to 5.2 bar (74.5 lbf/in^2).

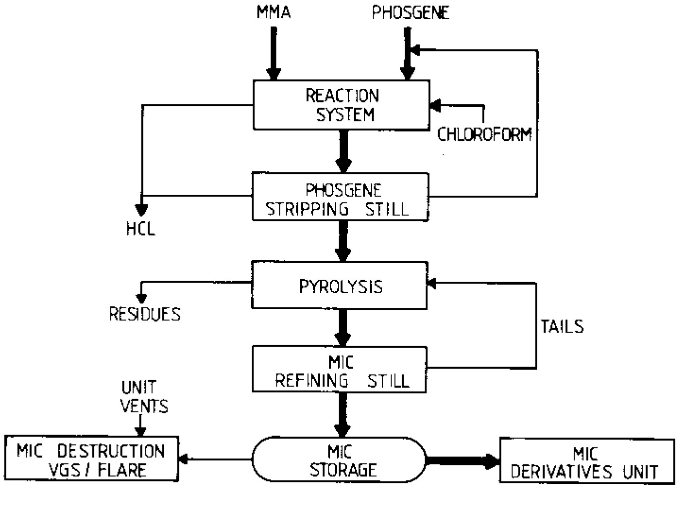

Figure 1.1 Simplified Process Flow Chart

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Piping arrangements allowed off-specification product to be either destroyed using the VGS or reprocessed at other locations within the plant.

The storage tanks incorporated a number of safety features in the form of the following instrumentation.

- Temperature indicator and alarm
- Pressure indicator and controller to regulate pressure by adding high purity nitrogen or by venting MIC vapour to the VGS and/or flare. NB. The controller did not automatically turn on the VOS caustic circulation pumps.
- A liquid level indicator and alarm for both high and low level.

All tanks were protected by safety valves set to relieve at 3.8 bar (54.5 lbf/in^2) with rupture discs to provide a positive seal between tanks and vent pipework. A pressure gauge installed on the outlet side of each disc was used to check that discs were intact.

The tanks' contents were mixed to ensure uniformity and samples were taken regularly to ensure that the specification was met.

Vent gas scrubber

The vent gas scrubber (VGS) was a 1.7 m diameter 18 m high packed tower with circulating caustic soda solution. During normal operation, one pump circulated the solution and the temperature, concentration and flow rate were monitored to ensure conditions were satisfactory. Low flow automatically engaged the auxiliary pump. Concentration of solution had to be measured daily and made up when necessary.

The VGS handled normal emissions from the Process Vent Header (PVH) and pressure reducing emissions from the MIC storage tanks.

Flare tower

The flare tower's main function was to burn vent gases from the carbon monoxide unit and the MMA vaporiser safety valve. It also burned gases vented from the MIC storage tanks, either directly or via the VGS, and gases from the MRS. The flare consisted of a shielded pilot flame and a flame front generator to ensure ease of re-lighting should the pilot be extinguished. As a further safety precaution, a seal tank was installed at the base of the tower to eliminate the possibility of backfiring in the vent lines.

Events leading up to incident

The events leading up to the incident began in June and are listed along with their consequences in the Event Timetable. This table was compiled from information given in Union Carbide Corporation's report.

Cause of incident

The residue in Tank 610, the tank in which the reaction took place, was found to contain a large number of complex organic compounds. Following extensive analysis and experimentation, the major components of the residue were reproduced and a theory proposed for the initial contents of the tank and the cause of the reaction.

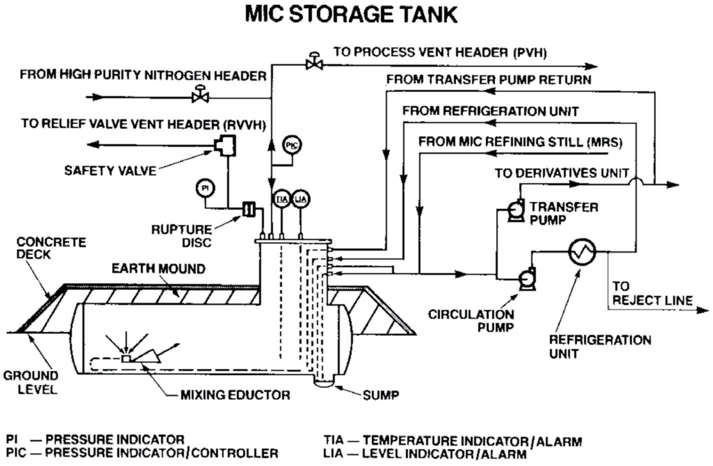

Figure 1.2 MIC storage tank and associated pipework.

MIC trimer	40% to 55%
1, 3 - Dimethylisocyanurate (DMI)	13% to 20%
1,3,5 - trimethylbiuret (TMB)	4% to 8%
1,1,3,5 - Tetramiethylbiuret (TRMB)	3% to 6%
Other complex organics	16% to 24%
MIC	0.2% to 1.0%
Chloroform	0.4% to 1.5%
Water	2%
Iron, chromium, nickel salts	0.18% to 0.26%

Table1: Significant residue components

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JUNE		REFRIGERATION PLANT FOR MIC STORAGE TANKS SHUT DOWN Me storage temperature from June to December approximately 15°C to 20°C. NB. Institute plant never lets MIC temperature exceed 5°C. TEMPERATURE ALARM DISCONNECTED AND NOT RESET AT HIGHER TEMPERATURE so no automatic reaction warning based on temperature
OCTOBER 18th — 22nd		MIC REFINING STILL OPERATED AT HIGHER THAN USUAL TEMPERATURE RESULTING IN HIGHER THAN SPECIFICATION CONTENT OF CHLOROFORM IN MIC OFF-SPECIFICATION MIC SENT TO TANK 610 INSTEAD OF OFF-SPECIFICATION TANK
OCTOBER 19th		MIXING OF TANK 610 CONTENTS STOPPED
OCTOBER 23rd		MIC PRODUCTION UNIT SHUT DOWN VENT GAS SCRUBBER (VGS) CIRCULATION PUMP SET TO STANDBY No automatic caustic circulation control — manual initiation only. TANK 610 PRESSURE — 1.1 bar (16.5 lbf/in^2)
DATE UNKNOWN		FLARE STACK INOPERATIVE DUE TO MAINTENANCE — exact date maintenance started is unknown.
NOVEMBER 30th		FAILURE TO PRESSURISE TANK 610. It is reported that the rupture disc was tested and found to be intact.
DECEMBER 1st		TANK 610 STILL NOT PRES5URISED PROCESS FILTER LINES CLEANED WITH WATER LINES NOT SLIP PLATED
DECEMBER 2nd	**10.20p.m.**	TANK 610 NOW PRESSURISED TO 1.1 bar (16.5 lbf/in^2) CONTENTS – 41 TONNES MIC (70% CAPACITY)
DECEMBER 2nd	**10.45p.m.**	SHIFT CHANGE
	11.00p.m.	TANK 610 PRESSURE — 1.7 bar (24.5 lbf/in^2) It is not known if the new operator knew the previous pressure in the tank. The temperature of the contents was not recorded. OPERATOR ASSUMES PRESSURE IS NORMAL Since the pressure was within limits (1.1 bar (16.5 lbf/in^2) to 2.7 bar (39.5 lbf/in^2) the operator was justified in this assumption. No consideration seems to have been given to sudden rises in pressure — rather than static pressure readings. MIC LEAK REPORTED IN PROCESS AREA. SOURCE NOT IDENTIFIED.
DECEMBER 3rd	**12.15a.m.**	MIC RELEASE REPORTED NEAR VGS AND MIC PROCESS FILTERS PRESSURE IN TANK 610 — 3.1 bar (45.5 lbf/in^2) RAPID INCREASE IN PRESSURE TO 4.8 bar (69.5 lbf/in^2) (TOP OF SCALE) Operator calls Supervisor who runs out to Tank 610. Heat is felt radiating and rumbling is heard from tank. Also, screeching from safety valve. SUPERVISOR STARTS VGS CIRCULATION PUMPS Flow indicator did not indicate flow started (although subsequent investigation suggested flow did occur).
DECEMBER 3rd	**12.20a.m.**	PLANT SUPERINTENDENT NOTIFIED
	12.25 a.m.	PLANT SUPERINTENDENT ARRIVES HIGH LEVEL OF MIC IS NOTED IN THE AIR
	12.45 a.m.	DERIVATIVES UNIT OPERATIONS SUSPENDED
	1.00a.m.	TOXIC GAS ALARM SOUNDED BY OPERATOR Plant Superintendent and operator confirm MIC is being emitted from VGS. FIREWATER MONITORS DIRECTED ONTO VGS WATER STREAMS DIRECTED ONTO TANK 610 MOUND — steam seen issuing
	1.30–2.30a.m.	SAFETY VALVE RESEATS Indicates pressure <3.8 bar (54.5 lbf/in^2) During the morning the tank contents cooled to create a partial vacuum indicating tank still intact. NITROGEN PUMPED IN TO TANK TO RAISE PRESSURE TO 1.5 bar (21.5 lbf/in^2)
DECEMBER 20th		Samples taken from Tank 610 for investigation.
DECEMBER 22nd		All remaining MIC stock converted to carbaryl insecticide by this date.

Table 2: Event timetable

The material required to form these products was concluded to be MIC, water (450 kg to 900 kg (1000 lb to 2000 lb)) and chloroform (700 kg to 1400 kg (1500 lb to 3000 lb)).

Ingress of water into Tank 610 would have caused the initial reaction resulting in a marked temperature increase. This would have led to the decomposition of chloroform to yield chloride ions, the resulting mixture being corrosive to the stainless steel tank. (The ratio of iron, chromium and nickel salts in the sample was consistent with the composition of type 304 stainless steel). The iron salts would have catalysed further reactions which, although complex, are recognised, and would have formed all the other components found in the residue.

The temperature in the tank must have exceeded 200°C in its latter stages in order for the suggested reactions to have occurred. It has also been calculated that to discharge the contents of the tank in the two hours that the safety valve is thought to have been open, the pressure must have averaged 13.4 bar (194.5 lbf/in^2) — well over four times the design pressure.

There are two major concerns relating to this incident.

1) Source of the initiating reaction components
2) Failure to identify and control the incident

Source of initiating reaction components

For the reaction described above to have occurred both water and chloroform must have been present in more than trace quantities. The following suggestions have been made for their routes of ingress into the tank.

Water

Two routes were proposed by Union Carbide. Water could have been added inadvertently or, deliberately via the nitrogen pressurisation line, which was located nearby to a water supply.

Alternatively, the water could have come via the process filter lines which were being washed with water shortly before the incident and had not been slip plated contrary to normal practice. Although this would have required a number of valves to have not been fully shut, the fact that Tank 610 could not be pressurised prior to the incident would suggest that there was indeed a leak. The route of nitrogen leakage was probably the route of water ingress.

Chloroform

Between 18th and 22nd October the MIC refining still was operated at a higher than usual temperature. MIC with a chloroform content of between 12% and 16% (Specification - max. 0.5%) was transferred to Tank 610 rather than the off-specification tank.

Samples taken on 5th and 9th December revealed contaminated product in the transfer lines to the derivatives unit.

Failure to identify and control the incident

The plant at Bhopal was designed and built with many safety features. However over the period from June until the incident many of these features were rendered inoperative (as detailed in the event timetable) without recognising that a hazard remained despite the discontinuance of MIC production.

- The flare stack was inoperative due to maintenance.
- The VGS was on standby without regular maintenance.
- The MIC storage refrigeration plant was shut down.
- The temperature alarm on MIC storage was disconnected.

Failure to slip plate lines during maintenance is a common cause of accidents. It is possible that this was the cause of water entering the tank. There was a shift change at the time of the accident — another common factor in accident scenarios. It is possible that lack of communication between the two shifts concerning tank pressure led to failure to recognise that there was something wrong early in the event. The fact that the MIC Storage refrigeration plant was shut down took away much of the 'room for error' which might otherwise have been provided. It is worth noting that Union Carbide's Institute Plant never lets the MIC storage temperature exceed 5°C.

Conclusion

The reaction which caused the release of MIC was caused by the ingress of between 450 kg and 900 kg of water into the tank containing MIC contaminated with chloroform.

The incident reached the proportions it did because of the incremental degradation of previously well designed safety measures.

Reference

Bhopal Methyl Isocyanate Incident Investigation Team Report, March 1985. Union Carbide Corporation, Danbury, Connecticut.

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