

REPORT ON SCIENTIFIC STUDIES  
ON THE FACTORS RELATED TO  
BHOPAL TOXIC GAS LEAKAGE

DECEMBER, 1985

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**This Report results from Studies**

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## C O N T E N T S

1.0	<b>INTRODUCTION</b>	
1.1	The Bhopal Pesticides Plant	1
1.1.1	MIC manufacturing process	2
1.1.2	MIC storage system	3
1.1.3	Vent gas scrubber	8
1.1.4	Flare tower	10
1.2	The Event	11
1.3	'Operation Faith'	14
2.0	<b>EXAMINATION OF TANK 610 AND ITS CONTENTS</b>	
2.1	Sampling	24
2.1.1	Core samples from the manhole nozzle	24
2.1.2	Samples from tank residue after opening the tank	27
2.1.3	Samples from pipelines	27
2.1.4	MIC samples from tank 611	27
2.1.5	Metal pieces cut from tank 610	28
2.2	Chemical Analysis	28
2.2.1	Physical appearance of samples of residue	28
2.2.2	Solubility characteristics	29
2.2.3	Qualitative analysis	29
2.2.4	Analytical procedures	29
2.2.5	Analytical results	30
2.3	Total Representative Sample of Residue and its Analysis	30
2.3.1	Product distribution	31
	Annexure 2.1	43
3.0	<b>CHEMISTRY OF FORMATION OF COMPOUNDS IN TANK 610</b>	
3.1	Experiments	55
3.2	Observations	55

3.3	Discussion	56
3.3.1	Material balance	59
3.4	Comments	59
3.5	Gaseous Products on Reaction of MIC	59
	Annexure 3.1	63
4.0	<b>AN ANALYSIS OF DESIGN AND ENGINEERING FEATURES</b>	
4.1	MIC and its Characteristics	71
4.2	Storage Tank	71
4.3	Nitrogen	73
4.4	Instrumentation and Control Systems	73
4.5	Refrigeration	74
4.6	Vent Gas Scrubber	74
5.0	<b>AN ANALYSIS OF THE EVENT</b>	75

## ABSTRACT

A major leakage of toxic gases took place on the night of 2/3 December, 1984 at the Union Carbide Factory in Bhopal from a buried stainless steel tank in which fortytwo tonnes of liquid methyl isocyanate (MIC) had been stored from October, 1984, resulting in loss of human life and injuries to thousands. Damages occurred to animals and plants. A further quantity of MIC in a second buried tank presented a serious hazard. Based on an appreciation of the chemical reactivity and properties of MIC, a number of measures were adopted to minimise the recurrence of another leakage and to contain the effects of such an eventuality. A risk management system was established and the material in the tank and in other containers was processed safely during 16th to 22nd December, 1984.

MIC reacts with itself and polymerises readily with explosive violence, especially under the influence of trace amounts of metallic catalyst contaminants. Commercial MIC is stated to be stabilised by the presence of a few hundreds parts per million of phosgene. Water also reacts with MIC, generating heat in proportion to the quantity of water. Heats of reaction from polymerisation or with water raise temperature resulting in conversion of unreacted MIC into a vapour or gas. An examination of several samples of residues removed from different sections of the tank from which leakage occurred has established the presence of over twelve chemical entities. These include MIC-Trimer (MICT), methyl ureas (DMU, TMU), trimethyl biuret (TMB), dimethyl isocyanurate (DMI), a cyclic dione (DIONE), and mono, di and trimethyl amines (MMA, DMA, TMA), besides large amounts of chloride and some amounts of sodium, iron, chromium and nickel salts. The relative proportions of all materials have been determined and the quantities present in the residue in tank 610, assuming they total 12.5 tonnes.

In order to determine the conditions of formation of the chemical entities found in the residue of tank 610, a large number of experiments on the transformation of MIC from tank 611 have been carried out in open and sealed containers at different temperatures. These include heating MIC alone or reacting it in presence of water, traces of ferric salts, and chloroform. The residues have been analysed in each case. It is shown that all products found in the residues of tank 610, with the exception



of DMI, DIONE and methylated amines (MMA, DMA, TMA) are found when MIC is heated in stainless steel closed tubes to temperatures upto 200°C with water and trace amount of ferric chloride. The formation of others require temperatures above 200°C. DIONE is formed only when chloroform is present in the initial mixture. The composition of residue in these trials is closest to that found in the residue of tank 610, when the sealed tube reaction mixture has been heated to 220°C - 250°C. It has also been shown that DMU and TMB which are products of reaction of MIC with water below 200°C, can be transformed to MICT, DMI, DIONE and Methylated Amines in further reactions in which MIC, trace metal and chloroform are involved. From a study of these chemical transformations and quantities of products found in the residue in tank 610, it is possible to arrive at a total materials balance. It is thus estimated that 12,087 kilograms of MIC and 595 kilograms of chloroform reacted with 512 kilograms of water to produce the residue containing 6,964 kg. of MICT, 2,675 kg. DMI, 391 kg. DIONE, 161 kg. DMU, 117 kg. TMB, 191 kg. TMU, 246 kg. DMA, 129 kg. MMA and 423 kg. TMA as well as 177 kg. of chloride. This represents in part the chloride and fully all other materials in the residue of tank 610. From the products found in the residue, the calculated amount of heats of chemical reactions and the extent of bulging of the exhumed tank, it is surmised that the temperature in the tank rose above 250°C at the time of the accident. It has been observed, in preliminary laboratory experiments that pure MIC, made by a route which does not involve phosgene or chloroform, when subjected to heating to 300°C produces small amounts of hydrogen cyanide. In the presence of chloroform, hydrogen cyanide formation is not found. Further experiments at higher temperatures are planned.

A detailed analysis of the features of design of the plant has been made together with the characteristics of MIC. MIC, when contaminated with traces of metallic impurities, which act as catalysts, undergoes a violent polymerisation, and the heat generated can volatilise a large proportion of MIC. The gas is highly toxic on inhalation. Use of iron, steel, aluminium, zinc, galvanised iron, tin, copper are prohibited from use in areas where MIC can come in contact. Commercially produced MIC contains phosgene which according to Union Carbide, acts as inhibitor of polymerisation. It is estimated that ingress of a few litres of water would lead to the elimination of phosgene and hydrolysable chlorides and produce hydrochloric acid which in turn can produce metallic impurities by reaction with the tank.

( iii )

There are no facilities for collecting MIC produced separately in each shift and the material is directly led into the storage tanks without batchwise analysis. There are no on-line analysers. Similarly, nitrogen from a neighbouring factory is fed directly into the storage tanks, without full intermediate storage and quality determination. Carbon steel sections are used in the connectors to the storage tanks. Copper tubes are used in connectors to the level instruments of the tank. The system of instruments for alarm to indicate sudden increase in temperature are not suited to the conditions of operation. Only a single refrigeration system for cooling of MIC in two tanks was installed and it had not been operated for some considerable time.

MIC has the combination of properties of very high reactivity with minimum contaminants, ready volatility to become gas and very high inhalation toxicity. The installed facilities provided for disposal of unstable liquid MIC in alkali or for the neutralisation of gaseous emissions from violent reaction, on examination are found to be not capable of meeting the objectives of such disposal in a very short time of two hours.

The ingress of about 500 kg. of water alone, without metallic contaminants, would have led to a reaction with three to four tonnes of MIC and gradual rise in temperature to 70°C, below the boiling point of MIC at the safety valve pressure. The very rapid explosive rise in temperature and pressure in the tank 610, implies conditions for a run-away trimerisation reaction already existed. Ingress of water and reaction with MIC would generate carbon dioxide evolution and cause mixing. The storage tank conditions would then equal those in a well mixed reactor, supplied with heat. Once initiated, the trimerisation reaction had features of auto-catalytic and auto-thermal reactions and temperatures increased rapidly to 250°C. The relief valve design could not permit free flow of large quantities of gases at the level at which they were generated and therefore further reactions continued.

The presence of sodium at levels of 50 to 90 ppm in the samples from residues of tank 610 indicates ingress of some alkali, possibly derived from the Vent Gas Scrubber Accumulator. It is known that the tank 610 could not be pressurised with nitrogen at any time after 22 October, 1984. The contents of tank 610 were virtually at atmospheric pressure from that date providing opportunities for entry of metal contaminants. From a

perusal of the reports of the events of the night of 2/3 December, 1984, it appears during the cleaning of choked filters with water in the Relief Valve Vent Header, such water, perhaps mixed with alkali from Vent Gas Scrubber Accumulator, could have entered the non pressurised tank and may have carried some metallic contaminants from the carbon steel portions of header pipelines. The rapid rise in temperature necessitates onset of metal catalysed polymerisation and could not result from water alone. The presence of chloroform has no influence whatsoever in initiating or accelerating the run-away reactions. The quantum of leakage is related not to the quantum of water but to the amount of MIC stored in a single container. If 42 tonnes of MIC had been stored in 210 stainless steel drums instead of a single tank, leakage by reactions or spillage would be no more than one fifth of a tonne.

Public preparedness for eventualities are dependent on information available on the toxicity and hazards. It appears that the factors that led to the toxic gas leakage and its heavy toll existed in the unique combination of properties of MIC and from the features of design of the plant. Storage of large quantities of such a material for unnecessarily long periods in single large tanks was made possible by the facilities installed. Insufficient caution in design, in choice of materials of construction and in instruments, together with lack of facilities for safe effective quick disposal of materials showing instability contributed to the event and to the adoption of guidelines and practices in operation and maintenance. The combination of conditions for the accident were inherent and extant. Some inputs of integrated scientific analysis of the chemistry, design and controls relevant to the manufacture would have avoided or lessened considerably the extent of damage.

## **1.0 INTRODUCTION**

The leakage of a large quantity of highly toxic gas from a buried tank in which Methyl Isocyanate was stored at the Union Carbide plant at Bhopal on the night of 2/3 December, 1984, led to the tragic loss of life and to serious damage and disabilities of thousands of people. This is the worst tragedy in the history of chemical industry. A further quantity of methyl isocyanate present at that time in another adjacent tank represented a serious hazard of a further leakage. Through a careful scientific review of the possible causes of the leakage, resulting from a violent chemical reaction and the identification of probable circumstances and origins of such an event, a number of measures were adopted to prevent a recurrence of such an explosive reaction. The Methyl Isocyanate was processed safely under 'Operation Faith'.

A scientific study of the chemical nature and reactions of Methyl Isocyanate, the features of the facilities and controls for its manufacture, storage, utilisation and disposal together with full examination of the buried tank and its constituents provides basis for outlining the factors and circumstances which led to the violent chemical transformations and rapid leakage of toxic gas. The results of such a study are presented in the Report.

### **1.1 The Bhopal Pesticides Plant**

Union Carbide has established a facility for the manufacture of Sevin (Carbaryl) and its formulations in their plant at Bhopal in India. From late 1977, Sevin was manufactured by using imported primary raw materials, viz. alpha-naphthol and methyl isocyanate (MIC). The MIC which was imported was made in Union Carbide's MIC plant in USA and shipped in stainless steel drums. However, from early 1980, MIC was manufactured in the Bhopal plant using the know-how and basic designs supplied by Union Carbide Corporation, USA (UCC).

The plant at Bhopal also produced carbon monoxide and phosgene as intermediates required for the production of MIC.

The manufacturing process for Sevin involves the reaction of a slight excess of alpha-naphthol with MIC in the presence of a catalyst in carbon tetrachloride solvent. The know-how for the manufacture of Sevin was provided by UCC.

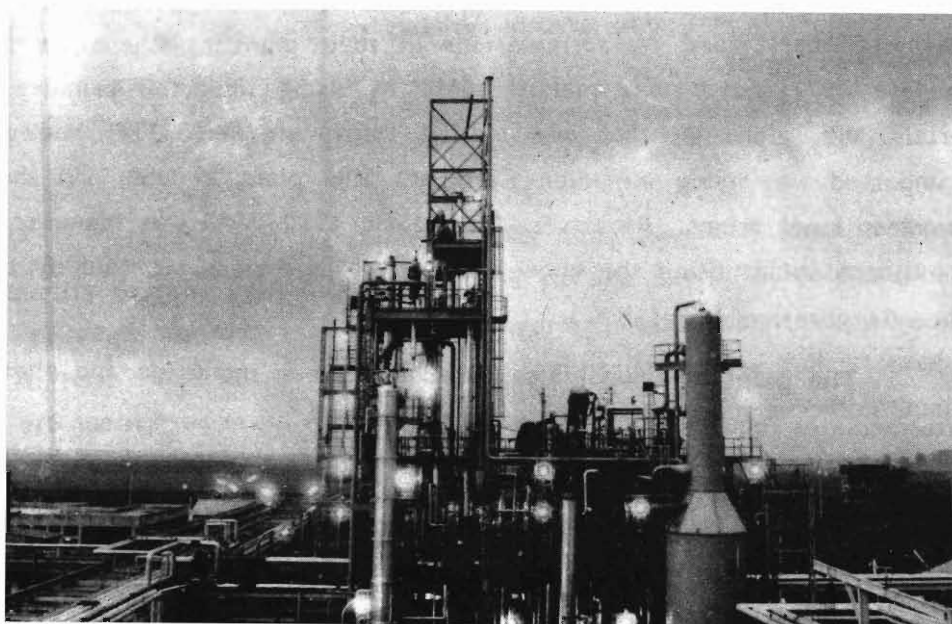
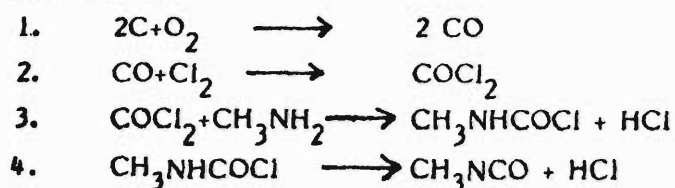
### 1.1.1 MIC manufacturing process

The raw materials used to make MIC are monomethylamine (MMA) and phosgene. Chloroform is used as solvent in the MIC process, and caustic lye for the neutralisation of any toxic material requiring disposal.

Phosgene is produced by reacting carbon monoxide and chlorine. Carbon monoxide is produced by reaction of petroleum coke with oxygen. Petroleum coke is obtained from an indigenous supplier, and oxygen is supplied from a neighbouring air separation plant. Chlorine, MMA, caustic lye and chloroform are brought in by tankers and stored in tanks. Facilities for storage of carbon monoxide and phosgene, both of which are highly toxic gases, were not provided. These were utilised for production of MIC as soon as produced.

MIC is produced by reaction of phosgene and MMA to methyl-carbamoyl chloride (MCC) and hydrogen chloride (HCl). MCC is then pyrolysed to yield MIC and HCl.

The Chemical reactions involved in the production of MIC via phosgene are as follows :



**MIC PLANT**

Phosgene and MMA are reacted in vapour phase to give MCC. The reaction products are then quenched in chloroform and fed to Phosgene Stripping Still (PSS). Unreacted phosgene is removed in PSS and recycled. The bottoms from PSS are fed to the pyrolyser where MCC is pyrolysed to give MIC and HCl and MIC and HCl are separated. The pyrolyser condenser feeds the MIC Refining Still (MRS). In MRS, the MIC is separated from the chloroform in the upper part and is led directly into the storage tanks. The bottoms of MRS are recycled to the process. The HCl formed is scrubbed with chloroform and extracted with water to produce aqueous HCl. Aqueous HCl is disposed off by neutralisation in a lime pit.

### 1.1.2 MIC storage system

MIC storage system comprises three horizontal mounded 15,000 gallon (57 M<sup>3</sup>) tanks and are designated as E-610, E-611 and E-619. Normally two of the three storage tanks are used to store the product of acceptable quality and the third tank is used for temporary storage of off-specification material. Generally, off-specification material is reprocessed. The two tanks can hold about 90 tonnes of MIC which can cater to about 30 days of production of Sevin using the stored MIC.

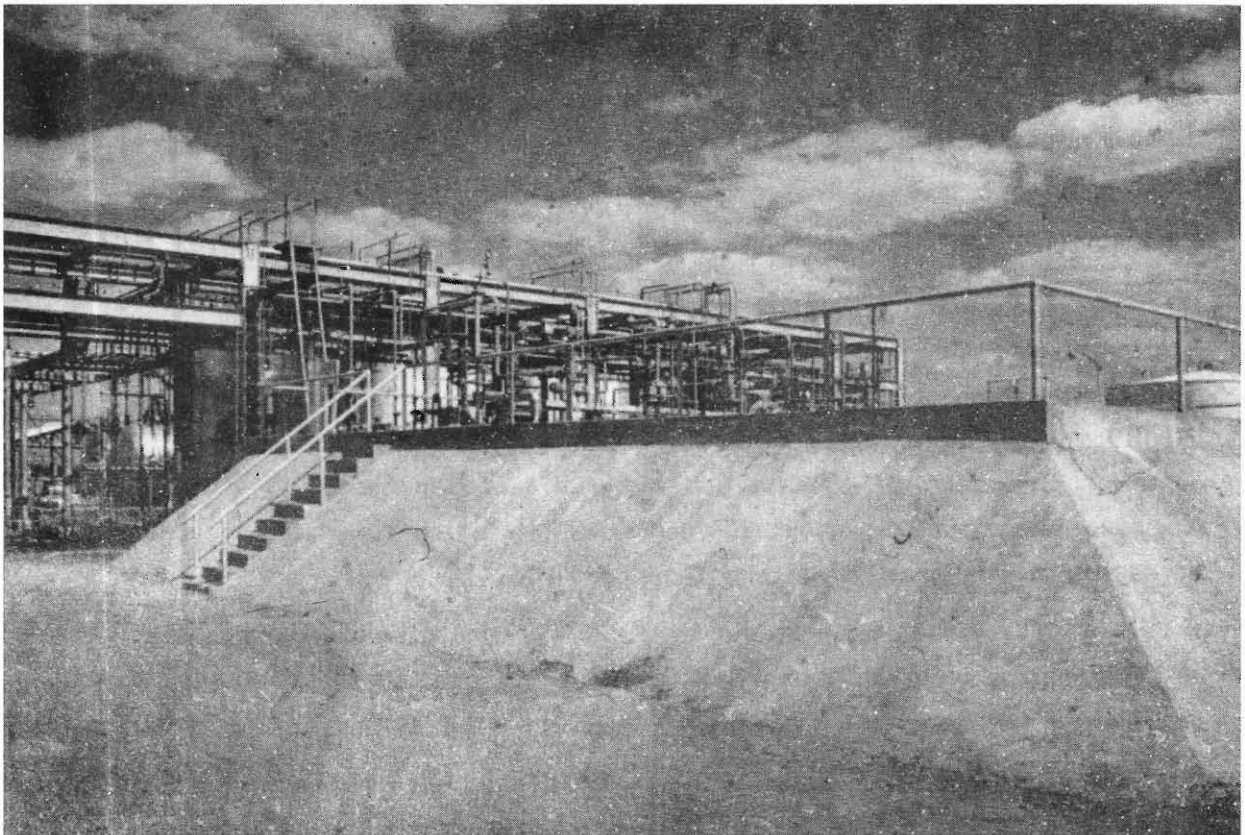
The tanks are made out of SS 304/SS 316, with nominal diameter of 2400 mm (8 feet) and nominal length of 12000 mm (40 feet). They are designed for full vacuum to 2.72 kg/cm<sup>2</sup>g (40 psig) at 121°C.

The schematic layout of the three MIC storage tanks with common headers is shown in Figure 1.1. MIC from MRS condenser in the MIC production facility (MIC structure) is led by a long common line of stainless steel to the MIC storage tank area and then branches off just before entry to the individual storage tanks.

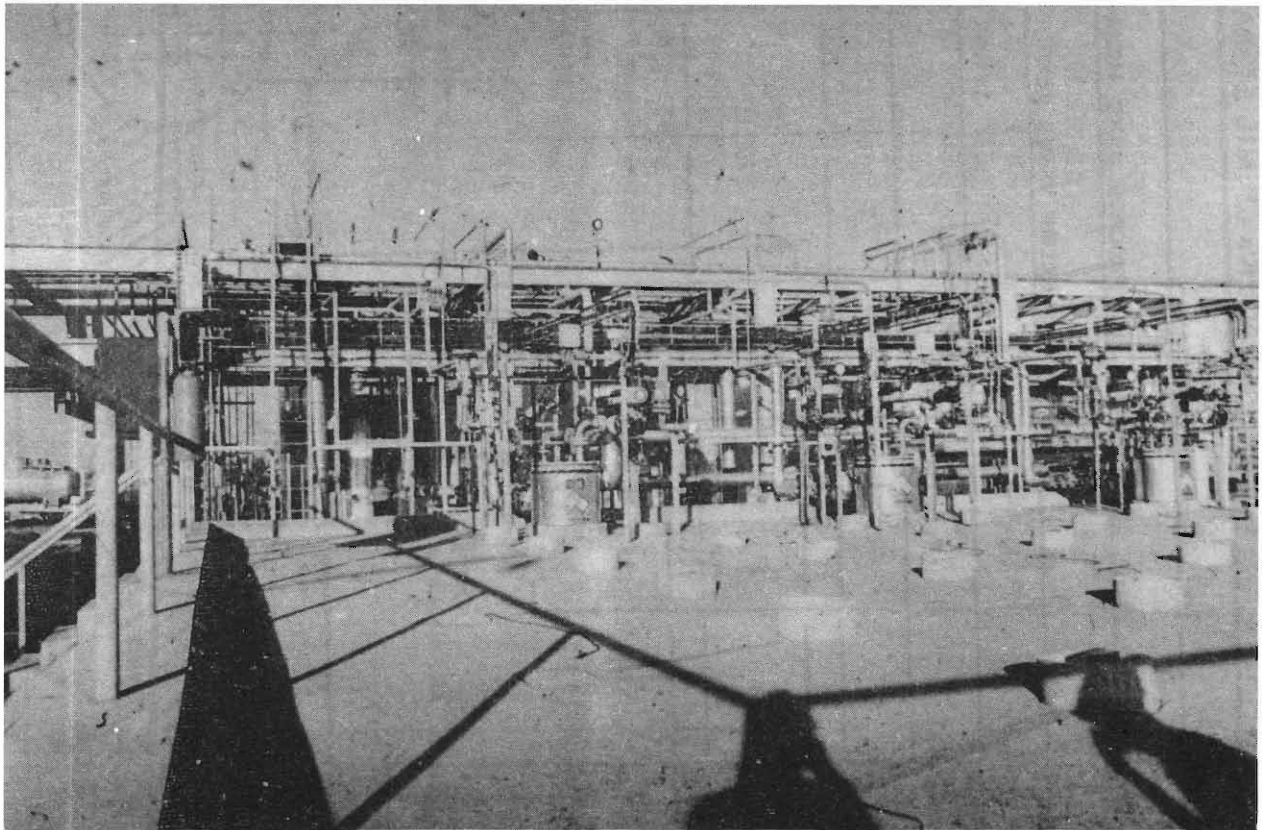
MIC is to be stored under high purity nitrogen pressure. The nitrogen is supplied to the storage tanks by a common header of carbon steel. Excess nitrogen from individual tanks is taken to a 50 mm (2") common Process Vent Header (PVH) of carbon steel. Similarly, the discharges from Safety Relief Valves (SRV) of individual storage tanks are also taken to a common 100 mm (4") Relief Valve Vent Header (RVVH) of carbon steel. The tank side PVH and RVVH are interconnected.

The transfer of MIC from the storage tanks to the Sevin unit is also through a common line.

The instrumentation and control system provided for individual MIC storage tanks is shown in Figure 1.2.



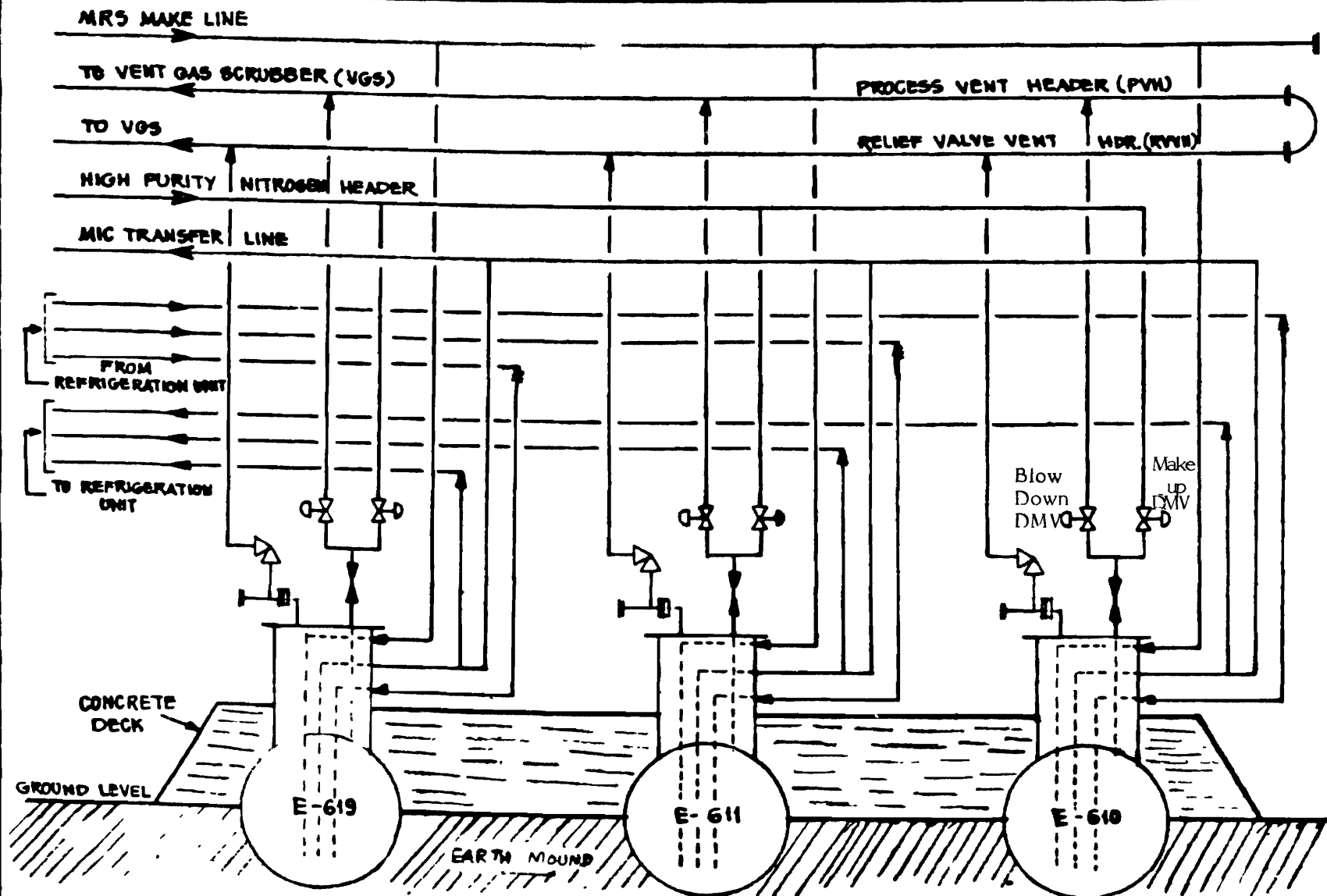
**VIEW OF MOUNDED MIC STORAGE TANKS FROM GROUND LEVEL**



**VIEW OF TOP OF MIC STORAGE TANKS**



FIGURE 1.1 SCHEMATIC LAYOUT OF COMMON HEADERS OF MIC STORAGE TANKS



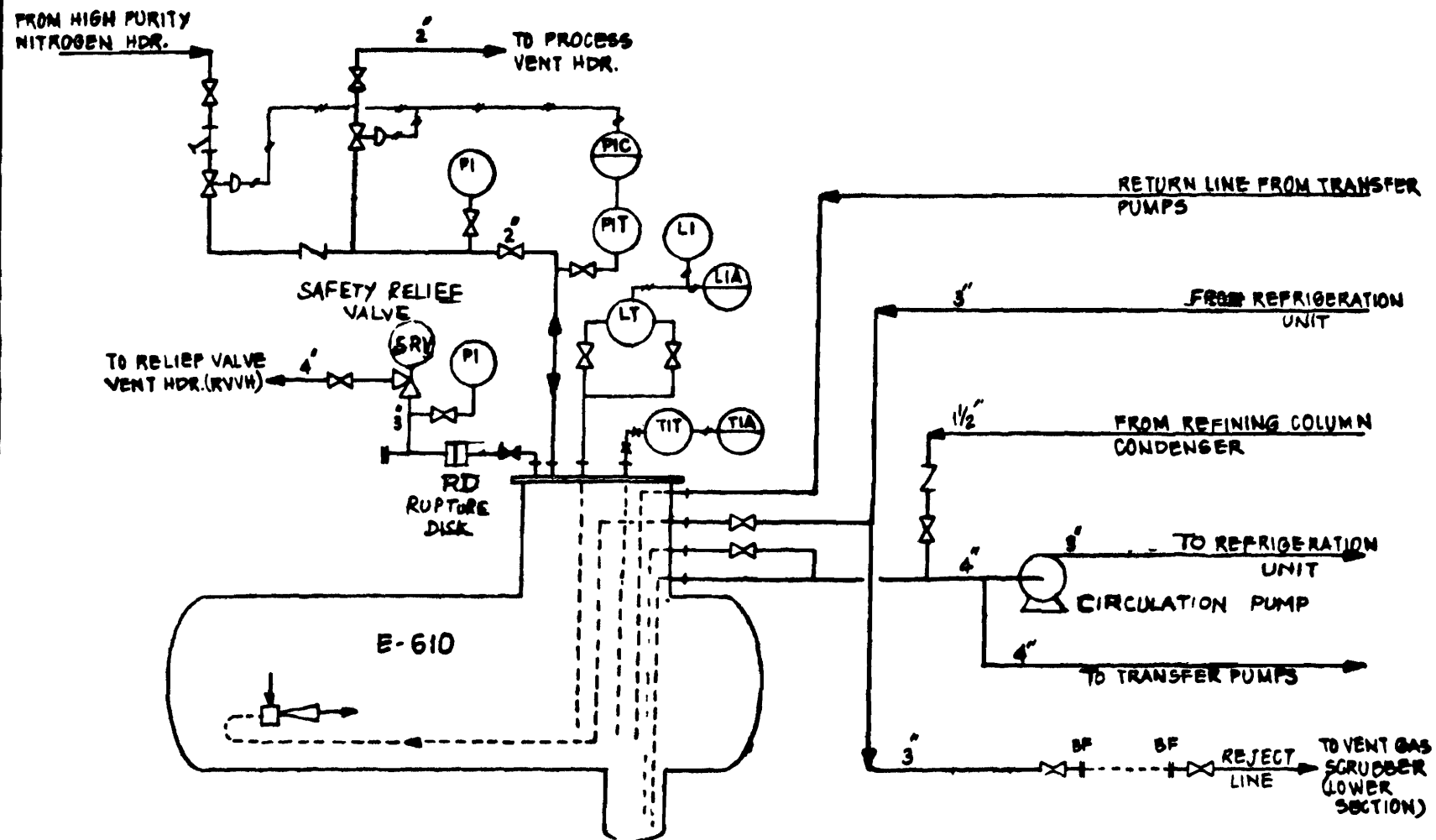


FIGURE : 1.2. MIC STORAGE TANK

MIC stored in the storage tanks is to be kept under an atmosphere of High Purity (HP) nitrogen. The recommended nitrogen pressure in the tanks is of the order of  $1.0 \text{ kg/cm}^2\text{g}$ . The tank pressure is indicated locally in the field as well as in the control room and controlled remotely from the control room by means of a pressure indicating controller. HP nitrogen is admitted into the tank through a make up control valve (make up DMV), the body material of which is carbon steel. In case the pressure is higher than the desired value, nitrogen is vented out into PVH through blow down control valve (blow down DMV), the body material of which is again carbon steel.

Each of the MIC storage tanks is provided with a temperature transmitter on the tank which indicates the temperature of MIC locally in the field as well as remotely in the control room. A high temperature alarm is provided to alert the operator in the control room in case the temperature of MIC in the tank rises beyond the desired limit.

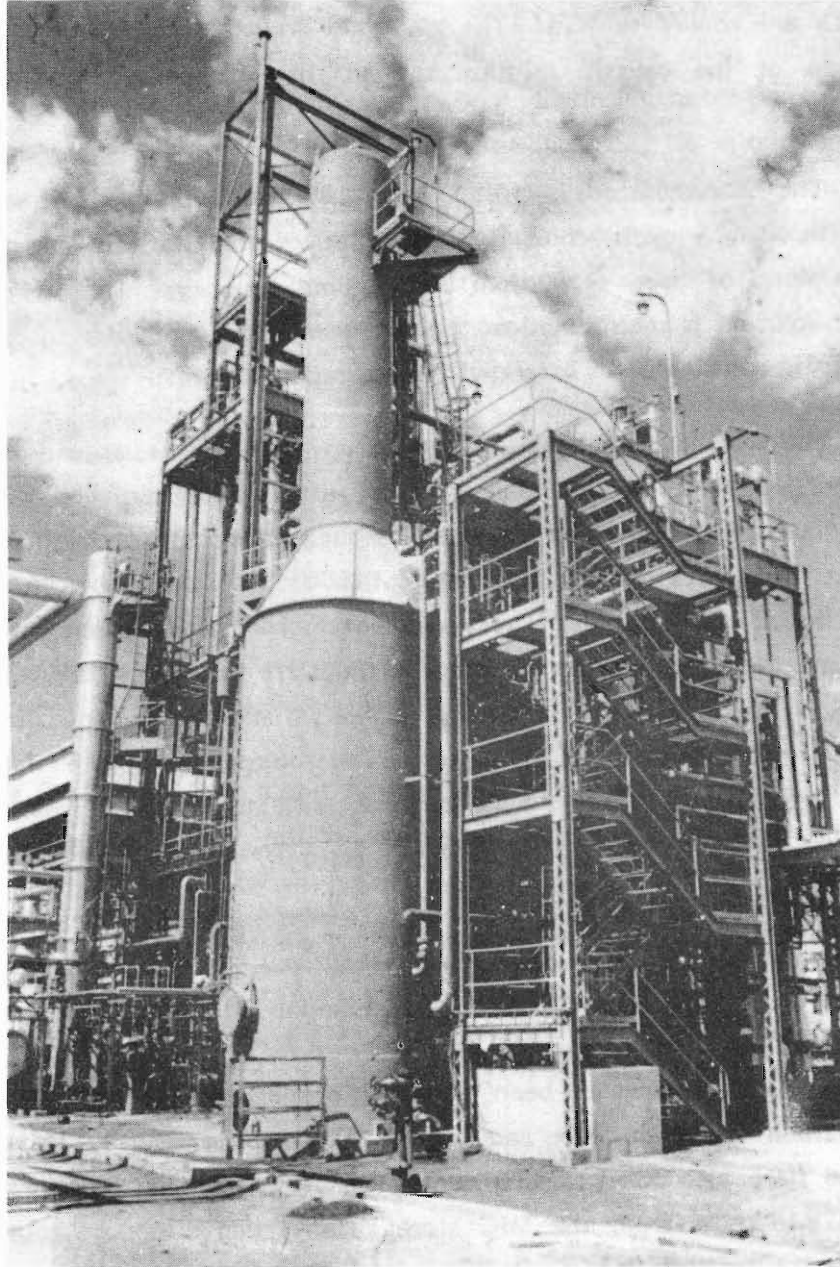
Each MIC storage tank is provided with a level transmitter to indicate the level of MIC in the tank. Nitrogen from Gas Blow Back Header (GBBH) is purged through MIC in the tank and the level is measured with back pressure. High and low level alarms are provided.

SRV is provided on each MIC storage tank. A graphite Rupture Disc (RD) is located on the pipeline between the tank and the SRV. There is a local pressure gauge provided in between the RD and the SRV. This would normally indicate atmospheric pressure. A rise in pressure would indicate failure of the RD. Failure of RD can be detected only through frequent inspection at the site of the tank. The outlet of SRV is of 100 mm (4") nominal diameter. Three outlets from three tanks are connected to a single common RVVH, which has 100 mm (4") nominal diameter.

A common line designed as MIC reject line is provided from the MIC storage tanks to send any off-specification material back to the MIC plant for reprocessing or to send any contaminated/off specification MIC to Vent Gas Scrubber (VGS), where it is neutralised with caustic solution.

#### **1.1.3 Vent gas scrubber :**

The Vent Gas Scrubber (VGS) meant to neutralise the toxic exhausts from the MIC plant and storage system consists of three sections. The upper section of 1650 mm diameter (5.5 feet) and 5540 mm (18.5 feet) height is packed up to a height of 4200 mm (14 feet) with ceramic Berl saddles. The middle section below the packing is of 1650 mm (5.5 feet) diameter and 2100 mm (7 feet) height. The third section comprises an



**VENT GAS SCRUBBER**

accumulator, 3600 mm (12 feet) diameter and 6900 mm (23 feet) height. The capacity of the accumulator is about 80m<sup>3</sup> (21000 gal). The material of construction of VGS is carbon steel.

Gases from RVVH, PVH, MMA Vaporiser SRV and chlorine evaporator SRV are routed to VGS. The gases get scrubbed in VGS by a counter current flow of the caustic solution through the packed-bed in the upper section of VGS.

The accumulator is filled with 10% caustic solution which is circulated through a cycle cooler to the inlet of the VGS by means of a circulation pump of about 4500 lpm (1200 gpm) capacity. The strength of the caustic solution is maintained at 9 to 10% in the accumulator by pumping in fresh caustic solution of 20% strength and process water.

The 20% caustic solution make up capacity is around 95 lpm (25 gpm). The gases entering the scrubber, after being scrubbed with the 10% caustic solution, are either released to the atmosphere through a stack at a height of approximately 30.5 meters (100 feet) from the ground or routed to the flare through a knock-out pot. The gases coming through the RVVH and PVH can also be diverted to the flare directly without passing through VGS.

It is intended that off-specification liquid MIC from MIC storage tanks can be disposed off by neutralisation in the VGS accumulator at a controlled rate.

#### 1.1.4 Flare tower :

A flare tower has been installed primarily to burn vent gases from the carbon monoxide unit and the MMA vapouriser safety valve discharge. The flare also burns normal vent gases from the MIC storage tanks, MRS and VGS. Vents from the MIC storage tanks can either be routed to VGS or directly to the flare. However, the flare tower is not expected to handle large release of MIC vapours directly.

## 1.2 The Event

Since the accident occurred in the MIC storage tank 610, it is important to consider information on aspects such as the chemical composition of the contents of the tank, the history of the material stored and the observations made by the plant personnel while loading and unloading the tank prior to the actual event.

At the start of the production run, i.e. 7th October, 1984, tank 610 contained 6.4 tonnes of MIC, presumably from production lots dating prior to that time. MIC production run was started on 7th October, and MIC was being led to tank 610 till 18th October, 1984. An additional 36 tonnes of MIC that was manufactured during that period was also filled in the same tank. On 18th October, about 23 tonnes of MIC were transferred to tank 611. From 19th to 22nd October, all the additional MIC produced in the plant was fed to and stored in tank 610. The production of MIC was stopped on 22nd October and at that time tank 610 contained approximately 42 tonnes of MIC. Tank 611 also contained MIC in quantities of the same order.

As per the operating practice, MIC in the storage tank was normally kept under nitrogen pressure of the order of  $1 \text{ kg/cm}^2\text{g}$ . Reportedly till 21st October, the pressure in tank 610 was maintained at  $1.25 \text{ kg/cm}^2\text{g}$ . However, during the night shift (22.45 hours to 06.45 hours) of 21st/22nd October, nitrogen pressure in tank 610 dropped to  $0.25 \text{ kg/cm}^2\text{g}$  abnormally and the material in tank 610 continued to be under a low pressure of  $0.1 - 0.25 \text{ kg/cm}^2\text{g}$  from 22nd October onwards. Recording of such low values is not an indication of any positive nitrogen pressure and denotes the tank contents were also nearly at atmospheric pressure.

The nitrogen pressure in the MIC storage tank is also utilised to transfer MIC from the storage tank to the Sevin unit. As liquid material is transferred, the gas pressure in the tank will show a gradual reduction. When the pressure in the tank drops to a considerably low value, the rate of transfer of MIC from the storage tank to the Sevin unit, would become low. The tank would need to be pressurised again to a higher value by admitting high purity nitrogen into the tank.

From 22nd October to 30th November, tank 610 was under nearly atmospheric pressure. No transfer of liquid MIC for Sevin manufacture took place from tank 610. During that period MIC was being transferred from tank 611 to the Sevin unit, whenever required. However, during the 30th November first shift, there were some problems in the pressurisation system of tank 611 and the pressure could not be increased. Therefore, attempts were made to pressurise tank 610 and transfer MIC from that tank to the Sevin Unit,

but it could not be pressurised. In the meantime, alternative system for pressurising tank 611 was made and then it could be pressurised. Transfer of MIC to the Sevin unit was then continued from the tank 611.

In the second shift of 1st December (14.45 hours to 22.45 hours) attempts were made once again to pressurise tank 610. However, this could not be accomplished to any significant extent. No further efforts to pressurise tank 610 were made.

On 2nd December, the first leak of MIC was noticed at 23.30 hours in the MIC structure area (MIC production facility) near VGS. The operators on the ground level in this area initially noticed some dirty water spilling from a higher level in the MIC structure. They also felt the presence of MIC in the atmosphere due to irritation of their eyes. They went up the stairs in the MIC structure and noticed that MIC and dirty water were coming out of a branch of RVVH on the downstream side of regeneration gas cooler Pressure Safety Valve (PSV). They also noticed that the PSV had been removed and the open end of RVVH branch line was not blinded. Around 00.00 hours on 3rd December, the operators went to the control room and informed the plant superintendent and the supervisor that there was an MIC leak. They were advised to spray water around the point of leakage.

At around 00.15 hours, when the control room operator was informed of the MIC leakage, he observed on the Pressure Indicator (PI) in the control room that the pressure in the tank 610 was shooting up and it was in the range of 25 - 30 psig.

Between 00.15 and 00.30 hours, PI of tank showed a reading beyond the maximum of the scale, i.e. higher than 55 psig.

The control room operator went to the storage area and heard a hissing sound from the Safety Relief Valve (SRV) downstream line, implying that SRV had popped off. He also noticed that the local temperature and pressure transmitters on the tank were indicating beyond their ranges (i.e.  $+25^{\circ}\text{C}$  and 55 psig).

At this point, the operator rushed back to the control room and started the VGS circulation pump from the control room. He, however, observed that the flow indicator in the control room did not show any circulation of the caustic soda solution through VGS. In the meantime, a gaseous

cloud was seen to be coming out from the stack by the field operator. Reportedly, the siren was sounded around 00.30 hours, and the plant personnel were alerted about the MIC leakage.

From around 01.00 hours, water was sprayed on the MIC structure, but reportedly, it did not reach the top of the stack from where the gases were coming out.

Around 03.00 hours, the SRV of tank 610 is reported to have sat back and the gas also stopped coming out from the stack.

Gas that had escaped into the atmosphere got condensed in contact with the cold air and due to atmospheric inversion phenomenon, settled down slowly on the ground. It then evaporated and spread in the atmosphere gradually due to low wind velocity, thereby affecting the population greatly.

The escape of such a large quantity of toxic material into the environment caused all the tragic loss of life, serious damage and disabilities to thousands of people. A part of the population of Bhopal city also suffered serious long-term effects which are still being evaluated.

Local authorities, the State Government and the Government of India and their agencies immediately reacted to this situation and provided medical relief and other measures. Medical personnel rushed to Bhopal from other parts of the country and supplemented the relentless efforts of local doctors and hospital staff. Supplies of medicine, food, oxygen and equipment were rushed to Bhopal. Disregarding potential risk and hazard from toxic material in the area, many volunteered to reach Bhopal and work there.

Within the Union Carbide Plant itself, everyone moved upwind, away from the emission and toxic gas flow direction. Only one person was affected to any extent and he recovered. One operator in the neighbouring oxygen/nitrogen factory unit died and others in the unit have suffered seriously.



### **1.3        'Operation Faith'**

Dr. S. Varadarajan, Director General (DG), Council of Scientific and Industrial Research (CSIR) and Secretary to the Government of India, reached Bhopal on 5th December, 1984, and was asked to coordinate all scientific efforts at Bhopal in relation to the situation following the leakage of toxic material. On his instructions, issued on 4th December, 1984, teams of scientists and technologists with expertise in environmental protection and toxicology for examination of the environment, reached Bhopal in the afternoon on 5th December, 1984 and assembled at the Regional Research Laboratory of CSIR at Bhopal.

The teams made an examination of the environment immediately to ascertain if the presence of any isocyanate or other related materials could be detected in air, water or surfaces. They also recorded observations on any visible damages in the environment such as changes in green plants, trees, aquatic life in the lake and the condition of animal and human population. Large number of people and animals had died by that time. Very large numbers of persons had serious irritation in eyes and breathing difficulties. The tests carried out did not show any presence of MIC or related toxic materials in the environment. Government authorities were advised accordingly. Public were advised to wash all vegetables and food articles with water and clean floors, walls and surfaces with water. These tests, collection of material and observations were continued in the next fortnight. Facilities for detection of specific toxic gaseous materials in a number of locations were established.

During the visit to the Union Carbide Plant on the morning of 5th December, 1984, the factory management provided Dr. Varadarajan a brief account of the gas leakage, the nature of facilities for storage of MIC and the associated controls. Visits to the MIC plant, storage area, the Sevin plant and VGS were made. At this stage, Dr. Varadarajan was informed that bulk quantities of MIC were stored in tanks E-610 and E-611 and the toxic gas leakage had taken place from tank E-610. It was estimated about 15 tonnes of MIC were present in tank E-611. The material in both tanks was from MIC production in October, 1984 and part of the material

had been transferred from tank 610 to tank 611. It was also noted that many pipeline systems for input into the three tanks and output from these were connected to common headers. It was realised that the MIC in tank 611 could also lead at any time to a further release of toxic gases and therefore presented a serious potential hazard to large population, remaining factory staff, visitors, officials in the vicinity and to personnel providing relief and medical attention. They were not aware of this further hazard and they had no knowledge of the precautions to be observed in the event of another toxic gas leakage. The crisis warranted immediate measures and a new crisis management system, for the following :

- Estimating the probability of a further leakage.
- Analysis of circumstances that led to the leakage on 2/3 December, 1984.
- Devising means to prevent, if possible, a leakage from tank 611.
- In the event of leakage occurring, precautions to be taken for minimising the damage to those present in the factory and to the public outside through various measures, including large scale evacuation of the population.
- Safe disposal of the material in tank 611.
- Outlining of precautions to be observed within the factory and in the vicinity of the factory to neutralise any toxic gaseous material that might be emitted.
- Provision of information to the Government authorities on steps to be taken to minimise effects of such potential toxic gases.
- Provision of information on precautions to be observed by the public in the event of any gas leakage and quick dissemination of warning, if an imminent leakage is indicated.
- Provision of authentic information to the press and public continuously to avoid confusion and panic.

- Reliable communication systems.
- Mobilisation of experienced scientists, technologists for various activities.
- Institution and coordination of all scientific efforts and establishment of an organisation.
- Collection of samples, data for current needs and future studies on the nature of injuries and damage to life systems and environment, to allow for therapy, rehabilitation.

The first task, on the morning of 5th December, 1984 at the factory of Union Carbide was the estimation of probability of further leakage. Material from production was fed from a common MIC distillation unit directly, without any intermediate day or shift storage into the tanks 610 and 611 through a common pipeline. Similarly, nitrogen from a common header was supplied without storage through a pipeline to the tanks. There was no reason to believe that the hazard from material in tank 611 was in any way different from that in tank 610. The rapid rise in temperature and pressure observed during the night of 2/3 December from tank 610 and the inadequacy of VGS to contain large releases, confirmed that any onset of reaction in material in tank 611 would lead to a rapid explosive release of toxic gases again and a repetition of the event of 2/3 December, 1984.

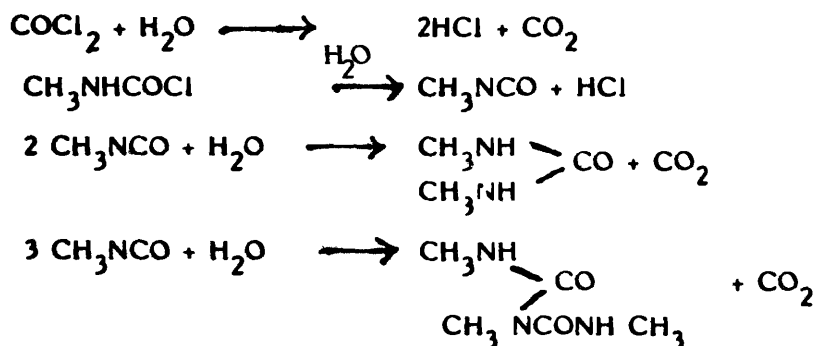
In the discussion on the morning of 5th December, 1984, between Dr. Varadarajan & Factory Management, it was concluded that MIC can react with water and the heat generated by reaction of about 40% of material would enable evaporation and expelling of remaining MIC as gas. About 1.5 to 2.5 tonnes of water would have been involved in the reaction in tank 610. Polymerisation or trimerisation of MIC could be initiated by traces of metal ions. In such an event, a third of the material undergoing reaction could produce sufficient heat to expel remaining material as gas. It was assumed at that time, following generation of heat by reaction with water or by catalysed polymerisation, temperature of liquid would rise to 80°C, the boiling point of MIC at 40 psig. The pressure generated by gaseous MIC as well as carbon dioxide, if any, would lead to a rupture of the graphite disc (RD) and lifting of the Safety Release Valve (SRV) and release of gas.

Depending on the rate of reaction, there would be further release of gas. It was then assumed that the pipelines/valves would have permitted free flow of gases without any obstruction through RVVH.

During further discussions on the evening of 5th December, a UCC brochure on MIC was made available, and it was stated that while pure MIC undergoes trimerisation, an exothermic reaction, without catalyst, commercial MIC of UCC does not. Phosgene present in MIC at a level of about 400 ppm acts as an inhibitor of such polymerisation and a minimum of 200 ppm of phosgene was required to ensure stability against polymerisation. These levels were prescribed by UCC in the specifications for control of quality of MIC. Phosgene was routinely estimated in MIC samples drawn from the outlet of MIC distillation unit leading to the MIC storage tanks. Such estimation of phosgene content was also made on each occasion when material from tanks was transferred to the Sevin unit. Phosgene was estimated by methods prescribed by UCC. This involved the addition of water to MIC, immediate liberation of hydrogen chloride from phosgene and estimation of the amount of hydrogen chloride by titration with alkali. A further modification involved addition of sodium iodide solution to MIC and estimation of iodine liberation by titration with sodium thiosulphate. The modified method was used only when abnormally high values for phosgene content were obtained.

These procedures were examined by Dr. Varadarajan on the morning of 7th December, 1984. He concluded that water could react readily with phosgene as well as methylcarbonyl chloride (MCC) present to give HCl. In the method involving alkali titration, the total of phosgene and MCC can be estimated. Similarly, in the second method also, while phosgene may liberate iodine quickly, the HCl formed from MCC would also produce hydrogen iodide and iodine by air oxidation. It would not be possible to estimate phosgene levels reliably by either procedure. This was experimentally verified in the Factory on the morning of 7th December, through estimations carried out by addition of specific amounts of HCl to MIC. In discussions with Factory Management, it was agreed that any water entering the material stored in MIC tanks, would react first with phosgene and MCC, and produce HCl. Reaction of water with MIC to produce Dimethyl Urea (DMU) or Tri-Methyl Biuret (TMB) is much slower than the reaction of water with phosgene

or MCC. The relevant reactions are listed below :



From these, it appeared that relatively small amounts of water of the order of a few litres, entering 42 tonnes of MIC in tank 610, would allow all the phosgene and MCC present to react, giving HCl. Phosgene and MCC would be totally absent or reduced to low level below the minimum prescribed by Union Carbide to act as inhibitor of polymerisation. With a slight excess of water, hydrochloric acid would be available and this may react with the material of the tank or with any small particle of metal which may have been present. This would produce ionisable metal chlorides. In the absence of the inhibitor, MIC could undergo polymerisation rapidly. Hydrochloric acid and metal chlorides may be expected to catalyse a violent and explosive polymerisation. The heat produced at any point, in the absence of inhibitor, would promote a chain reaction, leading to a very rapid increase in temperature, vaporisation, increase in pressure and leakage of gas.

The earlier appreciation<sup>was</sup> that 1.5 to 2.0 tonnes of water would have been required to account for the reactions, in tank 610. These fresh considerations on the role of water in destroying quickly phosgene present as inhibitor, led to a hypothesis whereby small amounts of water could lead to violent reactions. Since the tanks are buried and had material stored for a few years, without opportunities for cleaning or inspection, and since nitrogen and MIC were fed in, without analysis of quality of stored discreet batches, there may be possibilities for ingress of tiny amounts of metal or water, without being detected.

These necessitated urgent attention for the safe disposal of the material in tank 611 and for avoiding any ingress of small amounts of water or metal particles such as iron rust into the tank 611.

The measures introduced included of the following :

**i. Ultimate safe disposal of MIC**

To dispose MIC, four alternatives were considered. The first involved dumping liquid MIC into large quantities of water in a contained area near the factory. Such a facility could not be located. The reaction with cold water may take time and loss of vapour MIC into the atmosphere may not be precluded and hence this method was not practical and safe. The second envisaged dilution of MIC with carbon tetrachloride to act as a heat sink and subsequent feeding of the MIC carbon tetrachloride mixture into aqueous alkali in VGS. Carbon tetrachloride would settle in the bottom and displace alkali solution causing alkali to overflow. This was not therefore proceeded with. The third proposal was to feed liquid MIC into aqueous alkali in VGS. It was noted chloroform present in MIC would produce dichloro carbenes with highly obnoxious odour, the spread of which would create considerable panic in the city. While such a procedure would be inevitable, in the event of any indication of onset of reaction and rise in temperature in tank 611, this was not preferred. The fourth method consisting of conversion of MIC to Sevin by reaction with alpha-naphthol was considered suitable, as staff were trained in this operation and facilities were available.

**ii. Safeguards against entry of contaminants**

A thorough system review of the plant and associated facilities was made. Instruments were rechecked or replaced to ensure reliability of measurement of temperature and pressure. Except for certain lines needed for transfer of MIC, others connected to common header were blinded at the first isolation valve from the tank. The rupture disc was replaced. An additional filtration system was introduced in the nitrogen feed line to the tank to avoid contaminants being carried in. Checks were made on the quality of nitrogen supply from the neighbouring factory. Scientists were in position in the nitrogen factory to ensure adequacy of supply and of quality. Operators were posted to continuously monitor the pressure in the tank. Positive higher pressure would ensure contaminants would not enter the tank.

### **iii. Safeguards for containment in the event of onset of reaction**

The number of personnel in the factory was reduced to a minimum. Entry into the surrounding area was restricted. About 80,000 persons living in relatively open structures were evacuated to safe places. All educational institutions were closed. An alarm system was established by the Government to alert the public of any imminent leakage. The public were advised to go into closed buildings when an alert was sounded and use wet towels on their faces to filter air for breathing.

Within the factory, the VGS was kept in operation all the time. This was a departure from earlier factory practice by which VGS was shut down when MIC production stopped. The flare system was also continuously operated, which was also a departure from earlier practice.

Adequate large alkali supplies were mobilised to meet needs of neutralisation. It was realised that maximum contact with water should be established for any gases escaping from the top level VGS outlet. Hence the top of the stack open to atmosphere was cut and new pipes were welded on so that the gas outlet would be in a large cubical structure surrounded by a wet cloth tent. Water was sprayed on to this tent to ensure gaseous material contact water. Helicopters and small aircraft were mobilised and equipped to dump tonne quantities of water on to this outlet area. Fire hydrant hoses were positioned to spray water. In the entire factory wall perimeter, high level stands fitted with fixed cloth covers were erected and the cloth kept wet so that any leakage would pass on to the moist surface.

The surface roads and areas outside the factory were also covered with water sprays.

### **iv. Stabilisation of MIC**

The possibility of adding a quantity of phosgene into MIC in tank 611 was considered. Phosgene cylinders were brought in from various sources and a purification system was also established. However, since other steps made progress, this method was not pursued.

**v. Disposal of MIC**

Since the possibility of the material in tank 611, undergoing reaction was noted, there were suggestions, the material should be disposed off through reaction with alpha-naphthol and the processing should be started from 7th December, 1984. This was not accepted by Dr. Varadarajan on the following grounds :

i. There was reason to believe the reactions in tank 610 occurred due to ingress of some material, possibly small amounts of water and metallic contaminants.

ii. There were common header lines for the three tanks and they may contain water or metal contaminants. Use of these in some way <sup>may</sup> introduce contaminants into tank 611 and thereby start a violent reactions similar to those in tank 610. It was necessary to examine all potential sources for ingress of material and eliminate them before taking actions to transfer MIC from tank 611 for processing. Use of untested nitrogen without precautions might lead to such reactions.

iii. The material in tank 611 had been processed upto 2nd December, 1984 for conversion to Sevin and the quality of the material had been considered satisfactory. There was no indication of instability in tank 611 upto 7th December, 1984.

iv. Since the possibility of reaction occurring in tank 611 existed, all steps have to be taken to ensure minimum damage as outlined earlier. Therefore, these steps had to be given priority and had to be completed before attempts to dispose off MIC in tank 611. These included operation of VGS, mobilisation of additional alkali supplies, erection of water curtains around the top gas outlet and around the factory perimeter, evacuation of people around the factory and those in open structures, education of the public on pre-cautions and establishment of communication system and



risk management control organisation. Additional safety equipments such as air breathing packs and helmets had to be procured. Water spray systems for extensive coverage had to be brought to position.

v. Processing of MIC required pre-checking of all systems. In addition, chemicals such as alpha-naphthol, solvents and alkali had to be brought from distant locations in the country in adequate quantities and tested. Operators of Union Carbide and of Nitrogen Factory had to be located and brought back to function and given instruction and training to work under unusual conditions and to deal with any untoward emergencies. Reviews needed to be carried out and a total strategy for disposal of material had to be outlined. A large number of personnel in and outside the factory had to obtain full appreciation of all actions to be taken under different circumstances that may emerge.

Based on these, it was decided not to embark on processing and disposal of MIC in tank 611 from 7th December, 1984, and postpone such operations to a later date, after all reviews, modifications and arrangements had been completed. All concerned, after full discussions, agreed with this approach.

For purposes of reaction of MIC with alpha-naphthol, a complete detailed system of organisation and review was established. Samples of alpha-naphthol and solvents were brought in. All systems were thoroughly checked and detailed written procedures were issued. Wireless communication systems were established for constant contact with control cells in the Factory and at the State Secretariat. Special communication tele-links and hot-lines with Delhi and other centres enabled the mobilisation of materials, equipment, personnel. A number of senior scientists and technologists from research organisations and major chemical manufacturing units were involved in review and checks and control of operations. Senior-most officials of the Government of India and the Madhya Pradesh Government provided facilities and assistance for all these activities, and helped

to restore calm and order in an environment, which exhibited constantly the acute distress of suffering of thousands of citizens. These measures motivated the staff of factories, transporters, public utilities and services to take up work in public interest within the potentially hazardous areas.

The processing of MIC was termed 'Operation Faith' by the Chief Minister of the State, Shri Arjun Singh. The proposal to start such an operation was made public three days in advance, together with information on precautions to be observed. Radio and television were fully used for such communications. The Operation Faith started on the morning of Sunday the 16th December, 1984. A total of 21 tonnes of MIC in tank 611, one tonne from tank 619 and material from a number of stainless steel drums were reacted in one tonne lots with alpha-naphthol at the rate of three to four tonnes each day. The factory was made virtually free of all MIC. Operation Faith ended on 22nd December, 1984, successfully.

## **2.0        EXAMINATION OF TANK 610 AND ITS CONTENTS :**

In order to have an appreciation of the event, it was necessary to examine the tank, its associated piping and valves, samples of materials that collected in the pipelines and valves, and finally the residue remaining in tank 610.

On December 20, 1984, the line attached to the safety relief valve was disconnected and it was noted that the rupture disc which had broken had some solid material collected around it. A sample of this solid was collected from the rupture disc downstream of the spool piece and analysed. It was found to be essentially pure MIC trimer (MICT) which must have sublimed from the tank and collected there. Samples were also collected from the tank bottom using a stainless steel pipe as a drill core through the safety valve nozzle, and analysed. In February 1985, it was planned to take additional residue samples for further analysis. The tank was at an absolute pressure of 160 mm Hg. Nitrogen was first admitted to the tank to bring the pressure to normal level before opening the nozzles. All the 5 nozzles located on the manhole cover were opened one after another and the core samples withdrawn. This set of samples was also analysed.

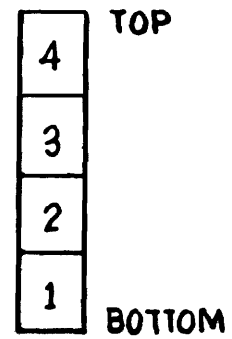
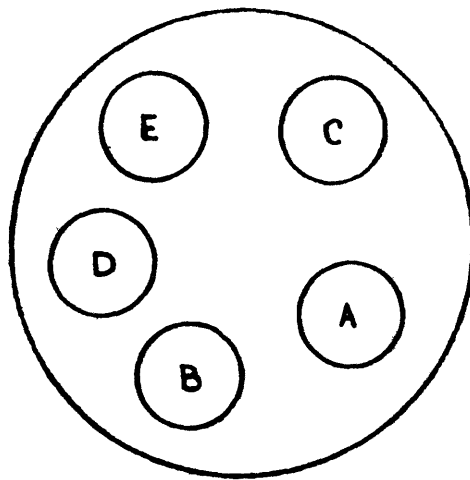
During March 1985, the concrete mound over the tank, which had already cracked during the event, was removed and excavation work around the tank completed to provide access to and enable inspection of the external wall of the tank.

It was decided to cut windows at specific points on the tank wall and examine the metal as well as samples of the residue throughout the length of the tank. In April 1985, tank 610 was evacuated first and then purged with nitrogen to remove volatiles and minimise odour. Plates were then cut at predetermined points and through these window holes samples of the residue were removed for analysis. Pieces of the metal plates were also subjected to physical and chemical analysis.

### **2.1.        Sampling**

#### **2.1.1.     Core samples from the manhole nozzle :**

All the five nozzles located on the manhole cover were opened one after another and core samples were drawn (see Figure 2.1). A pipe



CORE SAMPLE

- A. SAFETY VALVE
- B. PROCESS VENT
- C. SPARE
- D. THERMOWELL
- E. LEVEL INDICATION

FIG. 2.1, SAMPLE IDENTIFICATION

# SAMPLING SCHEDULE ON MIC TK E - 610

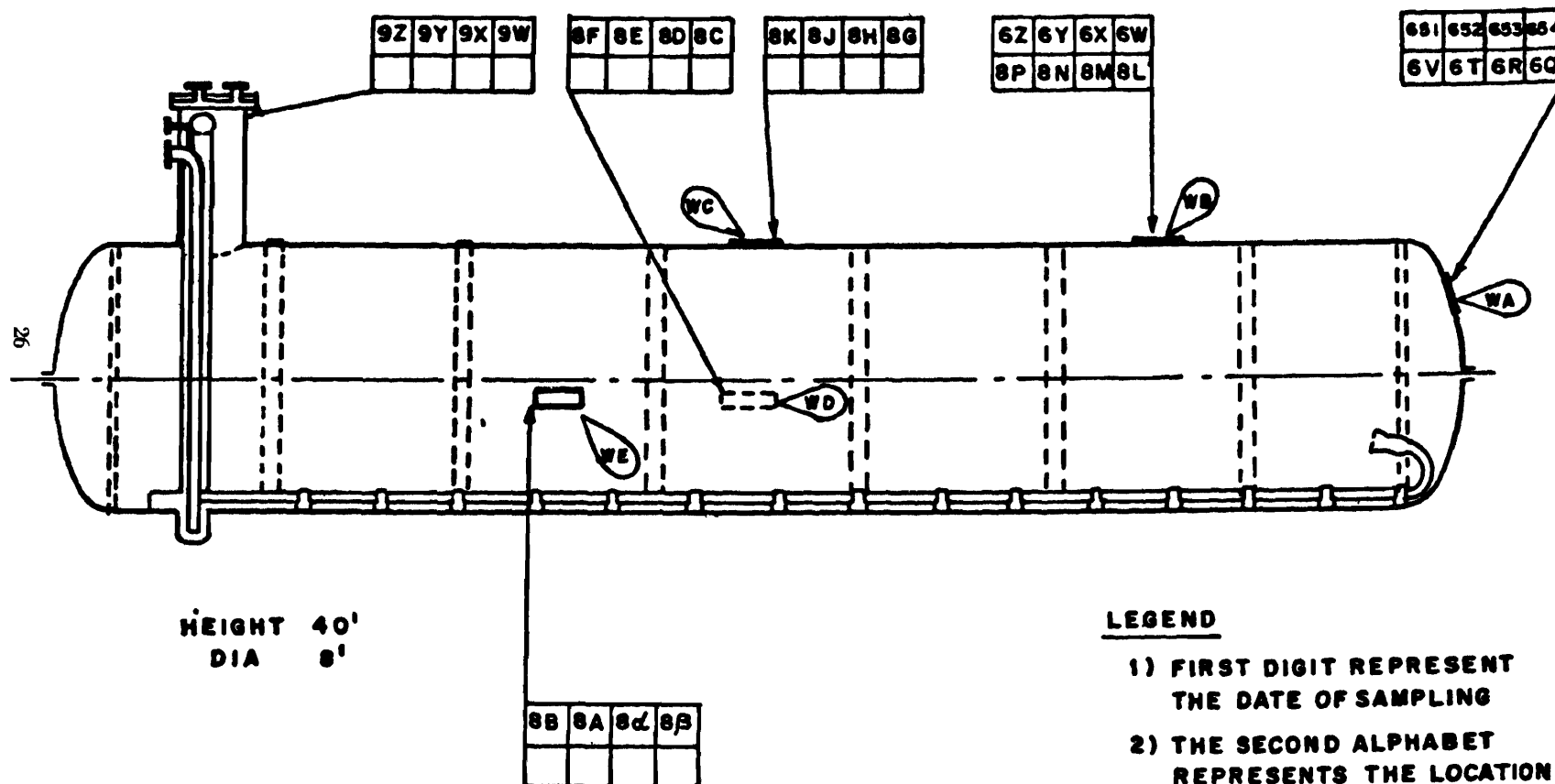
KEY:



SAMPLE NOS



WINDOW NOS



## LEGEND

- 1) FIRST DIGIT REPRESENT THE DATE OF SAMPLING
- 2) THE SECOND ALPHABET REPRESENTS THE LOCATION OF SAMPLE DRAWN FROM TANK

FIGURE - 2.2

section was mechanically forced inside the residue till it reached the bottom of the tank. The residue entering the pipe was pushed out by using a closely fitting pusher rod inside the pipe. The samples thus pushed out of the pipe section formed a cylindrical semi-solid mass. Each sample was divided longitudinally into 4 portions with the bottom material in contact with the vessel wall receiving identification number 1 of the respective series. Similarly, alphabets A to E were used for identifying the samples from different nozzles (see Figure 2.1)

#### **2.1.2. Samples from tank residue after opening the tank :**

Samples from various locations inside the tank were collected after cutting windows on the body of the tank. Various sampling points and windows on the body are presented in Figure 2.2. After cutting windows on the body of the tank, the inside of the tank was photographed. One of the important observations made during the opening of the windows was a very strong smell of amines. Four sets of samples were taken from each window. Samples were collected using a 5 cm dia. stainless steel pipe section and divided into 4 equal parts as described in 2.1.1. Each sample was properly marked and coded. For example, a sample marked 8-H-1 represents the bottom cross-section of the residue from window 'C' collected on 8th April. The time and date of sampling were also marked on the sample bottle tags. The tank residue was found to be about 52 cm deep.

#### **2.1.3. Samples from pipelines :**

Liquid samples were collected from RVVH/PVH in February, 1985 and May, 1985. Description of these samples along with their analyses is given in Table 2.1.

#### **2.1.4 MIC samples from tank 611 :**

MIC was stored in 3 storage tanks in the Union Carbide factory. The tanks are designated E-610, E-611 and E-619. During the night of December 2-3, 1984, the mishap occurred in tank E-610. Tank 611 still contained large quantities of MIC.

The samples of MIC from tank 611 had been collected in 200 ml capacity pressure bottles closed by spring-loaded ball valves. Each bottle contained about 125 to 150 ml of MIC. The samples were then analysed for specification tests. The MIC in tank 611 was as per the required specification and the data are given in Table 2.2.

#### **2.1.5. Metal pieces cut from Tank 610 :**

In April 1985, a team of experts examined the tank. The surface was found to be coated with bitumen with nylon fibre reinforcements. The bituminous layer was removed and examined. The tank had six numbers of steel stiffening rings welded all around. The tank had bulged significantly between the stiffening rings. The nature of the bulges indicated high internal pressures.

Several pieces were cut out from tank 610. The locations are shown in Figure 2.2. A round piece of metal (28 cm diameter) was cut out from the dished end away from the manhole (WA). Square pieces were cut out from locations WB, WC, WD and WE. All metal pieces were photographed. Physical examination of the pieces showed a blackish coating on the inside surface. The metal pieces cut out from the sides nearer to the residue levels showed deposits due to sublimation. The top portion of the tank (inside) showed only thin blackish deposits or sublimates. Examination through a microscope indicated crystals in the deposits. Metal pieces cut out from the sides or lower portions of the tank showed comparatively higher amounts of deposits.

### **2.2 Chemical Analysis**

#### **2.2.1 Physical appearance of samples of residue :**

All the samples from tank 610 were thick, semi-solid in consistency, and brownish in colour. The samples tended to absorb moisture on exposure to air and had the smell of amines. The consistency of the bottom portion was quite different from that of the top. The top portion of the residue appeared to be dark brown and was more hygroscopic and liquid-like in nature. The bottom portion appeared to consist of a high percentage of crystalline compound and was light in colour.

### **2.2.2. Solubility Characteristics :**

The solubility characteristics of the samples were studied initially for developing the analytical methods. Chloroform and acetone dissolved 70 to 85% of the samples. Hot toluene also dissolved a major portion of the samples. On cooling the toluene extracts, crystals separated and were identified as dimethylisocyanuric acid. Water was also found to dissolve the sample, but complete dissolution required large quantities of water.

### **2.2.3. Qualitative Analysis :**

**Smell :** The samples showed a strong smell of amines.

**Acidity or alkalinity :** The samples were highly acidic.

**Thin-layer chromatography (TLC) :** TLC carried out on silica gel indicated the presence of about 15 compounds. These were later identified by spotting standard compounds on the TLC plates.

**Chloride ions :** Residue samples indicated positive tests for chloride ions.

**Metal ions :** The residue after treatment with hydrochloric acid was tested for metal ions. Positive tests were obtained for the following metallic ions : iron, nickel, chromium and molybdenum

**Cyanide ions :** Residue sample showed negative test for cyanide ions.

### **2.2.4. Analytical Procedures :**

Different techniques were employed for the quantitative estimation of compounds in the samples. The organic compounds were determined by gas liquid chromatography (GLC). Except for the amines, all the organic compounds could be well separated on FFAP column or other columns as detailed in Annexure 2. Acetone was used as the solvent for the analysis. It was found that acetone in presence of dimethyl-amine (2%) dissolved about 95% of the residue. The acetone insoluble (approximately 3-6%) showed metal chlorides (approximately 1%). It did not contain amines or other identified organic compounds. The amines could be separated using a TEPA+ KOH column on Chromosorb 102. Most of the compounds were isolated from the residue using various techniques and their identity established by spectral data (IR, NMR and MS) by direct comparison with those of pure compounds.



The acid present in the samples and the chloride were determined by potentiometric titration.

Metallic ions as iron, chromium, nickel, calcium and magnesium were determined by atomic absorption and sodium by flame photometry.

Moisture contents in the samples were determined by Karl-Fischer titration.

Accuracy and reproducibility of analysis were established by using standard mixtures prepared from pure compounds.

#### **2.2.5. Analytical Results :**

The following compounds were identified in the residue samples taken from various locations in tank 610. The chemical structures of the first seven compounds are given in Figure 2.3.

1. Methylisocyanate trimer (MICT)
2. Dimethylisocyanurate (DMI)
3. Dimethyl urea (DMU)
4. Trimethyl urea (TMU)
5. Dione
6. Trimethyl biuret (TMB)
7. Tetramethyl biuret (TRMB)
8. Monomethyl amine (MMA)
9. Dimethyl amine (DMA)
10. Trimethyl amine (TMA)
11. Chloride
12. Metallic ions (Fe, Cr, Ni, Mo, Na, Ca, Mg)

The analytical results are summarised in Tables, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7 and 2.8.

#### **2.3. 'Total representative' sample of residue and its analysis :**

A total representative sample was prepared by mixing samples drawn from the various windows of the tank. The sample thus prepared as representative of the entire quantity of the residue <sup>was</sup> mixed and

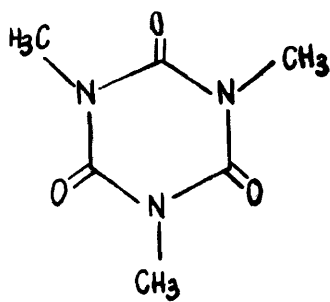
homogenised. This sample was prepared by mixing equal quantities from 22 different residue samples. These samples represent the bottom portions, middle portions and top portions at different axial positions along the 40 feet long storage tank. Two such samples were prepared initially, each of which was divided into 2 portions. These were then cross-mixed to provide two representative samples.

Total analysis was carried out on this sample and the analytical results were used to calculate various factors relating to the 'event'. The analytical procedures adopted were the same as described earlier. The results of the analysis are presented in Table 2.9.

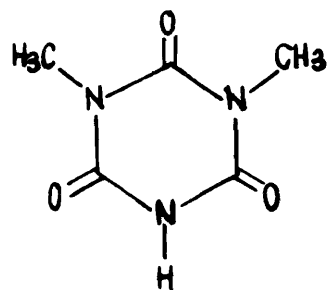
The total identified compounds in the sample add up to about 95%. As indicated earlier, the residue samples contain about 3-6% of unidentified tarry materials.

#### 2.3.1. Product distribution :

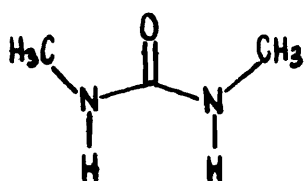
Besides the presence of various metal and chloride ions, the residue contains 10 organic compounds. These are presented as kg moles in the last column of Table 2.9. The tank residue contains 40.7 kg moles (or about 7000 kg of MIC trimer). The next highest molar concentration is that of DMI with 17.0 kg moles (2675 kg), followed by the chloride ions with a concentration of 15.2 kg moles (540 kg). All the amines taken together add up to 16.9 kg moles in the residue (800 kg). In all, a total of 97 kg moles of compounds are present in the residue, accounting for about 12 tonnes out of the 12.5 tonnes of the residue estimated to be present.



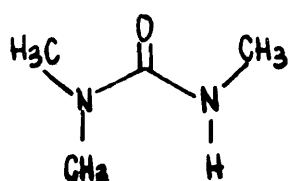
MICT  
MW = 171



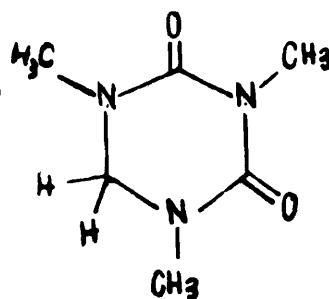
DMI  
MW = 157



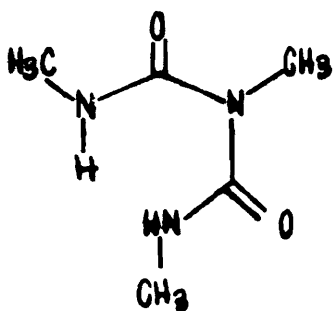
DMU  
MW = 88



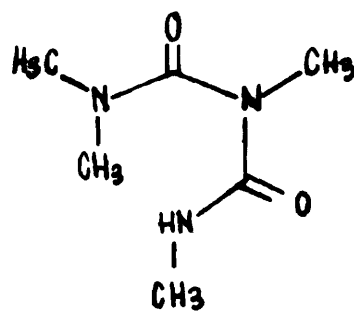
TMU  
MW = 102



Dione  
MW = 157



TMB  
MW = 145



TRMB  
MW = 159

FIG. 2.3 - STRUCTURES OF COMPOUNDS IN TANK-610

**TABLE 2.1****ANALYSIS OF LIQUID SAMPLES FROM RVVH/PVH**

Sl.No.	Sample	Chloride % $\text{Cl}^-$ w/w	Acidity % $\text{HCl}$ w/w	Alkalinity, % w/w $\text{Na}_2\text{CO}_3$ $\text{NaHCO}_3$	
1	2	3	4	5	6
<b>A. <u>Samples of February, 1985</u></b>					
A1	From PSV downstream bleeder of dryer.	1.37	-	-	-
A2	Side-stream cooler PSV d/s bleeder.	15.61	11.98	-	-
A3	RVVH drain bleeder on desuperheat on second level.	5.01	4.38	-	-
<b>B. <u>Samples of May, 1985</u></b>					
B1	PVH No. 7	1.42	Nil	13.62	13.31
B2	RVVH from bleeder on 2nd level B.F. towards Sevin.	1.50	-	7.67	12.06
B3	RVVH VGS line bleeder	1.15	-	8.59	20.62
B4	RVVH VGS line bleeder	1.16	-	-	23.93

**TABLE 2.2****ANALYSIS OF MIC SAMPLES FROM E-611**

Sl.No.	Component	Sample No.1 20.12.84 (%) w/w	Sample No.3 20.12.84 (%) w/w	Sample No.6 19.12.84 (%) w/w
1.	Methyl isocyanate	99.17	99.85	99.60
2.	Chloroform	0.314	0.334	0.332
3.	Moisture	N.D.	N.D.	N.D.
4.	Phosgene *	0.032	0.030	0.028
5.	Total Hydrolysable Chlorides *	0.040	0.028	0.032
6.	Non volatiles	0.130	0.110	0.090
<b><u>Trace metals (ppm)</u></b>				
(a)	Zinc	3.5	3.7	1.2
(b)	Iron	3.6	2.6	4.1
(c)	Chromium	0.9	1.0	1.0
(d)	Sodium	0.6	0.6	0.9
(e)	Copper	0.3	0.2	0.2
(f)	Nickel	0.2	0.2	0.2
(g)	Magnesium	0.03	0.02	0.02

\* As per Union Carbide Analytical Procedure.

**TABLE 2.3**  
**ANALYSIS OF CORE SAMPLES FROM THE MANHOLE NOZZLES**

Sl. No.	Description of sample	Code No.	Acidity as HCl % w/w	Chloride Cl % w/w	Fe ppm	Ni ppm	Cr ppm
1.	Safety valve nozzle	A-1	5.04	5.85	1160	100	260
2.	Safety valve nozzle	A-2	6.71	6.48	1180	120	365
3.	Safety valve nozzle	A-3	7.58	6.66	1600	155	360
4.	Safety valve nozzle	A-4	6.71	6.35	1780	135	375
5.	Process vent nozzle	B-1	4.51	4.63	1280	135	375
6.	Process vent nozzle	B-2	5.34	5.15	2030	270	380
7.	Process vent nozzle	B-3	6.95	7.29	1640	270	370
8.	Process vent nozzle	B-4	7.25	7.54	2180	170	500

**TABLE 2.4****ANALYSIS OF CORE SAMPLES FROM THE MANHOLE NOZZLES**

Description of samples	Code No.	Trimethyl Urea,TMU % w/w	MIC trimer MCT % w/w	Dimethyl Urea,DMU % w/w	Dione % w/w	Trimethyl biuret,TMB % w/w	Dimethyl isocynurate,DMI % w/w
1. Safety Valve Nozzle	A-1	1.1	59.6	1.8	3.1	-	12.6
2. Safety Valve Nozzle	A-2	1.9	47.9	0.9	4.4	-	16.0
3. Safety Valve Nozzle	A-3	1.6	35.6	3.4	4.2	-	23.1
4. Safety Valve Nozzle	A-4	1.8	34.0	3.6	4.1	-	25.9
5. Process Vent Nozzle	B-1	2.0	43.3	3.6	3.2	6.5	16.8
6. Process Vent Nozzle	B-2	2.0	37.3	6.4	4.1	8.2	20.6
7. Process Vent Nozzle	B-3	1.9	27.1	4.8	4.2	10.7	24.4
8. Process Vent Nozzle	B-4	2.5	24.9	3.8	4.2	13.5	25.0
9. Thermowell Nozzle	D-1	0.9	38.4	11.0	2.6	6.9	31.0
10. Thermowell Nozzle	D-2	0.8	38.2	3.7	2.6	9.4	31.8
11. Thermowell Nozzle	D-3	2.5	38.6	4.2	2.5	9.5	32.9
12. Thermowell Nozzle	D-4	2.4	41.9	3.4	3.2	2.6	22.9

Table 2.4 Contd.....

Description of samples	Code No.	Trimethyl Urea, TMU % w/w	MIC trimer MICT % w/w	Dimethyl Urea, DMU % w/w	Dione % w/w	Trimethyl biurate TMB % w/w	Dimethyl isocynurate, DMI % w/w
13. Safety valve nozzle (Bottom) I-1		0.8	66.5	0.3	1.8	-	11.0
14. Safety valve nozzle (Middle) I-2		1.6	47.4	0.9	3.6	-	15.1
15. Safety valve nozzle (Top) I-3		1.7	34.9	1.5	3.8	-	17.9
16. Diptube bottom piece	F-1	1.3	39.2	6.2	2.8	6.5	17.7
17. Diptube bottom piece	F-2	1.9	24.0	12.8	2.5	9.5	28.4
18. Diptube bottom piece	F-3	1.7	23.6	10.9	6.5	13.0	20.7
19. Diptube bottom piece	F-4	1.9	20.3	4.3	4.3	9.8	17.2



**TABLE 2.5****ANALYSIS OF SAMPLES OF TANK RESIDUES AFTER OPENING THE TANK**

Sr. No.	Sample No.	Acidity as HCl % w/w	Chloride Cl <sup>-</sup> % w/w	Fe ppm	Cr. ppm	Ni ppm
1.	Z-1	4.50	3.76	-	-	-
2.	Z-2	6.68	3.72	-	-	-
3.	Z-3	6.37	4.34	-	-	-
4.	Z-4	6.86	4.99	-	-	-
5.	M-1	6.72	5.81	230	Nil	10
6.	M-2	7.37	6.33	225	390	70
7.	M-3	8.22	6.65	1180	440	120
8.	M-4	9.39	7.78	480	455	90
9.	H-1	5.15	3.61	1050	Nil	100
10.	H-2	6.43	4.97	890	40	100
11.	H-3	8.78	6.99	1725	Nil	120
12.	H-4	8.98	6.85	330	Nil	100
13.	V-2	7.30	4.74	-	-	-
14.	V-3	6.20	5.34	-	-	-
15.	V-4	6.83	5.25	-	-	-

**TABLE 2.6****ANALYSIS OF SAMPLES OF TANK RESIDUES AFTER OPENING THE TANK**

<b>Sample No.</b>	<b>TMU % w/w</b>	<b>MICT % w/w</b>	<b>DMU % w/w</b>	<b>Dione % w/w</b>	<b>TMB % w/w</b>	<b>DMI % w/w</b>	<b>Amines (TMA, DMA, MMA) % w/w</b>	<b>Chlorides Cl<sup>-</sup> % w/w</b>
H-1	0.8	65.7	0.9	2.2	-	18.1	4.2	3.6
H-2	1.5	48.2	1.8	3.36	0.2	27.9	4.7	4.9
H-3	1.69	43.3	2.1	3.73	0.2	30.3	4.6	6.9
H-4	2.05	31.8	2.4	4.00	0.6	35.4	5.6	6.8
M-1	1.06	62.3	0.6	2.71	-	18.6	3.7	5.8
M-2	1.64	44.8	2.2	3.82	-	27.7	5.2	3.0
M-3	2.04	44.2	3.9	4.52	0.1	25.9	4.2	6.6
M-4	1.78	40.1	1.8	3.03	0.3	27.3	4.9	7.7
Z-1	1.43	56.3	3.1	5.28	3.1	21.9	3.3	3.7
Z-2	2.78	52.5	5.2	4.24	2.7	44.4	3.5	3.7
Z-3	1.62	47.3	3.5	2.88	1.4	29.0	5.5	4.3
Z-4	1.73	48.3	3.7	3.26	1.1	26.0	5.8	4.9
V-2	0.86	62.2	-	2.06	-	18.1	5.7	4.7
V-3	1.2	63.4	-	2.5	-	18.3	4.3	5.3
V-4	2.38	64.0	-	3.6	-	18.9	3.5	5.2

**TABLE 2.7**

**ANALYTICAL RESULTS OF SODIUM, CALCIUM AND  
MAGNESIUM IN THE CORE SAMPLE**

No.	Sample Code No.	Sodium ppm	Calcium ppm	Magnesium ppm
1.	G 1	50	-	-
2.	G 4	80	-	-
3.	H 1	55	-	-
4.	H 4	80	-	-
5.	L 3	80	-	-
6.	M 3	90	25	3

**TABLE 2.8****ANALYSIS OF AMINES BY GAS CHROMATOGRAPHIC METHOD**

Sl. No.	Sample Code	MMA % w/w	DMA % w/w	TMA % w/w	Total % w/w
1.	M-1	0.9	1.3	1.4	3.6
2.	M-2	1.0	2.0	2.1	5.1
3.	M-3	1.0	1.4	1.8	4.2
4.	M-4	1.1	1.4	2.3	4.8
5.	H-1	1.0	1.2	2.0	4.2
6.	H-2	0.9	1.8	2.0	4.7
7.	H-3	0.9	0.8	2.9	4.6
8.	H-4	1.0	2.1	2.4	5.5
9.	X-1	1.0	1.4	2.2	4.6
10.	X-2	1.0	1.1	2.0	4.1
11.	X-3	1.0	1.6	2.1	4.7
12.	X-4	1.0	1.3	1.8	4.1
13.	A-2	1.1	2.1	3.1	6.3
14.	A-3	1.1	2.0	3.0	6.1
15.	A-4	1.0	1.9	3.1	6.0
16.	B-1	1.0	1.4	2.5	4.9
17.	B-2	1.0	1.4	2.0	4.4
18.	B-3	1.0	1.2	2.2	4.4
19.	B-4	0.7	1.3	1.5	3.5
20.	I-1	1.0	0.9	1.4	3.3
21.	I-2	1.0	1.5	2.1	4.6
22.	I-3	1.1	1.7	1.9	4.7

**TABLE 29****ANALYSIS OF TOTAL REPRESENTATIVE CORE SAMPLE FROM E-610**

Sl. No.	Component	% w/w in residue *	Total Wt. kg	Kg moles
1.	TMU	1.52	191	1.87
2.	DMU	1.29	161	1.83
3.	DIONE	3.13	391	2.49
4.	TMB	0.94	117	0.81
5.	DMI	21.42	2675	17.04
6.	MICT	55.71	6964	40.72
7.	MMA	1.02	129	4.17
8.	TMA	3.384	423	7.17
9.	DMA	1.978	246	5.47
10.	TRMB	Traces	-	-
11.	CHLORIDE	4.33	540	15.21
12.	METAL CONTENT	Fe		1275 ppm
		Cr		260 ppm
		Ni		95 ppm
		Ca		20 ppm
		Mg		3 ppm
		Na		60 ppm

Based on the total weight of the residue as 12.5 tonnes.

\* Tarry material (4.7%) not characterised.

## **ANNEXURE 2.1**

### **Gas liquid chromatography (GLC)**

The first ten compounds of the tank residue listed under 2.2.5 were estimated by GLC. Various columns were investigated for separation and quantitative estimation. The following three columns were found suitable for the separation of first seven compounds and their quantitative estimation. The procedure used for determination of amines is described separately.

1. FFAP - 3 - 10%
2. OV-210 + OV-17 - 3-5%
3. Carbowax 20 M TPA - 5-7%

Variation in the load of the phase helps in eluting all the components in shorter time.

### **Determination of MICT, DMI, Dione and Ureas**

#### **Sample preparation :**

About 3g of the sample was weighed in a 100 ml beaker and repeatedly extracted with acetone containing 2% dimethylamine. The extraction was repeated four times with 15 ml portions of the acetone containing dimethylamine. Dimethylamine ensures the dissolution of all the organic compounds excepting the tarry compounds in the sample. The extracts were made up to 100 ml and the solution (0.4  $\mu$ l) was injected into the GLC. About 3 to 6% of tarry residue remained undissolved. Only metal chlorides (0.8%) could be identified in the insoluble residue. The results were calculated by the reporting integrator. The accuracy of the results was checked by injecting known samples into the GLC.

In the case of analysis done using internal standard quantitation, concentration of internal standard was kept constant for standards as well as samples.

The reliability and reproducibility of the methods were checked by analysing known standard samples. The results obtained by absolute calibration curve method are tabulated in Table 2.9. Reliability test used for the external standard methods was the determination of standard deviation for each standard compound. The results of reliability tests using internal standard are recorded in the Tables A-2.3, A-2.4 and A-2.5.

All the values obtained by using different methods are within the acceptable range for GLC analysis.

**Standard solutions :**

The standard solution of each compound was prepared by using purified compounds, with a concentration to match the quantity of that compound actually present in the samples. All the standard compounds (synthesised or isolated) were characterised by their spectral data. Acetone was used as a solvent for preparing the solutions. Standard solutions of various concentrations of each compound were prepared to match the peaks of the sample matrix.

**Instruments and chromatographic conditions :**

The following three instruments were used for the gas chromatographic analysis.

1. **Shimadzu gas chromatograph RIA coupled with reporting integrator**

**GLC conditions :**

Column - FFAP 10% on chromosorb WAW (SS column of 1/8" ID x 6')

Detector - Flame Ionisation Detector (FID)

Carrier gas - nitrogen (60 ml/min)

Column oven temperature - 180°C

Injection port temperature - 250°C

Detector temperature - 250°C

Injection volume - 0.4 µl

Total analysis time - 43 min.

Quantitation method - absolute calibration curve method 44.

2. **Hewlett Packard - 5730 A with 3380 A computing integrator**

**GLC conditions :**

Column - OV-210+OV-17 3-5% w/w on chromosorb W-HB 80/100 (glass column 2 mm ID x 180 cm)

Detector - Flame Ionisation Detector (FID)

Carrier gas - nitrogen (30 ml/min)

Column oven temperature - 155°C  
Injection port temperature - 250°C  
Detector temperature - 300°C  
Injection volume - 2 µl  
Total analysis time - 15 min  
Quantitation method - external standard

**3. Carlo Erba - Fracto vap 2450 coupled with spectra physics - sp-4100 - computing integrator :**

**GLC conditions :**

Column - FFAP 3% on chromosorb 2-HP  
(glass columns 2 mm ID x 100 cms)  
Detector - Flame Ionisation Detector (FID)  
Carrier gas - nitrogen (35 ml/min)  
Column oven temperature - 190°C  
Injection port temperature - 225°C  
Detector temperature - 225°C  
Injection volume - 2 µl  
Total analysis time - 15 min  
Quantitation method - internal standard

Several compounds were tried as internal standards, out of which dibutyl phthalate was selected since its retention time did not interfere with any other component of the sample matrix.

**Standard solutions with internal standard :**

Standard solutions of all the compounds with equal amounts of internal standard were prepared. Concentrations of these standard solutions had a wide range. This was necessary for area matching as in the case of external standard.

**Retention time data and order of elution :**

Retention times and elution data for all the compounds on all the columns are given in Tables A-2.1 and A-2.2. Copies of representative chromatograms are attached in Figures A.1 and A.2.



**TABLE A-2.1**

**RETENTION TIMES OF DIFFERENT COMPOUNDS ON FFAP  
(10% AND 3%) COLUMN**

No.	Compound	10% FFAP Retention time, min	3% FFAP Retention time min
1.	TMU	1.6	0.94
2.	MICT	3.95	2.0
3.	DMU	4.96	2.55
4.	Dione	10.48	4.79
5.	TMB	12.61	5.80
6.	DMI	32.28	12.68
7.	Internal standard Dibutyl phthalate	-	8.15

(Conditions as given in pages 44 and 45).

**TABLE A-2.2**

**RETENTION TIME OF DIFFERENT COMPOUNDS ON  
OV-210 + OV-17 3% W/W COLUMN**

Sl.No.	Compound	Retention time, min
1.	TMU	1.42
2.	DMU	1.78
3.	MICT	5.55
4.	TRMB	6.04
5.	TMB	6.66
6.	DMI	8.32
7.	Dione	10.80

( Conditions as given on page 44 ).

### Determination of amines

Various columns were investigated for the separation and quantitative analysis of amines by GLC. The column described below was developed and was found to be suitable for the quantitative estimation of amines. (Fig A-3)

#### **Sample Preparation**

About 1 g of the sample was extracted with 50 ml water and injected in the Gas Chromatograph. The percentages of amines were calculated directly.

#### **Standard Solutions**

Standard mixture, containing MMA, DMA and TMA were prepared from the corresponding standard solutions of amines. Standard solutions (0.5  $\mu$ l) were injected into the Gas Chromatograph. The ID Table was prepared and filed. The reliability of the method was checked by injecting known concentration of the amines in the Gas Chromatograph.

Retention times of amines were as follows :

Monomethylamine	-	3.85 min
Dimethylamine	-	5.29 min
Trimethylamine	-	5.99 min

#### **Reliability Tests**

<u>Compounds</u>	<u>Wt. taken g/100 ml</u>	<u>Wt. found g/100 ml</u>
MMA	0.36	0.36
	0.72	0.70
	1.44	1.52
DMA	0.46	0.45
	0.92	0.94
	1.84	1.76
TMA	0.26	0.25
	0.52	0.53
	1.04	1.12

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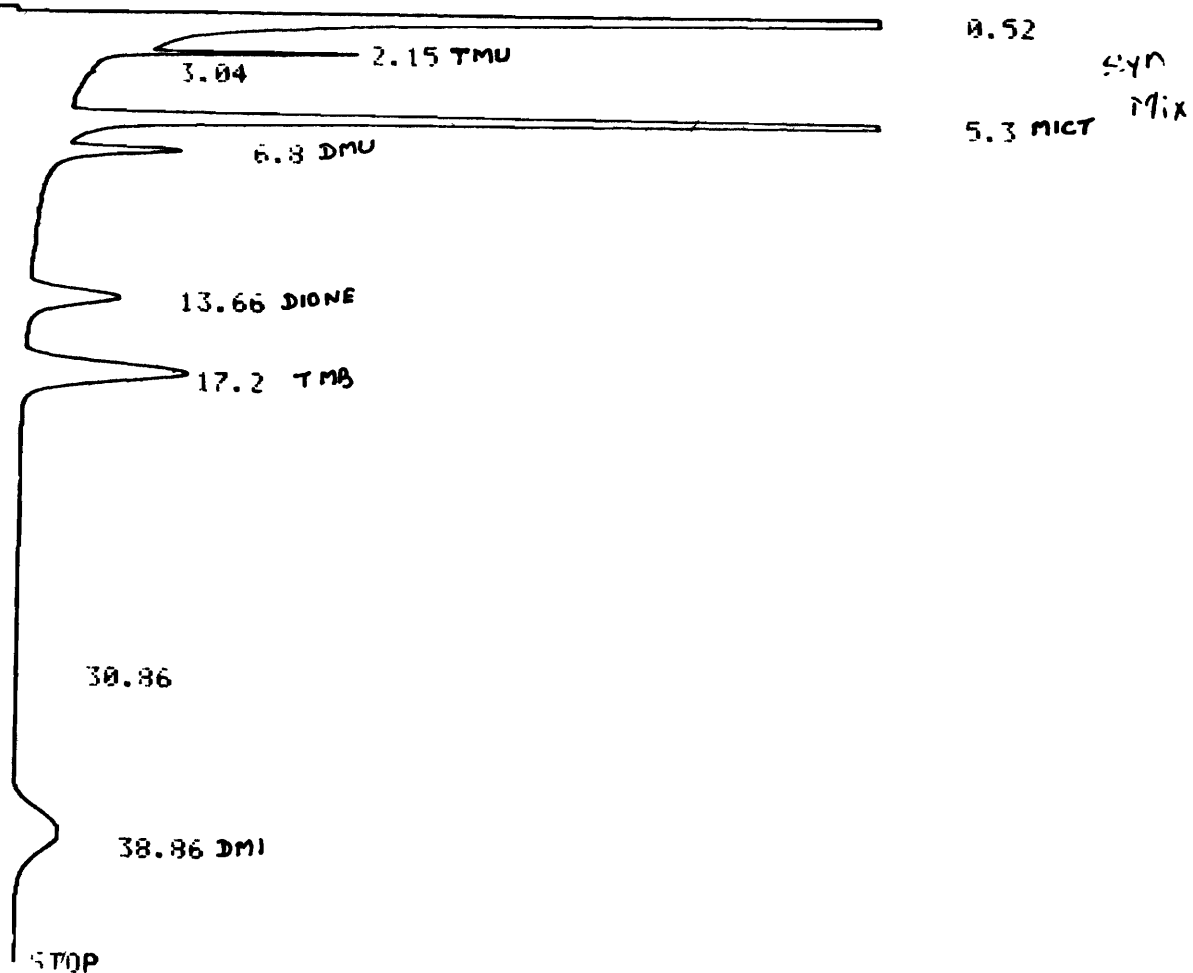


FIG. A-1

INJECT TIME 01:31:44

FFAP - 3X

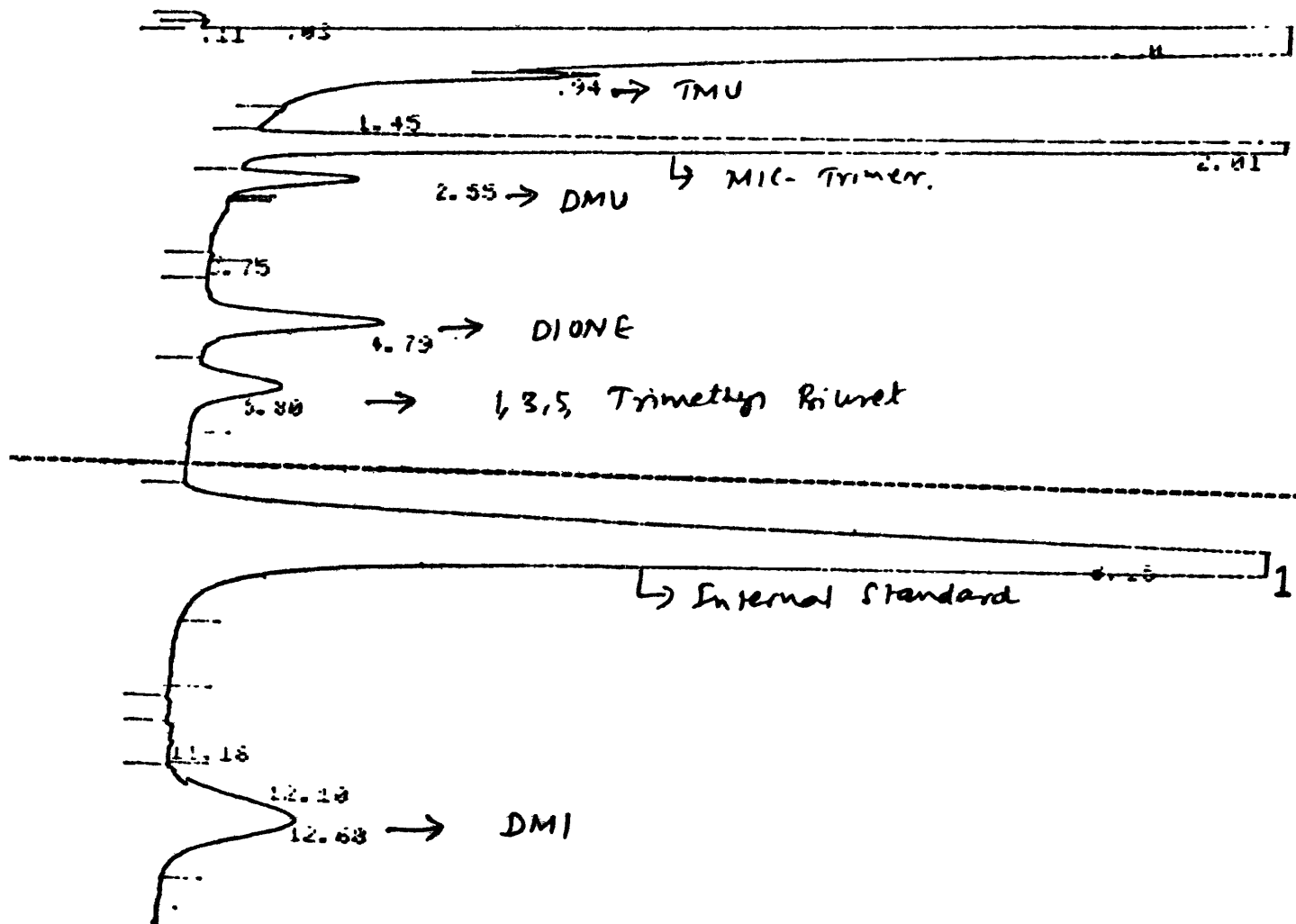


Fig. A.2

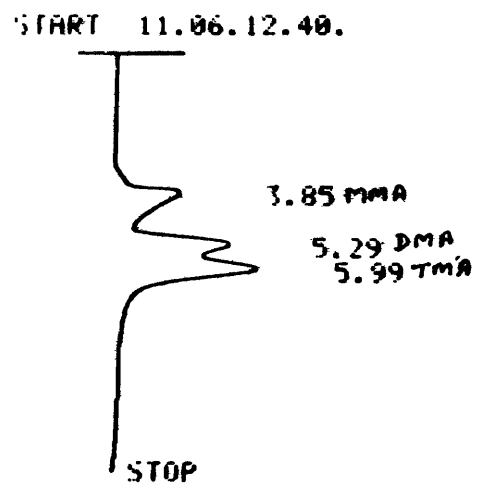


FIG A-3

### **Instrument and chromatographic conditions**

Shimadzu Gas Chromatograph RIA coupled with the reporting integrator was used for all chromatographic estimations. The performance of the chromatograph was checked periodically by injecting standard mixtures.

### **GLC conditions**

Column - 8% TEPA + 2% KOH on chromosorb 102  
(SS column of 1/8" ID x 6 feet)

Detector - Flame Ionisation Detector (FID)

Carrier gas - nitrogen (50 ml/min)

Column oven temperature - 85°C

Injection port temperature - 150°C

Detector temperature - 225°C

Total analysis time - 15 min

Quantitation method - Absolute calibration curve method 44

### **Determination of Chlorides by Potentiometric Titration**

Chloride content ( $\text{Cl}^-$ ) was determined by titrating against standard silver nitrate solution potentiometrically. Residue samples from tank 610 as well as other samples were determined by this procedure. All the samples after diluting with water were made acidic with dilute nitric acid before titration.

### **Reagents and Apparatus**

A R Grade reagents were used for all the work.

1. 0.1 N silver nitrate was prepared by dissolving 85 g of silver nitrate in 5 litres of deionised-distilled water. The solution was standardised using sodium chloride as standard.
2. Mettler automatic titrator was used for all the titrations. ORION CHLORIDE ion selective electrode along with a double junction reference electrode was used as the indicator electrode system.

A magnetic stirrer was used for stirring the solutions during titrations. The end point of the titration was determined by plotting mV against volume of standard  $\text{AgNO}_3$  added. The end point potential was set at + 300 mV .

## Procedure

About 0.5 to 1 g of a sample was accurately weighed using a Sartorius Balance. The weighed sample was transferred into a 250 ml beaker and diluted to about 80 ml with distilled water. The solution was made acidic by adding 5 ml of 1:3 dilute nitric acid. The chloride ion selective electrode and the reference electrode (D/J reference electrode with sodium nitrate in the outer compartment) were introduced into the solution and kept on the magnetic stirrer. A Teflon coated magnetic needle was used as the stirring bar. The electrodes were connected to the automatic titrator. The end point of the titrator was set at + 300 mV. Before starting the titration, the solution was stirred well to ensure that all the chlorides are dissolved in the solution. The stirring was continued throughout the titration. The burette addition automatically stopped when the potential reached + 300 mV. The volume of silver nitrate solution added was noted down after the titration was over.

The chloride content in the sample was calculated by using the equation

$$1 \text{ ml of } 0.1\text{N AgNO}_3 = 3.55 \text{ mg Cl}^-$$

## Preparation of Standard Compounds

### Trimethyl Urea

NN - Dimethylamine in ether was treated with MIC in ether at 0-5°C. The product was isolated after keeping the reaction mixture under stirring overnight. The reaction mixture was filtered and washed with ether. A colourless crystalline product was obtained in quantitative yield.

### 1, 3, 5 Trimethyl Biuret

MIC and sym-dimethylurea (dry) were heated at 100°C in s.s. bomb for 2 hr. The reaction mixture was left at room temperature overnight. The following day the reactor was opened and the excess MIC was evaporated by keeping the reactor in a hot water bath. The residue was crystallised from hot benzene.



### **1,1,3,5 - Tetramethylbiuret**

Attempts to prepare tetramethyl biuret by heating trimethyl-urea with excess MIC in a s.s. bomb at 100°C resulted in a mixture of compounds. The resulting products were analysed by GC and MS and the presence of unreacted trimethyl urea, traces of MIC trimer, tetramethyl biuret and trimethyl biuret were confirmed.

### **Dione**

Dione was prepared by condensation of methylal with 1,3,5-trimethyl biuret in sulfuric acid. The purity was confirmed by M.P. and spectral data.

### **MIC Trimer**

MIC trimer was isolated from the tank residue and characterised by spectral data.

20 g of the residue from tank 610 was extracted with chloroform. The chloroform layer was evaporated. The residue was collected in a stoppered long tube. The tube containing the residue was introduced in an oil bath and heated to about 150°C. The sublimate at the colder portions of the tube was collected and characterised by IR, NMR and M.S.

### **Dimethyl Isocyanuric Acid**

Dimethyl isocyanuric acid was isolated from the tank residues and characterised by spectral data.

About 20 g of the sample was extracted with about 150 ml of toluene under reflux. The hot toluene solution was decanted from the residue and cooled. The crystals formed on cooling were filtered off and recrystallised from toluene and characterised by IR, NMR and MS.

### **Amine Hydrochlorides**

The amine hydrochlorides were prepared from the corresponding amines by standard procedures and checked for their purity.

### **3.0      CHEMISTRY OF FORMATION OF COMPOUNDS IN TANK 610 :**

Having established the presence of the compounds described in Section 2 and listed in 2.2.5 in the residue in tank 610, it was desirable to find conditions and circumstances leading to the formation of each chemical entity. It also became necessary to gain some understanding of the complex chemistry of the reactions that occurred and the various plausible routes by which the products found could have been formed.

#### **3.1      Experiments :**

Since simulation of the exact conditions of the total event that occurred in tank 610 was not possible, experiments were carried out by taking small quantities of MIC and subjecting them to different reaction conditions. The MIC used for these experiments was from material collected from tank 611 from the Bhopal plant. Its composition is given in Table 2.2. It contained  $\text{CHCl}_3$  and hydrolysable chlorides.

Two sets of experiments were carried out :

- a) In the first set, a few experiments were done with MIC which was taken in loosely stoppered pyrex tubes essentially at atmospheric pressure, and reacted with different reagents.
- b) In the second set of reactions, MIC and/or its derivatives, with or without reagents, was taken in stainless steel containers, sealed and heated to and maintained at different temperatures for predetermined times. After cooling, the seal was broken and the residue was examined. Gaseous products have not been examined in these experiments. Further work will be done to identify and estimate the gaseous products as well.

Summaries of a few representative experiments are given in Table 3.1. Experimental procedures along with details of laboratory experiments (Table A-3.1) are given in Annexure 3.1.

#### **3.2      Observations :**

Based on the above mentioned experiments, the following observations were made :

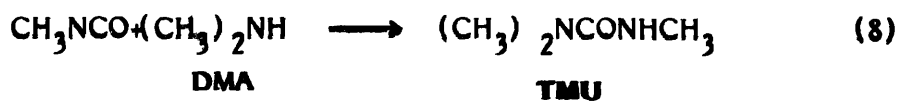
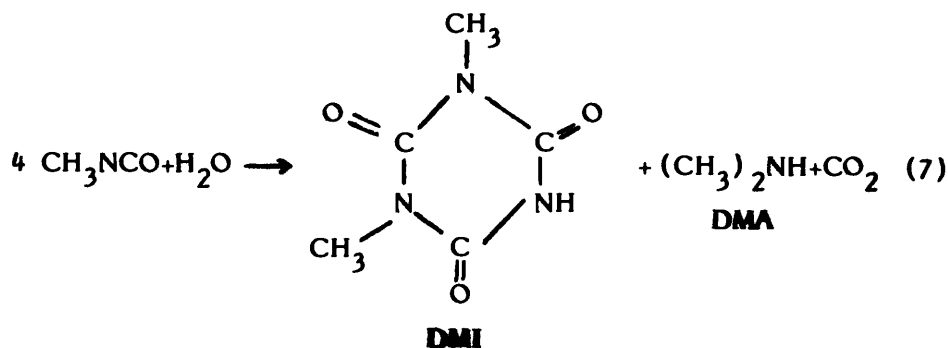
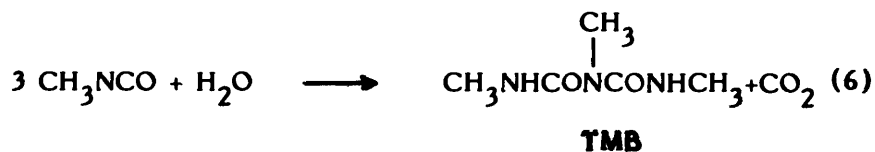
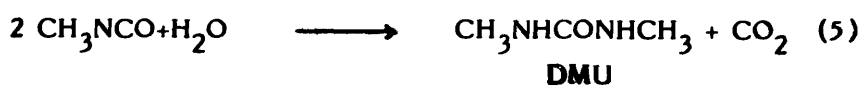
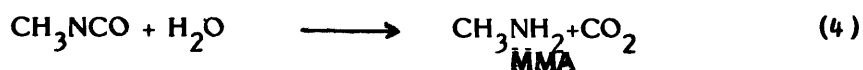
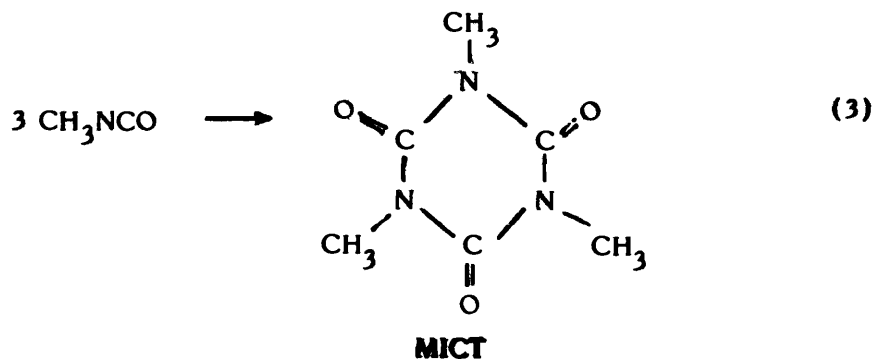
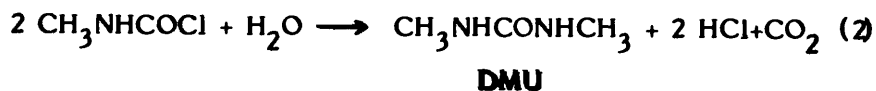
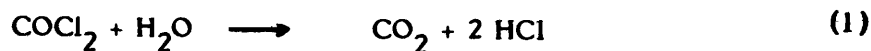
- i. MIC reacts with small quantities of water slowly at room temperature, with a half life of 3 to 4 hours.
- ii. Addition of a trace of ferric chloride to the above reaction mixture at room temperature results in a vigorous reaction after an induction period.
- iii. DMU and TMB are readily formed by reaction of MIC with water.
- iv. MICT is formed readily from MIC. (Presence of MICT has also been noted in various parts of the plant). It can also be formed from TMB by heating. It is very stable product and is not easily transformed into other products.
- v. The formation of DMI is not noticed below 200°C. TMB alone on heating to temperatures above 200°C also gives DMI.
- vi. Dione formation was noticed only above 200°C and the quantity increases as the temperature is raised.
- vii. Presence of chloroform is considered necessary for the formation of Dione.
- viii. It appears that part of the chloride present has come from chloroform present in MIC when the reaction temperatures exceed 200°C.
- ix. The reaction of MIC with small quantities of water and chloroform at 250°C gives all the products formed in tank 610 with the exception of tetramethyl biuret. Formation of amines and amine hydrochlorides was also noticed.

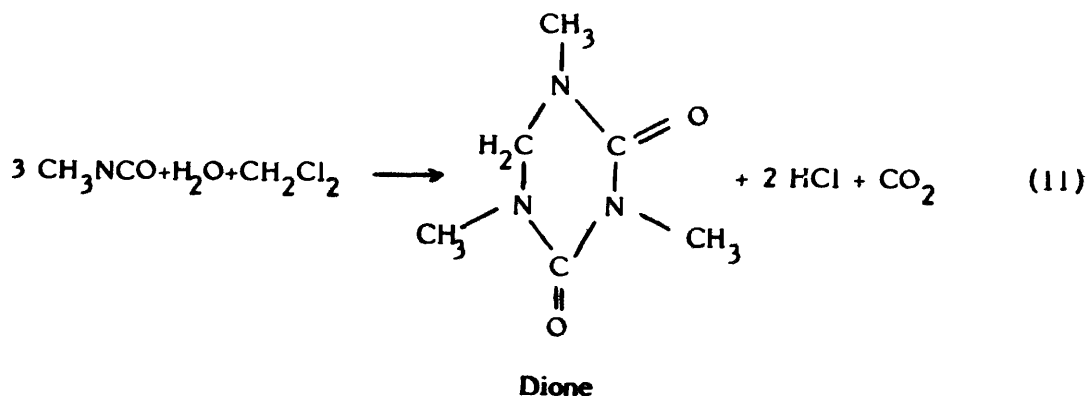
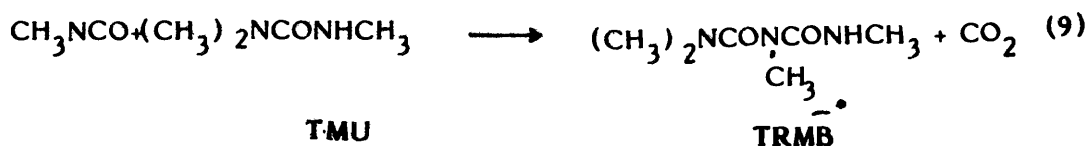
### **3.3 Discussion:**

Based on the above observations and on the composition of the residue given in Table 2.7, the following statements can be made :

Compounds found in the residue can be accounted for by the reaction of MIC with small quantities of water and chloroform.

Assuming the residue composition, and the nature and quantity of each chemical entity present as given in Table 2.9, the following stoichiometric equations can be written for the chemical reactions involved :





### Assumptions

- i. The above reactions represent initial reactants and final products without specifying possible intermediates.
- ii. Chloroform present could enter into reactions only above 200°C. at which stage, all the water present would have been consumed by reaction with MIC. Chloroform or its thermal decomposition products could be available to react with DMU or TMB to produce the Dione.
- iii. The formation of DMI takes place at high temperatures. It is assumed that N-alkylureas are converted to DMI with the simultaneous formation of alkylamines.
- iv. The gaseous products emitted are assumed to be mainly MIC, carbon dioxide, methylchloride ( $\text{CH}_3\text{Cl}$ ), methylene dichloride ( $\text{CH}_2\text{Cl}_2$ ) and carbon tetrachloride ( $\text{CCl}_4$ ). Some alkylamines may have been present in very small amounts.
- v. Phosgene ( $\text{COCl}_2$ ) and MCC ( $\text{CH}_3\text{NHCOCI}$ ) present in very small amounts are readily hydrolysed with water to give hydrogen chloride.

- vi. A part of the chlorine of chloroform is converted to hydrogen chloride. The hydrogen chloride produced is present in part as hydrochloride of amines and as metal chlorides.

### **3.3.1 Material Balance**

Based on the chemical reactions described above, a material balance has been worked out to give the water required for these reactions and the MIC that was used up. These are given in Table 3.2.

Approximately 512 kg. of water and 12.0 tonnes of MIC were used up. About 80 kg. of ammonia and 1.25 tonnes of carbondioxide evolved and escaped from the tank.

### **3.4 Comments**

The residue contains iron, chromium and nickel, almost in the same ratio as in stainless steel 304/316. This could be due to corrosion of the material due to the hydrochloric acid produced as envisaged in the reactions mentioned earlier.

Sodium is present in the residue to the extent of 50-90 ppm. The process water contains only 15 ppm sodium. If all the sodium in the residue is to be accounted from process water only, it had to enter the tank in enormous quantity. Hence one has to look for other sources of sodium e.g. alkali solution in the VGS.

The cause of the presence of 20-30 ppm calcium and of 2 ppm magnesium in the residue, is being investigated.

The exploratory laboratory experiments carried out so far provide sufficient information to enable a logical and plausible scenario to be developed for the chemical reactions that occurred in tank 610.

### **3.5 Gaseous Products of Reaction of MIC**

In the above set of experiments on the chemical transformation of MIC under different conditions and the analysis of the residue, it was not possible to collect gaseous products and examine them. Facilities for such collection of gaseous material are being established.

In preliminary experiments, MIC, water and ferric chloride were placed in a stainless steel tube as described under Annexure 3.1. The tube was closed with cap to which was attached a pressure valve and a thin pipe. The valve was closed and the tube heated to 300°C and maintained at the temperature for half an hour. The tube was then cooled to -5°C and the end of the pipe was placed

in a known quantity of dilute aqueous alkali. The valve was opened and the tube and contents were warmed up to 30°C to volatilise gases and low boiling materials. The gaseous products were thus trapped in the dilute aqueous alkali. The aqueous alkali was examined for the presence of cyanide by standard APHA methods. Cyanide was not detected.

The behaviour of MIC prepared by a different route, namely from sodium azide and acetyl chloride has been studied. When heated in sealed glass tubes to 300°C and the contents examined, the presence of hydrogen cyanide in small amounts has been noted. Under the same conditions, it has been found that MIC sample from tank 611 does not yield hydrogen cyanide. It was felt that the chloroform present in the samples from tank 611 may have an influence on thermal degradation. Therefore, small amounts of chloroform were added to the chloroform free MIC made through sodium azide and acetyl chloride route and the material was heated. In this case, hydrogen cyanide could not be detected. It appears chloroform inhibits the break down of MIC to hydrogen cyanide. It is also possible that minor components present in MIC prepared by the sodium azide-acetyl chloride route may act as activators for formation of hydrogen cyanide. For such studies on inhibitors and activators, highly purified MIC is required. It is found that highly purified MIC tends to polymerise very readily at room temperature. By suitable storage, it is proposed to keep highly purified MIC non polymerised and then examine the influence of minor additives to MIC on thermal decomposition at high temperatures.

MIC, DMI, Dione, DMU and TMB are all products found in the residue in tank 610. It has been estimated by detailed calculation that about 500 kg. of water which had entered the tank, would have reacted with MIC before the temperature rose to 150°C. At temperatures above 200°C, the five materials listed would be in the main products and the possibility of these producing hydrogen cyanide at further higher temperature has been examined. Weighted amounts (100-150 mg) of each material in sealed glass vials have been heated for half an hour at 300°C, the cooled vial placed under dilute alkali in standard flasks and the seal broken to release material. The solution made up to 100 ml was analysed for cyanide by standard procedures. Only traces could be detected in some cases. Thus, there seems to be little or no formation of cyanide from these five materials even in the absence of chloroform. Further detailed work on behaviour at higher temperatures and on influence of other components is planned.

TABLE 3.1

## REPRESENTATIVE LABORATORY EXPERIMENTS WITH MIC &amp; DERIVATIVES

Expt. No.	Reactants	Reaction Temp. °C	Time (Minutes)	GLC of Acetone Extract (Approx. %)
1.	MIC + H <sub>2</sub> O + trace HCl	Rose 23 to 28	6	Not analysed. Temp. rose from 23° to 28°, remained at 28° for 15 minutes and started decreasing.
2.	MIC + H <sub>2</sub> O + trace HCl + trace FeCl <sub>3</sub>	1. Rose 23 to 29 2. 29 to 31 3. 31 to 45	3-5 60 in a few minutes boiled off	Residue was a solid mass which analysed for DMU, TMB and MICT qualitatively.
3.	MIC + CHCl <sub>3</sub> + H <sub>2</sub> O	100	40	DMU (7), MICT (5) TMB(84)
4.	MIC + CHCl <sub>3</sub> + H <sub>2</sub> O	190	40	DMU (3), MICT (60), TMB (36) Dione (Trace)
5.	MIC + CHCl <sub>3</sub> + H <sub>2</sub> O	200	15	DMU (1), TMB (54), MICT (45), Dione (0.5)
6.	MIC + CHCl <sub>3</sub> + H <sub>2</sub> O	250	45	TMU (2), DMU (14), MICT(41), TMB (2.5), DMI (6), Dione(3)
7.	TMB + MIC + CHCl <sub>3</sub>	240	40	TMU (1), DMU (45), MICT(80) TMB (3), DMI (6), Dione (5)
8.	TMB + CHCl <sub>3</sub>	245	45	TMU (2.5), DMU (40), MICT (6), TMB (4), DMI(9), Dione (2)
9.	TMB	250	45	DMI (4), Dione (nil) TMB(1), MICT (29), DMU (61), TMU (trace)
10.	DMU	280	45	DMU (100)
11.	DMU + MIC + CHCl <sub>3</sub>	250	45	TMU (3), DMU (13), MICT (52), TMB (8), DMI (4), Dione (2)
12.	TMU + MIC + CHCl <sub>3</sub>	251	45	TMU (10), DMU (1.5), MICT (47), TMB (3.5), TRMB (2), DMI (12), Dione (2)
13.	MICT + CHCl <sub>3</sub>	280	45	MICT (100)
14	MICT + CH <sub>3</sub> NH <sub>3</sub> Cl	300	45	MICT (100)

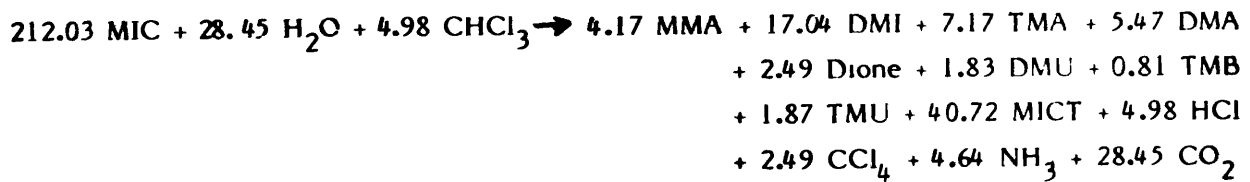


**TABLE 3.2**

**MATERIAL BALANCE**

Chemical Reaction	Product	Kg. mole (kg.)	MIC Consumed kg.	Water Consumed kg.
1	2	3	4	5
$\text{MIC} + \text{H}_2\text{O} \rightarrow \text{MMA} + \text{CO}_2$	MMA	4.17 (129)	237.7	75.0
$\text{MIC} + \text{H}_2\text{O} \rightarrow \text{DMI} + \text{TMA} + \text{DMA} + \text{NH}_3 + \text{CO}_2$	DMI	17.04 (2675)	3792.2	277.4
	TMA	7.17 (423)		
	DMA	5.47 (246)		
$3 \text{ MIC} + \text{H}_2\text{O} + 2\text{CHCl}_3 \rightarrow \text{Dione} + 2\text{HCl} + \text{CO}_2 + \text{CCl}_4$	DIONE	2.49 (391)	425.8	44.8
$2 \text{ MIC} + \text{H}_2\text{O} \rightarrow \text{DMU} + \text{CO}_2$	DMU	1.83 (161)	208.6	32.9
$3 \text{ MIC} + \text{H}_2\text{O} \rightarrow \text{TMB} + \text{CO}_2$	TMB	0.81 (117)	138.5	14.6
$3 \text{ MIC} + 2\text{H}_2\text{O} \rightarrow \text{TMU} + \text{NH}_3 + 2\text{CO}_2$	TMU	1.87 (191)	319.8	67.3
$3 \text{ MIC} \rightarrow \text{MICT}$	MICT	40.72 (6964)	6964.0	-
			12086.6	512.0

**Overall reactions**



## ANNEXURE 3.1

### EXPERIMENTAL PROCEDURE :

- a) The reactions at atmospheric pressure and room temperature were carried out either in a pyrex or stainless steel tube with a loosely fitting cork through which a thermometer was fixed to observe the temperature of the reaction. The rise in temperature due to the exothermic reaction was noted. In the reaction, wherein a trace of iron catalyst was added (Expt. No. 17 of Table A-3.1), after an induction period of about 1 hr a vigorous trimerization reaction set in. The temperature rapidly rose to 40-45°C, and MIC boiled off through the loosely fitting cork.
- b) The reactions were carried out in closed stainless steel bombs at specified temperatures and predetermined times as given in Table A-3.1. The bombs were cooled to 0°C or less and the product extracted, first with acetone and then with water. The residue from the acetone extract was subjected to direct GLC analysis. Both an OV-210 plus OV-17 on a chromosorb column, which shows tetramethylbiuret (TRMB) as a clear separate peak, and FFAP on a chromosorb column, were used for analysis. Details of analytical instrumental conditions and methods of standardisation and peak matching are given in Annexure 2.

The values in parentheses reported in column 7 of Table A-3.1 represent the approximate percentages of these components present in the total acetone extract for the particular experiments.

TABLE A-3.1

## LABORATORY EXPERIMENTS WITH MIC &amp; DERIVATIVES

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm		GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
				Acetone extract	Water extract		
1.	MICT (2.00g), $\text{CHCl}_3$ (9.09g)	200	120	-	-	MICT (100)	-
2.	MICT (1.30g), $\text{CHCl}_3$ (3.00g)	200	120	-	-	MICT (100)	-
3.	MICT (0.41g), $\text{CH}_3\text{NH}_3\text{Cl}$ (0.14g)	200	120	-	-	MICT (100)	-
4.	MICT (0.43g), $\text{CH}_3\text{NH}_3\text{Cl}$ (0.29g) DMU (0.48g)	200	120	-	-	MICT + DMU(qualitative)	-
5.	MICT (0.52g), $\text{NH}_4\text{Cl}$ (0.23g)	200	120	-	-	MICT (100)	-
6.	DMU (2.20g), urea (3.00g)	200-230	300	-	-	DMI (1) + unknowns	-
7.	Methylcarbonyl chloride (MCC) + Dimethyl Allophanyl chloride (DMAC) (0.50g) + Aq $\text{NH}_3$ 5ml	27	30	-	-	MICT, DMU TMB (qualitative)	-
8.	MCC + DMAC (2.35g) + $\text{MeNH}_2$ (excess) in solvent $\text{CH}_2\text{Cl}_2$	0-5	30	-	-	MICT, DMU, TMB (qualitative)	-
9.	MCC + DMAC (3.08g) + MIC (4.0g) kept at room temperature for 24 hr mixture treated with excess $\text{MeNH}_2$ in $\text{CH}_2\text{Cl}_2$	27	30	-	-	MICT, DMU, TMB (qualitative)	-

: 2 :

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract    Water extract		GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
10.	MICT (4.7g), CHCl <sub>3</sub> (0.22g), H <sub>2</sub> O(0.1g), HCl 20% (0.05g)	200	120	-	-	MICT (100)	-
11.	MIC (3.0g), CHCl <sub>3</sub> (0.150g), H <sub>2</sub> O (0.1g), HCl 20% (0.075g)	Mixture temp rose from 23° to 25°, was constant for 1/2 hr and then started decreasing		-	-	Not analysed	-
12.	MIC (2.5g), HCl 20% (0.075g), H <sub>2</sub> O (0.1g)	Mixture temp went up from 23° to 28°, constant for 15 min. at 28° and started decreasing		-	-	Not analysed	-
13.	CHCl <sub>3</sub> (4.5g), H <sub>2</sub> O (4.0g)	200	120	-	-	CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> (qualitative)	HCOOH detected
14.	MIC (3.2g), CHCl <sub>3</sub> (0.225g), H <sub>2</sub> O (0.1g)	200	15	2.65	-	DMU (1.13), TMB(53.6) MICT(45), Dione(0.5)	Cl ions - nil, HCOOH-0.3%
15.	MIC (3.4g), CHCl <sub>3</sub> (0.35g), H <sub>2</sub> O (0.1g)	240	45	2.31	1.23	MICT (84), TMB(2.0) Dione(1)	-
16.	MIC (2.5g), FeCl <sub>3</sub> (0.005g)	Temp rose from 23 to 29° in 5 min and then came down to 27°		-	-	Not analysed	

: 3 :

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract    Water extract		GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in
		<u>Rise in temp</u>	<u>Time</u>				
17.	MIC (2.5g), FeCl <sub>3</sub> (0.04g), H <sub>2</sub> O(0.05g), HCl(20%)(trace)	1. 23 to 30 2. 29 to 31 3. 31 to 45	3-5 60 in a few min. MIC boiled off	-	-	MIC evaporated at 45°C solid mass left analysed DMU, TMB, MICT detected qualitatively	-
18.	CHCl <sub>3</sub> (4.5g), H <sub>2</sub> O (4.0g)	200	120	-	-	CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> (qualitative)	HCOOH estimated (0.3)
19.	MIC (3.1g), CHCl <sub>3</sub> (0.22g) H <sub>2</sub> O (0.1g), MCC + DMAC (0.34g)	200	45	3.24	0.52	TMU(0.64), DMU(15) MICT (53), TMB(12) Dione (0.5), DMI(2.3)	
20.	MIC (3.5g), CHCl <sub>3</sub> (0.22g), H <sub>2</sub> O (0.1g)	200	40	2.65	0.37	CHCl <sub>3</sub> (0.1), CH <sub>2</sub> Cl <sub>2</sub> (1.06) DMU(1.5), MICT(66), TMB (30.4), Dione (0.25)	-
21.	MCC + DMAC (1.43g), DMA (0.68g) in pet.ether	10	15	1.85	-	TMU(17), MICT(8.76) Dione(3), TRMB (appreciable quantity), DMI (2)	-
22.	MICT (2.8g), CHCl <sub>3</sub> (0.15g), H <sub>2</sub> O (0.1g), HCl(trace)	245	45	2.84	0.1	MICT (100)	0.0126

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract    Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in Water extract
23.	TMB (0.66g), CHCl <sub>3</sub> (0.075g) H <sub>2</sub> O (0.05g) HCl (trace)	245	45	0.2g -	DMU(27), MICT(1.15), TMB(1.64), Dione(1.42)	0.02
24.	MCC + DMAC (0.45g), MIC (4.30g)	245	45	1.7g 0.08	TMU(traces),DMU(0.27) MICT(73.6),TMB(4.2) DMI(5.1),Dione(0.5)	-
25.	DMU (4.00g), MIC (4.8g) (Prepn of TMB)	120	120	6.8g (cryst from benzene)	TMB (100)	-
26.	MIC (6.8g), CHCl <sub>3</sub> + HCl (gas) (80 ml)	27	720	- -	MCC+DMAC +MICT (trace) qualitative	-
27.	MIC (6.5g) MCC + DMAC (1.6g)	245	45	5.6g 2.02	TMU(trace),DMU (1.5) MICT(103), TMB(2) DMI(3.2), Dione (0.8)	0.05
28.	TMB(0.93g), MIC (3.5g), CHCl <sub>3</sub> (0.375g)	240	40	3.65g 0.5	TMU(1),DMU(4.68),MICT (90),TMB(3.1),DMI(5.6) Dione(4.7)	0.096
29.	TMB (1.12g), CHCl <sub>3</sub> (0.35g)	245	45	1.25g 0.06	TMU(2.5),DMU(40),MICT (6.1), TMB(4.0),DMI(9.3), Dione (1.7)	0.004
30.	TMB (0.88g)	250	45	0.86 -	DMI(3.7), Dione(nil) TMB(1.36), MICT(29) DMU(61), TMU(trace)	-

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract    Water extract		GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
31.	MICT(0.450g) + CH <sub>3</sub> NH <sub>3</sub> Cl(0.150g)	280-300	1 20	0.41	-	MICT (100)	-
32.	MIC(3.0g) + DMU(1.05g) CHCl <sub>3</sub> (0.225g)	250	45	3.125	0.68	TMU(3.5),DMU(26),MICT (44.4), TMB(3.7), DMI(13.0), Dione (5)	0.04
33.	DMU (3.00g)	280	45	3.033	-	DMU(100)	-
34.	MIC(4.2g) + CHCl <sub>3</sub> (0.225g) H <sub>2</sub> O (0.2g)	250	45	3.420	0.056	TMU (1.94), DMU(14.03) MICT (41), TMB (2.35) DMI(6.1), Dione (2.79)	0.006
35.	MICT (0.55g) + CHCl <sub>3</sub> (1.5g)	280	45	0.63	-	MICT (100)	-
36.	MIC(4.5g) + DMU(1.05g) + CHCl <sub>3</sub> (0.225g)	250	45	4.05	0.052	TMU(1.6), DMU(18), MICT (76), TMB(6.9), DMI(4.5) Dione (3.05)	0.03
37.	MIC (3.1g) + CHCl <sub>3</sub> (0.3g) + H <sub>2</sub> O (0.1g)	250	45	2.90	0.18	TMU(1.1), DMU(13), MICT(44), TMB(3), DMI(6.3) Dione(2.23)	0.3
38.	MIC (3.1g) + DMU (1.0g) + CHCl <sub>3</sub> (0.225g)	250	45	3.750	0.14	TMU(2.7), DMU(12.5), MICT(52), TMB(8), DMI(4), Dione (2)	0.02
39.	MIC (3.2g) + DMU (1.07g)	250	45	3.530	0.014	TMU(1), DMU(31.6), MICT(36), TMB (8.4), DMI(1), Dione (1)	Nil
40.	MIC(3.2g) + DMU (1.13g) + CHCl <sub>3</sub> (0.225g)	280-300	45	4.250	0.056	DMU(18), TMU(0.75), MICT(46), TMB(10) DMI(3) Dione(2)	0.006

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract      Water extract		GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
41.	MIC (3.4g) + DMU (1.02g) + CH <sub>2</sub> Cl <sub>2</sub> (0.225)	240-250	45	4.130	0.14	TMU(1.36), DMU(9), MICT(49), TMB(6.4), DMI(5), Dione (2.4)	0.01
42.	MIC (3.5g) + DMU (1.01g) + CHCl <sub>3</sub> (0.45g)	215	40	4.20	0.25	TMU(0.7), DMU(12), MICT(41), TMB(4.5), DMI(11), Dione(1)	0.07
43.	TMU(0.44g) + MIC(1.5g) + CHCl <sub>3</sub> (0.3g)	215	45	1.64	0.21	TMU(10), DMU(1.4), MICT(46.5), TMB(3.4), TRMB(1.7), DMI(12), Dione(1.6)	0.05
44.	MIC(3.5g) + CHCl <sub>3</sub> (0.225g) + H <sub>2</sub> O (0.1g)	100	40	1.09	0.02	DMU(7.4), MICT(5), TMB(83.5)	0.001
45.	MIC(3.5g) + CHCl <sub>3</sub> (0.225g) + H <sub>2</sub> O (0.1g)	190	40	2.64	0.02	DMU(3), MICT(70), TMB(36) Dione(traces)	0.005
46.	MIC(3.5g) + CHCl <sub>3</sub> (0.225g) + H <sub>2</sub> O (0.1g)	215-220	40	3.40	0.07	TMU(0.15), DMU(5.13), MICT(60), TMB(15), DMI(6), Dione(1.22)	0.005
47.	TMU(3.43g) + CHCl <sub>3</sub> (0.3g)	220	40	2.50	-	TMU(64), DMU(13), TetMU (present)	nil
48.	MIC(3.2g) + CHCl <sub>3</sub> (0.45g), H <sub>2</sub> O (0.1g)	215-220	40	2.91	0.08	TMU(1), DMU(7), MICT(52) TMB(14), DMI(5), Dione(1.6)	0.008



: 7 :

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract    Water extract		GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
49.	MIC(3.4g) + DMU (1.04g) CHCl <sub>3</sub> (0.6g)	220	40	4.48	0.23	TMU(0.6),DMU(10), MICT(44), TMB(6.5), DMI(8), Dione(2)	Nil
50.	Mic(3.6g) + CHCl <sub>3</sub> (0.6g) H <sub>2</sub> O (0.3g)	220	45	2.84	0.40	TMU(0.5),DMU(21), MICT(9), TMB(20), DMI(14), Dione (3)	0.1
51.	MIC (1.5g), TMU(0.47g), CHCl <sub>3</sub> (0.450g)	215	45	2.52	0.13	DMU(3.5), TMU(22) MICT(42.6), TRMB(2), TMB(5), DMI(4.3) Dione(1.5)	0.026
52.	MIC(5.0g), H <sub>2</sub> O (0.2g)	20-29	48	1.02	-	MICT(1), TMB(52.3), DMU(49.4)	-
53.	DMU(1.55) + CHCl <sub>3</sub> (0.3g)	220	60	1.33	0.04	DMU(96.9), TMB(2.02)	0.025
54.	TMB(0.208g) + CH <sub>2</sub> Cl <sub>2</sub> (0.15g)	220	60	0.197	0.019	DMU(39.3), TMB(50), MICT, DMI & Dione not seen	Nil
55.	TMB(0.820g) + CH <sub>2</sub> Cl <sub>2</sub> (0.45g)	250	60	0.68	-	TMU(0.92), MICT(12.9), DMU(39.4), Dione(4.4), TMB(30), DMI(1.5)	-

#### **4.0        ANALYSIS OF DESIGN AND ENGINEERING FEATURES :**

##### **4.1        MIC and its Characteristics :**

MIC is a highly reactive, toxic, volatile and inflammable chemical. According to the UCC brochure, MIC is usually stored and handled in stainless steel 304 and 316 equipment. Iron or steel, aluminium, zinc or galvanized iron, tin, copper or their alloys are prohibited from use.

Purified MIC will react with itself under the influence of a catalyst to form a cyclic trimer or a high molecular weight polymer. Strong bases such as sodium hydroxide, sodium methoxide and sodium acetate, certain metal chlorides such as ferric chloride and stannic chloride catalyse trimerisation. Since the reaction is quite exothermic, contamination of MIC with traces of the catalysts can cause violent reactions.

Highly purified MIC will polymerise spontaneously to a linear polymer/trimer.

Water reacts exothermically to produce heat and carbon dioxide. As a result, the tank pressure will rise rapidly if MIC is contaminated with water. The reaction may begin slowly, especially if there is no agitation, but it will become violent. Aqueous sodium hydroxide solution will react with MIC quite rapidly.

MIC with the above mentioned characteristics should be considered as an explosive in addition to it being a highly toxic chemical.

As per the UCC brochure, the storage temperature should be maintained below 15°C and preferably at about 0°C. The storage tank is to be equipped with dual temperature indicators that will sound an alarm and flash warning lights if the temperature of the stored material rises abnormally. The tendency of valves on storage tanks to be clogged with solids is also stated in the brochure.

The brochure further states that the cooling medium in the heat exchanger should not be one that reacts with MIC or catalyses the reactions. While chloroform is an example of a safe coolant, use of water does create a hazard.

## **4.2      Storage Tank**

The highly toxic and explosive nature of MIC requires that the storage system and its related instrumentation/control be of high reliability.

Inspection of MIC storage tanks is difficult, since they are buried. Tank 610 was reportedly cleaned and inspected in 1982. Varying quantities of MIC from production runs at different periods have been filled into tank 610. Similarly, varying quantities of MIC have been removed at different periods.

Commercially produced MIC contains hydrolysable chloride in the form of phosgene and MCC. Ingress of even a small quantity of water of the order of 40-50 ml per tonne of MIC, will lead to the reaction of water with the hydrolysable chloride to provide hydrogen chloride and with a little more of water, aqueous hydrochloric acid. This leads to corrosion of stainless steel, the material of construction of the storage tank, leading to the formation of ferric chloride which can catalyse the violent run-away reaction.

The Sevin unit could process MIC of the order of 3 to 4 tonnes per day. The inventory of MIC in the storage tank was of the order of 90 tonnes, equivalent to nearly 30 days production.

It is normal plant practice to have intermediate batch tanks to hold production from a single shift or for a day. The product collected in these tanks is analysed, its quality ensured and then it is transferred to the bulk storage tank. Such a facility of batch tanks had not been provided. MIC was directly fed to the bulk storage tanks from MRS without any batch tank.

Alternatively, an online analyser could have monitored continuously the quality of MIC before it entered the storage tank. An alarm could have been provided to alert the operator regarding off-quality MIC and enable him to take quick action to prevent contamination of the bulk storage tank with off-quality material. There was no provision for such an online analyser/ alarm system.

Water is used as the cooling medium in the multi-tubular MRS overhead condenser. Water circulated in the shell side is at a higher pressure than the pressure of MIC inside the tubes. Even a pin hole in any of the tubes could lead to a small quantity of water entering the MIC make line which is taken directly to the bulk storage tank.

### **4.3        Nitrogen :**

MIC is kept under a pressure of nitrogen which is supplied by a carbon steel header common to all the storage tanks. There is a strainer in the nitrogen line. Subsequent to the strainer the pipe is of carbon steel and leads to make-up DMV which also has a body of carbon steel. Similarly, the blowdown DMV is also of carbon steel body. These carbon steel parts may be exposed to MIC vapours and get corroded, providing a source of contaminant which can enter the MIC storage tank.

The level in MIC tank is measured by purging of nitrogen. The header supplying this nitrogen is made of carbon steel and the connection from the manifold to the level instrument is by a copper tube. There is no strainer or filter in this line which can prevent entry of rust or metallic particle entering the tank along with nitrogen.

### **4.4        Instrumentation and Control System :**

The pressure in the MIC tank increases rapidly if MIC is contaminated with water. There is no high pressure alarm to alert the operator about the build-up of pressure.

There is a graphite rupture disc between the tank and the safety valve. This graphite rupture disc may break because of pressure surges even under normal conditions. There is no provision for an alarm to bring such a breakage of rupture disc to the attention of the operator.

For the storage of a lethal chemical such as MIC, two instruments in parallel (one for control/indication and another for alarm) are normally provided. No such provision is made. For example, quite often the level readings have not been recorded, reportedly because the level system used to be out of order very often due to choking problems. In fact, after the event, since the only level monitoring system provided for tank 611 was not functioning, it was not possible to ascertain the exact quantity of MIC in that tank. An additional level measuring system would have helped in such a situation.

Ingress of contaminants or water can start a reaction with MIC which will begin slowly and produce a rise in temperature of the tank contents.

However, the range of the temperature transmitter provided was only  $-25^{\circ}\text{C}$  to  $+25^{\circ}\text{C}$ , with a high alarm setting at  $+11^{\circ}\text{C}$ . The contents of the tank were being stored at ambient temperature, which varies approximately from  $+15^{\circ}\text{C}$  to  $+40^{\circ}\text{C}$  at Bhopal. The temperature of MIC in the storage tanks for most part of the year was higher than the high temperature alarm setting, i.e.  $+11^{\circ}\text{C}$ . Indeed the temperature of material in the tank was higher than the maximum of the range of the temperature transmitter, i.e.  $+25^{\circ}\text{C}$ . In such circumstances the actual temperature was not known and the transmitter was of no value. Further, provision of "rate of rise in temperature" alarm would have invited the operator's attention to the start of such a reaction. No such provision was made.

#### 4.5 Refrigeration

There is only one common compressor and chiller system for all the three MIC storage tanks. For such a hazardous material as MIC, where maintaining it at a low temperature is considered very important, a spare compressor and chiller system would have ensured proper chilling even when the main compressor and chiller system is under repairs or maintenance. This provision of spare compressor and chiller has not been made.

#### 4.6 Vent Gas Scrubber

The VGS is designed to neutralise a maximum of about 3.5 tonnes (7700 lb) of MIC at a maximum rate of about 9.6 tonne/hr (21200 lb/hr) in a vapour form.

The accumulator volume of  $80\text{m}^3$  (21000 gal) if filled with the recommended 10% caustic solution can neutralise a maximum of about 13 tonnes of MIC. Also, operation of VGS at temperatures above  $70^{\circ}\text{C}$  for extended periods is not recommended since absorption will be poorer and the heat of neutralization is not completely removed by the cooler in the VGS system.

With the caustic make up pump capacity at 95 lpm (25 gpm) of 20% caustic solution, additional MIC that can be neutralised is also limited to about 2 tonne/hr.

## **5.0 AN ANALYSIS OF THE EVENT:**

The background and circumstances, the study of the properties of the materials, examination of tank residue, experiments on conditions for formation of various chemical entities, critical examination of relevant features of design have all been described in the previous chapters. This provides a basis for outlining factors which led to the event, which are given in the following paragraphs:

- MIC readily undergoes chemical reactions with explosive violence, which produce a large amount of heat, and allow a large portion of stored liquid MIC to vapourise. This is inherent to the nature of the material. Neither the precise conditions under which such run-away reactions could be initiated in MIC nor its manner of prevention are well known.
- A large quantity of MIC was stored in underground tanks which have many inlets and outlets that can permit entry of contaminants which can trigger off explosive reactions.
- The studies described earlier indicate that a reaction was initiated and the temperature rose rapidly. There was no 'rate of rise in temperature' alarm to indicate the rising temperature which would have alerted the operator to an early detection of a run-away reaction.
- Any emergency dumping of liquid MIC into the VGS would not have been feasible because the alkali available in the accumulator is grossly insufficient. Further more, this would also lead to an abnormal temperature rise in the VGS.

- It is conceivable that gaseous MIC would be emitted due to a rapid reaction inside the tank. This gas is expected to be neutralised by circulating alkali solution in the packed section of VGS. This system is also grossly inadequate to handle quantities of vapourised MIC as large as were emitted during the event. Calculations show that even if the normal design load for VGS is taken into consideration, the VGS is inadequate to neutralise a discharge of 28 tonnes of vapourised MIC in about 2 hours.
- Therefore, neither the liquid nor the gaseous disposal system was capable of handling the event which occurred on the night of December 2, 1984.
- The relief valve design could not permit free flow of large quantities of gases, certainly at the level at which they were generated during the event. Thus, the tank contents were subjected to pressures much higher than 40 psig and correspondingly high temperatures.
- From the examination of the tank residue and from the conditions of formation of the residue, it is surmised that the temperature reached in the bulk storage tank may have been around 250°C. The total energy balance on the tank also indicate that the probable temperatures would be in the range of 200 to 250°C. Information from the mechanical examination of the tank indicate that the pressures may have reached 11 to 13 kg/cm<sup>2</sup>g with the corresponding temperatures in the range of 200 to 350°C.

The chemical analysis of the tank residue clearly shows the evidence of entry of approximately 500 kg. (1100 lb) of water. The fact that the tank 610 was not under pressure of nitrogen for approximately two months prior to the accident also indicates that conditions existed for entry of contaminants such as metallic impurities through the high pressure nitrogen line. As emphasised earlier, many such impurities have a catalytic effect on the possible reactions MIC can undergo.

The hydrolysis of MIC with about 500 kg. (1100 lb) of water by itself and in the absence of other contaminants is not expected to lead to thermal run-away conditions. The presence of this quantity of water would have possibly resulted in reaction with about three to four tonnes of MIC, generation of carbon dioxide, breaking of the rupture disc and release of CO<sub>2</sub>. The temperature of the tank content would have gradually risen to about 60-70°C, below the boiling point of MIC at that pressure. It is surmised that no more than 50 to 100 kg/hr (110-220 lb/hr) of CO<sub>2</sub> along with small quantities of MIC, ca 100-150 kg/hr (220 - 330 lb/hr) would have been released. Such emissions will cease once the water has been consumed.

The presence of trace amount of metallic contaminants derived from the material of the tank or its attachments or from extraneous sources, may not necessarily initiate a violent reaction under dry conditions. Small amounts of local trimerisation may take place, as noticed throughout the pipelines and plant. However, the ingress of water, would provide for active species of initiator to be generated and distributed in the liquid.

This implies that conditions which were ripe for the initiation of a run-away trimerisation reaction already existed in tank 610 on the day of the event, and that entry of water would generate active initiators and



the hydrolysis of MIC would provide the necessary heat also for the trimerisation reaction to take off with explosive violence. The carbondioxide evolved upon hydrolysis would provide the necessary mixing leading to even more rapid chemical reactions. The storage tank thus equalled the conditions of a well mixed tank reactor, supplied with heat.

Once initiated, the trimerisation reaction rapidly led to a temperature increase leading to levels as high as 250°C with autocatalytic and auto-thermal features. At these high temperatures, secondary chemical transformation occurred leading to the complex mixture of products actually found in the tank 610 residue.

500 kg (1100 lb) of water could have entered the tank 610 either from the MRS condenser (through condenser tube leaks) or through RVVH/PVH lines. The fact that about 50-90 ppm of sodium was found in the tank residues is also significant. The observed sodium levels are substantially higher than what would have normally been present due to the entry of 500 Kg (1100 lb) of water (below 0.5 ppm).

Entry of water from the MRS condenser appears less likely as the MRS make line from MRS condenser to tank 610 was flushed with nitrogen, evacuated and blinds were inserted in the line between 23 to 25 October, 1984. Water could have entered from the MRS prior to 23 October but it would have probably reacted much earlier than 2 December, 1984.

A detailed analysis indicates that water entry through RVVH/PVH lines is quite likely. It has been reported that around 9.30 P.M. on 2 December, 1984, an operator was clearing a possible choke of the RVVH lines downstream of phosgene stripping still filters by water flushing. Presumably the 6" isolation valve on the RVVH was closed but a slip blind

had not been inserted. Under these conditions when the filter lines are choked, water could enter into the RVVH, if the 6" isolation valve had not been tightly shut or passing.

Furthermore, it is likely that alkaline water could have backed up from the VGS accumulator into the RVVH and PVH under certain conditions. Indeed, several litres of alkaline water was drained from the RVVH/PVH lines in the MIC structure in May 1985, lending credence to such a possibility.

Furthermore, RVVH/PVH lines are made of carbon steel. Back up water or alkali through these lines increase the possibility of metal contaminants entering the tank, especially in the absence of positive nitrogen pressure.

The water that entered RVVH at the time of water flushing along with backed up alkali solution from the VGS already present could find its way into the tank 610 through the RVVH/PVH lines via the blow down DMV or through the SRV and RD. To account for say 60 ppm of sodium in the residue quantity equivalent to 25 litres (about 6.5 gal) of 5% sodium hydroxide would have been sufficient. Such an eventuality would have required that the blow down DMV was malfunctioning or the SRV was not tightly shut and rupture disc had been damaged.

The absence of practically any nitrogen pressure on tank 610 for over a month and the observation that MIC was leaking out of a branch of RVVH on the downstream side of Regeneration Gas Cooler Pressure Safety Valve at 23.30 hours on the night of 2 December, 1984 indicated the possibility of malfunctioning of blowdown DMV.

Opportunities for intrusion of water, alkali and metal contaminants into tank 610 thus existed from 22nd October, 1984 and into tank 611 as well during 30th November to 1st December, 1984, when there was negligible positive nitrogen pressure in these tanks.

Trimerisation of MIC to solid material in small quantities and consequent choking of lines leading to tank was a frequent occurrence and seems to have been well accepted by the plant operating staff. Similarly, cleaning and purging with water of lines associated with the storage tanks was also accepted as a routine procedure. The hazards presented by ingress of water or other contaminants which could cause trimerisation and lead to choking was not appreciated and the tank 610 was allowed to stay without positive nitrogen pressure from 22nd October to 2nd December, 1984.

The UCC brochure on MIC makes reference to the reaction of water to produce DMU and TMB. The heat generated would be related to the quantity of water. The brochure also mentions metallic contaminants could lead to violent reactions of MIC which has the unique combination of properties of explosive reactivity, ready volatility and high inhalation toxicity. It seems possible that small amounts of water in presence of trace amounts of metallic contaminants could set off explosive reactions and leakage not containable in the inadequate VGS system.

It was entirely unnecessary to provide facilities for storage of such large amount of MIC in tanks. The quantities stored were quite disproportionate to the capacity of further conversion of MIC in downstream unit. This permitted MIC to be stored for months together without appreciation of potential hazards.

The events on 2nd/3rd December, 1984 arose primarily from these facilities and accepted practices.

The rapid rise in temperature and violent reactions that occurred necessitate the onset of metal ion catalysed polymerisation. The presence of chloroform has no influence whatsoever in initiating or accelerating the run-away reactions. The chloroform present was involved in chemical transformations when the temperature had risen above 200°C at which stage all the water would have already been consumed by reactions.

- The quantum of toxic leakage by violent chemical reaction is not related to the amount of metal and water which initiate the reactions but to the quantity of MIC stored in a single container. If 42 tonnes of MIC had been stored in 210 stainless steel drums of 200 litre capacity each, as alternative to a single tank, there would be no possibility of leakage of more than one fifth of a tonne and effects of even such a leakage could be minimised by spray of water or alkali.
- It has been reported that a large number leakages of MIC in comparatively small quantities have occurred from storage vessels and tanks in Union Carbide. The causes for such leakages have not been made known. While Union Carbide product brochure refers to chemical properties and reactivity of MIC, including possibilities of violent reaction as well as of possibilities of spillages from drums and tanks during transport, no information is provided on the extraordinarily lethal toxic effects of inhalation. Public preparedness for eventualities arising out of leakage would have been substantially greater if information on these had been generally available. For instance, substantial care is exercised in the storage and transport of explosives or in handling even weakly radioactive materials or in the use of X-ray equipment, due to the awareness of hazards.

In retrospect, it appears the factors that led to the toxic gas leakage and its heavy toll existed in the unique properties of very high reactivity, volatility and inhalation toxicity of MIC. The needless storage of large quantities of the material in very large size containers for inordinately long periods as well as insufficient caution in design, in choice of materials of construction and in provision of measuring and alarm instruments, together with the inadequate controls on systems of storage and on quality of stored materials as well as lack of necessary facilities for quick effective disposal of material exhibiting instability, led to the accident. These factors contributed to guidelines and practices in operations and maintenance. Thus the combination of conditions for the accident were inherent and extant. A small input of integrated scientific analysis of the chemistry, design and controls relevant to the manufacture would have had an enormously beneficial influence in altering this combination of conditions, and in avoiding or lessening considerably the extent of damage of December, 1984 at Bhopal.



