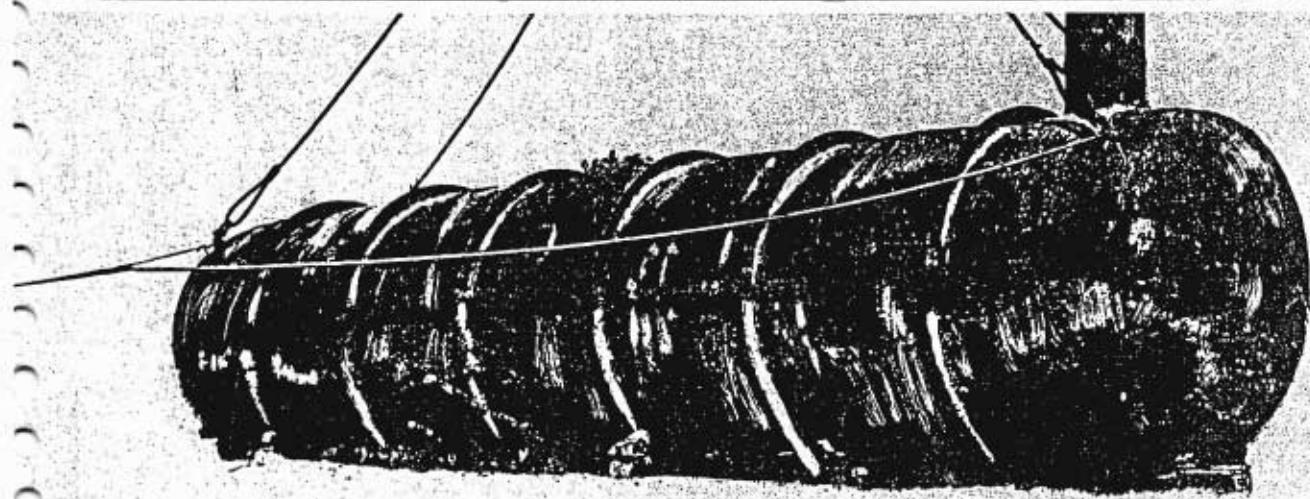
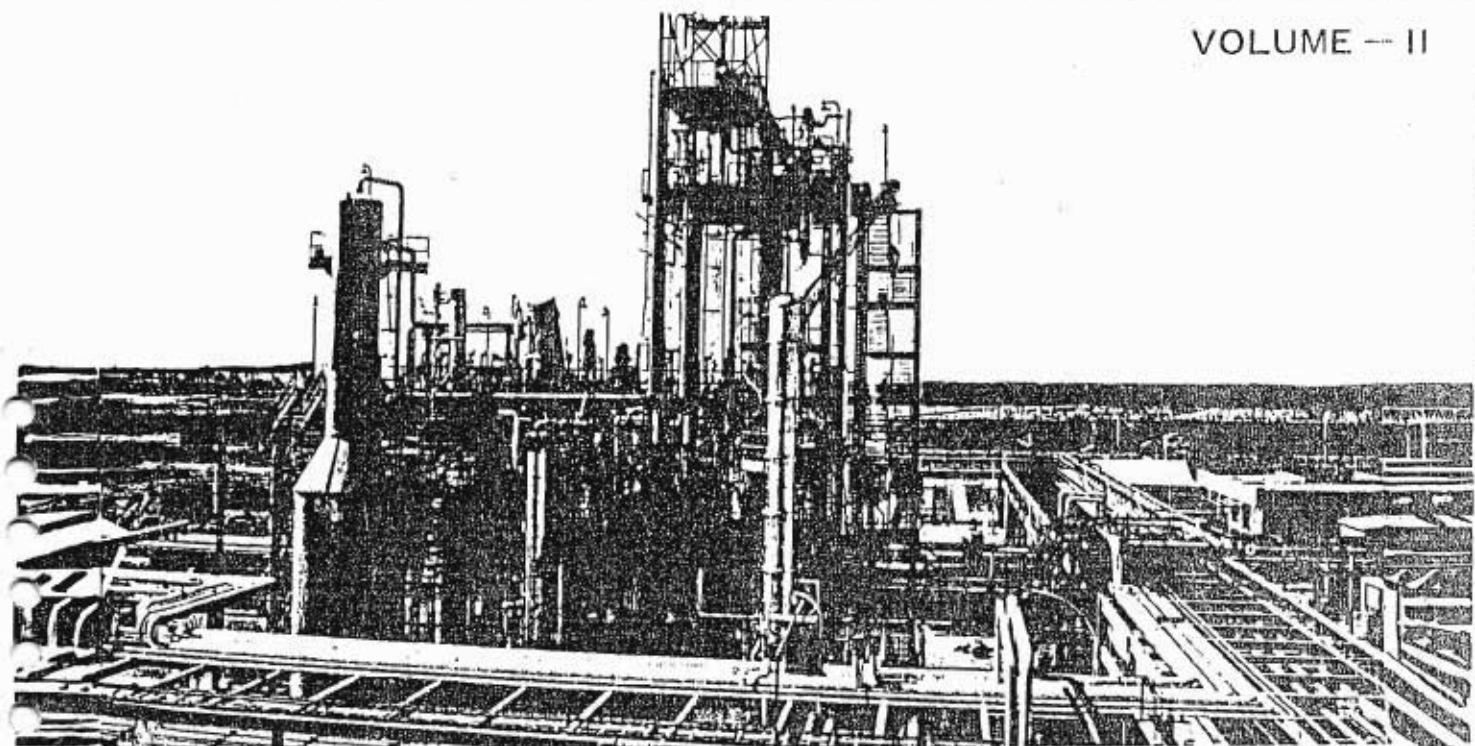


VOLUME - II



COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
RAFI MARG, NEW DELHI-110001

RESTRICTED

**THE CHEMICAL PHENOMENA LEADING TO
THE TRAGIC TOXIC GAS LEAKAGE AT
THE UNION CARBIDE PESTICIDE PLANT,
BHOPAL AND AFTERMATH**

VOLUME – II



**COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
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NATIONAL CHEMICAL LABORATORY
PUNE

THE BHOPAL ACCIDENT
REPORT ON
CHEMICAL REACTION ENGINEERING ANALYSIS

1986

A report on the investigations by National Chemical Laboratory (NCL), Pune, could be found in the following pages. NCL, which belongs to the Chemical Sciences Group of laboratories of the Council of Scientific & Industrial Research, undertook the task of studying the chemical and reaction engineering aspects of MIC leakage. The results are dealt with in Part I and Part II.

Part I begins with a presentation of analytical procedures and results of various chemical samples collected from the tanks, pipings, etc. at the site of the accident including core samples from the ill-fated Tank 610. The analysis reveals the existence of a large number of compounds which must have been formed during the event. Possible chemistry of the events and details of experiments to verify the postulates are also given. The experiments carried out have conclusively shown that a mixture of MIC, chloroform and water when heated to 225°C to 250°C in a stainless steel reactor gives all the products found in Tank 610, though not in the same quantitative proportion. The concluding section gives the experimental studies to determine the ways in which hydrogen cyanide (apparent cyanide poisoning in many patients having been observed) could have been formed.

Part II presents a modelling and computer simulation of the Bhopal accident. The model is based on the essential findings in Part I. These data, together with experimental data on the key reactions between MIC and water, MIC trimerization, etc. were analyzed to obtain the rate kernel. The mathematical model is developed subsequently with a number of simplified assumptions. The three stage model, thus developed, is discussed further. This particular model helps in putting quantitative bounds on the temperature and pressure reached in the accident tank and provides an approximate description of the dynamics of the whole process during the event.

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1. INTRODUCTION

A major leakage of toxic gases took place on the night of December 2, 1984 at the Union Carbide factory in Bhopal from a buried stainless steel tank (tank 610) in which forty two tonnes of methyl isocyanate (MIC) had been stored. This event resulted in enormous loss of human life and injuries to a significant proportion of the population. Whereas the consequences of such a major event have been obviously tragic, the causes have not been well understood. The National Chemical Laboratory was assigned the tasks of examining the chemical and reaction engineering aspects of the accident. This report provides the details of the investigations carried out by NCL team of scientists.

The report is presented in two parts. Part I deals with the chemical aspects and Part II deals with the reaction engineering aspects of the problem. The method of enquiry in Part I is largely experimental in nature while Part II uses the essential findings from Part I as the basis to construct an engineering model to describe the events leading to MIC leakage.

Part I begins with the analysis of samples which were recovered from the ill-fated tank 610 after the accident. The details of the methods of analysis and composition of residue are presented in Section 2. The analysis reveals the existence of a large number of compounds which must have been formed during the event.

Section 3 discusses the possible chemistry of the event and gives details of experimental studies carried out to verify these postulates. The experiments carried out have conclusively shown that a mixture of MIC, chloroform and water when heated to 225° to 250°C in a stainless steel reactor gives all the products found in Tank 610, though not in the same quantitative proportion. Finally, Section 4 is devoted to the experimental studies to determine whether HCN could have been formed during the event.

The analysis in Part II begins with the main results derived in Part I as its basis. Section I of this part therefore highlights the essential findings of Part I which are germane to the development of a mathematical model. Section 3 analyses the experimental data on the key reactions between MIC and water, MIC trimerisation, etc. with a view to obtain the rate kernel. The mathematical model is developed subsequently with a number of simplifying assumptions, which have been clearly outlined. Section 4 discusses NCL's three stage model of the Bhopal accident. The important implications of the results are discussed in Section 5. In particular the model helps in putting quantitative bounds on the temperature and pressures reached in the accident tank and also provides an approximate description of the dynamics of the whole process during the event.

2. ANALYSIS OF SAMPLES

In order to reconstruct the event, it was necessary to obtain reliable analytical results of various chemical samples connected with the event. Samples were collected from the site of the accident in various batches. The first samples of residue from the tank were collected in February 1985 through the manhole nozzles of the tank. Later, windows were cut at the specific point of the tank and further samples were collected. Samples from various pipelines, especially, RVVH/PVH and associated pipelines were also collected.

In all, samples were collected in five batches. The list of the samples alongwith their code nos and dates of collection are attached as Annexure 2.2.

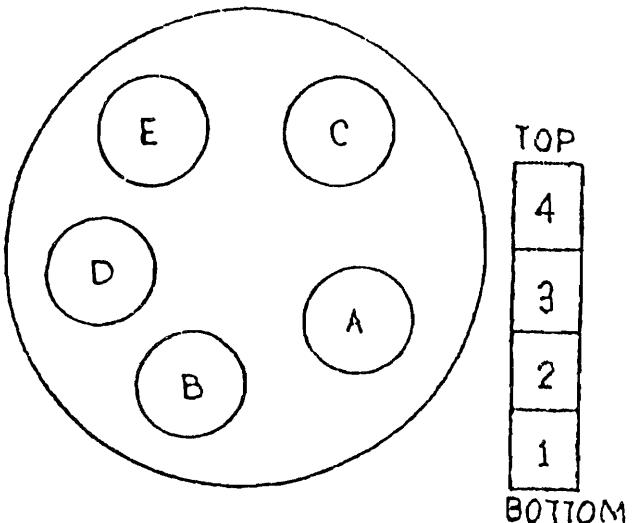
2.1 Sampling

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). A pipe 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



CORE SAMPLE

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

Fig. 2.1: Sample Identification

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.

SAMPLING SCHEDULE ON MIC TK E - 610

KEY:

SAMPLE NOS



WINDOW NOS

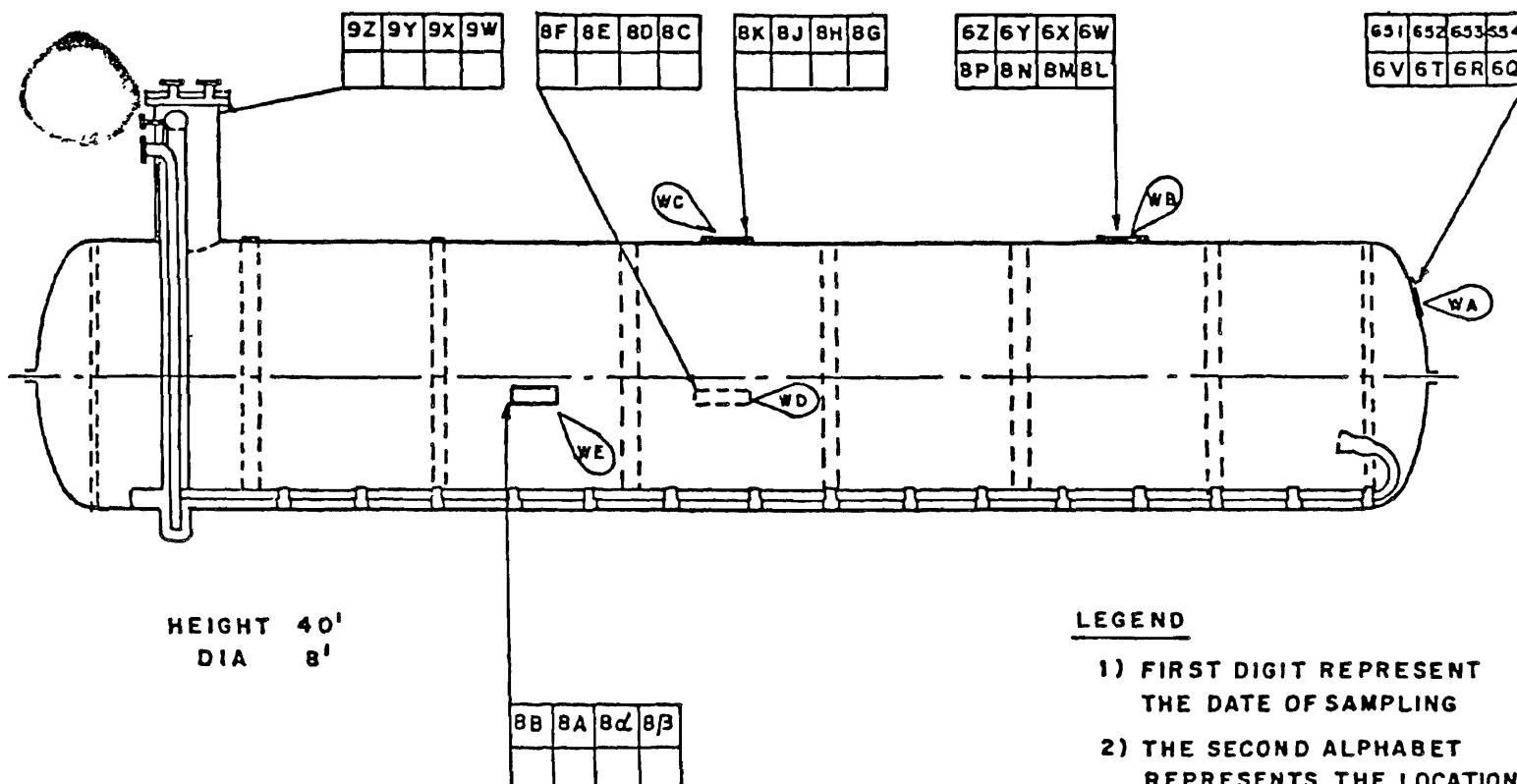


Fig. 2.2:

2.1.3 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.

A sample of MIC from tank 619 was collected on 14.3.85 at 1.20 p.m. Earlier, 2 samples of MIC were collected from the chiller line to tank 610 on 4.12.84. The analysis of these 3 samples are given in Table 2.2a. They were all of specification.

2.1.4 Samples from pipelines, valves and other equipments

Liquid samples were collected from RVVH/PVH and other equipment in February and May, 1985. Description of these samples given in Annexure 2.2 and their analyses of chloride ion, acidity and alkalinity are given in Table 2.10.

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 manhold (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 sublimes. 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 liquidlike 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 2.1. 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:

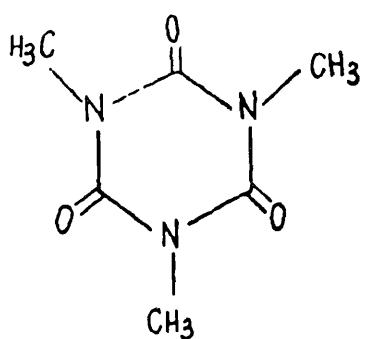
A total representative sample was prepared by mixing samples drawn from the various windows of the tank. The sample thus prepared as representative of the entire quantity of the residue was mixed and homogenised. This sample was prepared by mixing equal quantities from 22 different residue samples. These samples represent the bottom portions, middle 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.

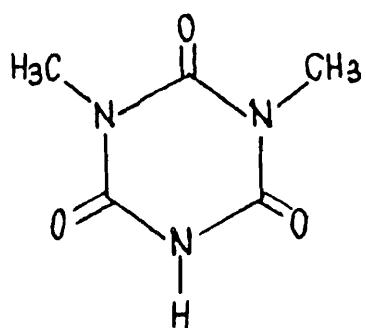
The total identified compounds in the sample add up to about 95%. As indicated earlier, the residue samples contain about 3-6% of unidentified tarry materials.

2.3.1 Product distribution

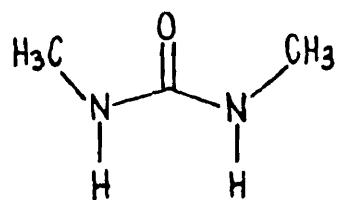
Besides the presence of various metal and chloride ions, the residue contains 10 organic compounds. These are presented as kg moles in the last column of Table 2.9. The tank residue contains 40.7 kg moles (or about 7000 kg of MIC trimer). The next highest molar concentration is that of DMI with 17.0 kg moles (2675 kg), followed by the chloride ions with a con-



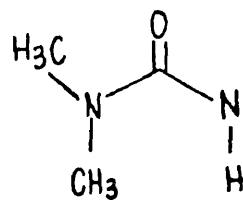
MICT
MW = 171



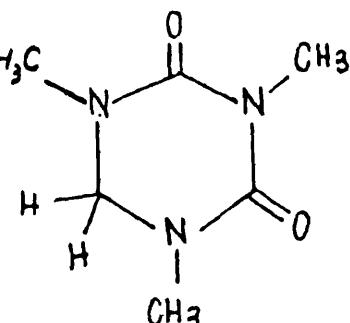
DMI
MW = 157



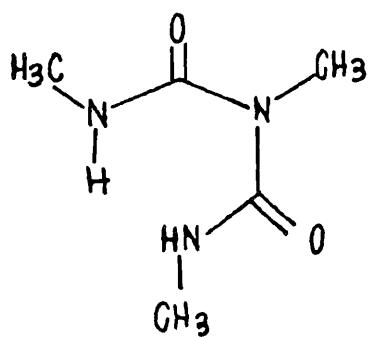
DMU
MW = 88



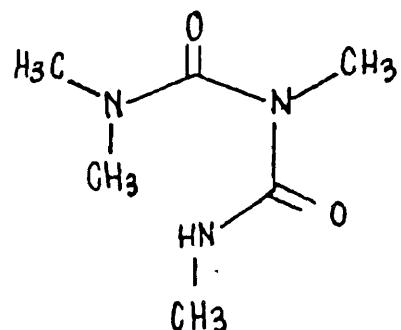
TMU
MW = 102



Dione
MW = 157



TMB
MW = 145



TRMB
MW = 159

Fig. 2.3: Structures of compounds in tank-610

centration 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.

2.4 Reactions involved

The percentages as well as the total quantities of all components found in the tank residue are presented in Table 2.9.

MIC, in the absence of external reagents but in the presence of catalyst, can trimerize to give 1,3,5 trimethyl isocyanurate (MICT). The residue has been found to contain MICT to the extent of 40 mole percent.

Examination of the analytical results reveals that the residue mass contains products which could be considered as derived from the MMA - MIC reaction. MMA can also be produced by the reaction of water and MIC. It can therefore be concluded that either water or MMA entered the MIC storage tank E 610.

Reaction sequences that take place when either water or MMA enters the MIC tank are depicted in Chart I.

The chemical structures of the compounds are shown in Fig 2.3.

From simple stoichiometric calculations, the total quantity of water required for all the reactions involving water can be calculated. This amounts to about 450 kg.

CHART - 1

Reaction sequences:

1. Formation of MMA and CO₂



2. Formation of DMU



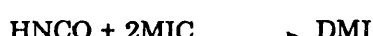
3. Formation of Trimethyl biuret



4. Formation of DMA



5. Formation of DMI



6. Formation of TMU



7. Formation of TMA and DMI



8. Formation of dione and chloride



9. Formation of MICT

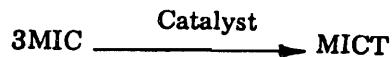


TABLE 2.1
Analysis of Liquid Samples from RVVH/PVH

SL No.	Sample Designation	Chloride % Cl ⁻ w/w	Acidity as % HCl w/w	Alkalinity % w/w	
				Na ₂ CO ₃	Na ₂ HCO ₃
A. SAMPLES COLLECTED IN FEBRUARY, 1985					
A1	Sample of liquid from PSV down-stream bleeder of dryer	1.37	-	-	-
A2	Side-stream cooler PSV d/s bleeder sample	15.61	11.98	-	-
A3	Sample from RVVH drain bleeder on desuperheat on second level.	5.01	4.38	-	-
B. SAMPLES COLLECTED IN MAY, 1985					
B1	30/5/PVH liquid sample No.7	1.42	Nil	13.62	13.31
B2	RVVH liq. from bleeder on 2nd level B.F. towards Sevin dt. 31/5 sample No.21 Sr. 8	1.50	-	7.67	12.06
B3	RVVH VGS line bleeder liq. 31/5 sample No.31	1.15	-	8.59	20.62
B4	RVVH VGS line bleeder liq. 31/5 sample No. 31	1.16	-	-	23.93

TABLE 2.2

Analysis of MIC Samples from E-611

Sample Code No.		Sample No.1 20.12.84	Sample No.3 20.12.84	Sample No.6 19.12.84
1. Methyl isocyanate	(%)w/w	99.17	99.85	99.60
2. Chloroform	(%)w/w	0.314	0.334	0.332
3. Moisture	(%)w/w	N.D.	N.D.	N.D.
4. Phosgene	(%)w/w	0.032	0.030	0.028
5. Total Hydrolysable Chlorides	(%)w/w	0.040	0.028	0.032
6. Non Volatiles	(%)w/w	0.130	0.110	0.090
7. Trace metals (ppm)				
(a) Zinc		3.5	3.7	1.2
(b) Iron		3.6	3.6	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

TABLE 2.2a
Analysis of MIC Samples from E-610 and E-619

Sr. No.	Component	Sample from Tank 619 on 14.3.85 Time 1.20 pm Sample No.1	Brown sample from Tank 610* Sample No.2	Sample from MIC Tank 610 4.12.84 at 17.30 hrs Sample No.
1)	Physical appearance	Pale Yellow with grey residue at the bottom	Dark brown liquid	Pale Yellow
2)	Total hydrolysable chloride Cl ⁻	0.0683%	0.155%	0.0455%
3)	Phosgene -COCl ₂	0.0587%	0.0305%	0.0338%
4)	Chloroform CHCl ₃	0.70%	4.7%	5.41%
5)	Non volatiles - evaporation residues	11.59%	10.34%	5.92%
6)	Assay - MIC	89.7%	84.22%	87.39%
	Trace Metals (ppm)	SN I	SN II	SN III
1)	Iron - Fe	0.14%	0.093%	0.090%
2)	Nickel - Ni	0.014%	0.0056%	0.0035%
3)	Chromium - Cr	0.035%	0.014%	0.015%
4)	Sodium - Na	0.0033%	-	-

* Sample collected from the chiller line.

TABLE 2.3
Analysis of Core Samples from the Manhole Nozzles

S.No.	Description of sample	Code No.	Acidity as HCl % w/w	Chloride Cl % w/w	Fe ppm	Ni ppm	Cr ppm
Sample from							
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 MICT % w/w	Dimethyl Urea, DMU % w/w	1, 3, 5 Triazine Dione % w/w	Trimethyl biurate TMB % w/w	Dimethyl isocynurate, DMI % w/w
1	2	3	4	5	6	7	8
1. Safety Valve Nozzle	A-1	1.1	59.6	1.8	3.1	-	12.6
2. Core sample MIC Tank E-610 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	39.6	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
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. Sample from diptube bottom piece tank 610	F-1	1.3	39.2	6.2	2.8	6.5	17.7
17. Sample from dip tube bottom piece tank 610	F-2	1.9	24.0	12.8	2.5	9.5	28.4
18. Sample from dip tube bottom piece tank 610	F-3	1.7	23.6	10.9	6.5	13.0	20.7
19. Sample from dip tube bottom piece tank 610	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.	Sample No.	Acidity as HCl % w/w	Chloride Cl- % 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

Sample No.	TMU % w/w	MICT %w/w	DMU % w/w	Dione % w/w	TMB % w/w	DMI % w/w	Amines (TMA, DMA, MMA) % w/w	Chlorides % w/w
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	4.0	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	6.3
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	5.2	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

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.	X 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
23.	39	1.0	-	1.0	2.0

TABLE 2.9
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	229	2.24
2.	DMU	1.29	193	2.2
3.	DIONE	3.13	469	3.0
4.	TMB	0.94	140	0.97
5.	DMI	21.42	3210	20.45
6.	MICT	55.71	8357	48.86
7.	MMA	1.02	155	5.00
8.	TMA	3.38	508	8.6
9.	DMA	1.98	295	6.56
10.	TRMB	Traces	-	-
11.	CHLORIDE	4.33	648	18.25
12.	METAL CONTENT	Fe Cr Ni Ca Mg Na	1275 ppm 260 ppm 95 ppm 20 ppm 3 ppm 60 ppm	

Based on the total weight of the residue 15.0 Tonnes

* Tarry material (4.7%) not characterised.

TABLE A-2.10
*Analysis of Chloride Ion, Acidity & Alkalinity
 Samples from 1st Batch*

	Samples	Acidity as HCl % w/w	Chlorides as HCl % w/w
		1	2
9)	Nozzle B, N ₂ /Outlet outside of core sample	6.35	10.26
22)	Solids from R/D v/s/ and D/S spool (2)	0.78	0.496
23)	Solids from E-610 R/D v/s/ spool piece (3)	0.68	0.41
24)	Solids R/D v/s/ isovalve D/S side (4)	0.51	0.340
25)	Solids from R/D D/S spool piece (5).	0.83	0.523
26)	R/D D/S spool piece end flange side solids E-610 tank (7)	0.82	0.352
27)	Sample from RVVH dead end bleeder towards 200 TR shed (11)	7.82	7.68
28)	Sample of liquid from PSV downstream bleeders of dryer (9)	-	1.37
29)	Side stream cooler PSV d/s bleeder sample 2Pc	11.98	15.61
30)	Sample from RVVH drain bleeder on desuper-heat on 2nd level.	4.38	1.97
31)	Top core section MIC tank E-610	9.37	5.01
32)	Mid core section MIC tank E-610	6.54	4.87
33)	Bottom core section MIC tank E-610	4.89	4.26
34)	Solids from E-610 Thermowell	5.77	1.75
35)	Liquid sample collected from MIC tank GIL PSV p/s line (RVVH)	3.06	4.9
36)	Solid sample collected from MIC tank 610 PSV D/s valve D/s line RVVH	2.93	1.66

	1	2	3
37)	RVVH bleeder above decanter after reopening RGC PSV D/S valve.	4.33	7.4472
38)	Solid from MIC tank 610 process vent nozzle spool piece	0.95	0.228
39)	Solid sample : i) D/S side below of DMV ii) D/S and v/s common N ₂ make	1.22	0.814
40)	PSV d/s bleeder of phosp vapouriser E-101		0.407
41)	Solid samples from D/S pipe line between D/S isolation valve and blow off DMV	6.46	12.69
42)	MIC transfer recirculation inlet line to MIC tank E-610 dropped piece	0.49	2.56
43)	Sample No. I 'Anode' white powdery sample near manhole MIC tank 610	-	0.046
44)	Sample 2 collected near Dished end towards MIC structure tank E-610 (ANODE) (S oil sample around anode at above mentioned place)	-	0.1277
45)	Sample from phos-vapouris-or safety valve D/S bleeder	Neutral	0.42
46)	VGS Caustic from pump discharge bleeder No.3	Alkalinity 7.6% NaOH w/w	1.03
47)	VGS Caustic pump discharge bleeder No.1	7.68% NaOH w/w	1.11
48)	VGS Caustic from pump discharge bleeder No.2	7.74 "	1.11
49)	VGS Caustic from pump discharge bleeder No.4	7.64	1.19
50)	Unlabelled bottle (1)	-	2.6
51)	Unlabelled bottle	-	1.15

Sample from II Batch

	Sample	Acidity	Chlorides
1)	Sodium hydroxide in approx. Core sample V ₁	-	1.24
2)	2nd from bottom from E-610 Core sample V ₂	7.30	4.74
3)	3rd from bottom from E-610 Core sample V ₃	6.20	5.34
4)	Top layer from E-610 Core sample V ₄	6.83	5.25
9)	Dip tube, E-610 Tank DT ₁	0.92	0.24
10)	Dip tube (middle portion) E-610 tank DT ₂	2.08	0.40
11)	Dip tube Near Bottom DI ₃	1.13	0.68
12)	WS ₃	1.63	0.11
13)	E-610 (Manhole from bottom of manhole tank) MH ₁	0.95	1.1
14)	MHRV	0.38	0.11
15)	E-610 E ₁	8.39	7.3
16)	E-610 8A ₁	8.95	8.27

Results Table: Samples from IVth Batch

Sl. No.	Sample Designation	Chlorides	Acidity as HCl	Alkalinity % w/w		
				Total as NaOH	Na ₂ CO ₃ 8.5 pH	as NaHCO ₃ from 8 to 4 pH
1	2	3	4	5	6	7
1.	30/5/RVVH Spool piece sample No.1	1.4% w/w	0.51% HCl w/w	-	-	-
2.	30/5/RVVH PVH line solid sample Sample No.4	2.3	"	1.27 "	-	-

1	2	3	4	5	6	7
3.	30/5/RVVH-PVH line solid sample Solid Sample No.5	1.9 "	1.38 "	-	-	
4.	30/5/PVH liquid sample No.7 Sample No.8 (Sr. No.5)	1.42 "	-	16.62	13.62	13.31
5.	Sample No. 8 Sr. No.5	1.37 "	-	16.41	12.05	11.81
6.	30/5/PVH Solid Sample before NRV Sample No.10	25.82 "	10.47 "	-	-	-
7.	30/5/PVH-Solid Sample No.11 before NRV	25.07 "	14.82	-	-	-
8.	Solid sample from RVVH 1st level lead end (Towards 200-TR) dt. 31/5 11.20 AM. Sample No.17	18.02 "	16.41 "	-	-	-
9.	Solid sample from RVVH 1st level Dead and (Towards 200 TR) Dt. 31/5 11.20 AM Sample No.16	15.63 "	16.08 "	-	-	-
10.	RVVH liq. from bleeder on 2nd level B.F. towards sevin dt. 31/5	1.49 "		10.58	8.199	9.24
11.	RVVH liq. from bleeder on 2nd level B.F. towards Sevin dt. 31/5 Sample No.21 Sr. No.8	1.50 "		10.56	7.67	12.06
12.	Solid from RVVH 2nd level dead end towards Sevin Unit dt. 31/5 Sample No.24	1.52 "		11.01	8.75	9.56
13.	—"— Sample No.25	1.50 "		11.63	8.56	10.85
14.	Solid from 4" RVVH flange at B.L. dt. 31/5 14.50 hrs No.27	0.35 "	2.3 "	-	-	-
15.	—"— 15.00 hrs. No.28	0.35" "	1.3 "	-	-	-
16.	RVVH VGS line bleeder liq. 31/5 Sample No.31	1.15 "		16.85	8.59	20.62

1	2	3	4	5	6	7
17.	—”— No.32	1.16 "		17.04	-	23.93
18.	31/5 Sample from PV H dead end towards 200 TR/No.33	Nil	0.54 "	-	-	-
19.	Tarcole sample collected from the half lower portion and the MIC tank 610 from whole water from below at 15.50 hrs.	-	0.14 "	-	-	-
20.	Water sample (found around MIC tank 610) at 8/3/85	0.03%	0.07 "	-	-	-

Samples from Vth Batch

Sr.	Description of the Samples	Chlorides % w/w	Acidity as HCl % w/w	Alkalinity % w/w		
				as NaOH	as Na ₂ CO ₃	as NaHCO ₃
1)	15/6 RVVH-II level bleeder towards 20C TR liq. sample No.2	1.58	-	10.91	8.23	9.838
2)	17/6/VGSD Drain Sample before taking fresh caustic No.3	0.11	-	0.97	1.07	0.35
3)	14/6/VGS Caustic Sample before transfer to spent caustic tank No.3	0.6	-	6.67	8.29	0.86
4)	14/6 Caustic Sample before transfer to spent caustic tank No.4	0.6	-	6.68	8.29	0.88
5)	Sample No.4. 15/6/PVH IIInd level 4" x 3" Reducer liq. Sample 4	1.95	-	15.75	9.77	17.52
6)	17/6/VGS Drain Sample before taking fresh caustic/No.4	0.15	-	0.93	1.06	0.28
7)	15/6 RVVH IIInd level bleeder towards Sevin liq. Sample No.6	1.79	-	11.26	8.64	9.99
8)	15/6 RVVH-I level bleeder towards Sevin liq. Sample No.8	2.48	2.97	-	-	-

Sample from VIth Batch

Water Analysis	Hardness
(1) Lake water	87 ppm as CaCO ₃
(2) Process water	88 ppm as CaCO ₃

Gas liquid chromatography

The first compounds of the tank residue listed under 2.3 were estimated by gas liquid chromatography. Various columns were investigated for separation and quantitative estimation. The following three columns were found suitable for the separation of all these compounds and quantitative estimation.

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

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

Experimental results are given in the following section 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 coupled with reporting integrator.

G.C. conditions

Column - FFAP 10% on chromosorb WAW
Detector - Flame Ionisation Detecter (FID)
Carrier gas - Nitrogen (Flow 60 ml/min.)

Temperatures

Column oven - 180°C
Injection Port - 250°C
Detector - 250°C
Injection volume 0.4 l

To analysis time - 43 min.

Method employed for quantitative analysis -
Absolute calibration curve method 44.
1. Hewlette Packard - 5730 A with 3380 A Computing integrator.

G.C. Conditions

Column - OV-210+OV-17 3-5% w/w on chromosorb
W-HP 80/100
2 mm ID x 180 cms - glass
Detector - Flame Ionisation Detecter (FID)
Carrier gas - IOLAR-1 nitrogen 30 ml/min.

Temperature

Column oven - 155°C
Injection port - 250°C
Detector - 300°C
Injection volume - 2 μ l
Total analysis time - 15 min.
Method employed for quantitative estimation.
External standard quantitation.

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

G.C. conditions

Column - FFAP 3% on chromosorb W-HP

2 mm ID x 100 cms

Detector - Flame Ionisation (Detector (FID))

Carrier gas - IOLAR - 1 nitrogen 35 ml/min.

Temperatures

Column oven - 190°C

Injection port - 225°C

Detector - 225°C

Injection volume - 2 µl

Total analysis time - 15 min.

Method employed for quantitative estimation - Internal standard.

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

Standard solutions with internal standard

Standard solutions of all the compounds with equal amount of internal standard were prepared. Concentration of these standard solutions had 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 A-2.2 Copies of representative chromatograms are attached in Figs. A.1, A.2.

Analysis procedure

Determination of organic compounds by GLC:

Sample preparation:

About 3 gms. of the sample was weighed in a

100 ml beaker and repeatedly extracted with acetone containing 2% of dimethylamine. The extraction was repeated 4 times with 15 ml. portions of the acetone containing dimethylamine. The dimethylamine insures the dissolution of all the organic compounds excepting the tarry compounds in this sample. The extracts were made up to 100 ml. and the solution (0.4 µl) was injection into the Gas Chromatograph. About 3 to 6% of tarry residue remained undissolved. Metal chlorides (0.8%) only could be identified in the insoluble residue. The results were calculated by the reporting integrator. The accuracy of the results were checked by injecting known samples into the GC.

In 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 44 are tabulated in Table 2.9. Reliability test used for the external standard method was the determination of standard deviation for each standard compound.

The values of reliability test using internal standard are recorded in Tables.

All the values obtained from the different methods are within the acceptable range for G.C. analysis. In the case of DMI the percentage variation exceeds 5% and is due to a somewhat skewed-peak. However, the analysis at lower concentrations and in internal standard are quite reliable; peaks are normal.

Determination of Amines by Gas Chromatography

Various columns were investigated for the separation and quantitative analysis of amines by Gas Chromatography, the column described below was developed and was found suitable for the quantitative estimation of amines.

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.

G.C. conditions		Reliability Test		
Column: 8% TEPA + 2% KOH on Chromosorb 102.		Compound	Wt. taken gms/100 ml.	Wt. found gms/100 ml.
		MMA	0.36	0.355
Temperature			0.72	0.702
Inj.	150°		1.44	1.52
Column	85°	DMA	0.46	0.45
Detector	FID		0.92	0.94
Carrier gas	Nitrogen	TMA	1.84	1.76
Fuel	Hydrogen 50 ml/min		0.26	0.25
Nitrogen flow	20 ml/min.	Samples	0.52	0.53
Air	50 ml/min.		1.04	1.12
Range	2			
Attn.	3			
Chart speed	3 mm/min.			
Quantitation	Absolute calibration curve method 44.			
Procedure:		Determination of Chloride		
Standard mixture containing MMA, DMA and TMA were prepared from the corresponding standard solution of amines. Standard solutions (0.5 µl) 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 G.C.		Chloride content (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.		
Retention time of amines:		Reagents and Apparatus:		
1. Monomethylamine 3.85 min. 2. Dimethylamine 5.29 min. 3. Trimethylamine 5.99 min.		Analar Grade reagents were used for all the work		
		1. 0.1 N silver nitrate was prepared by dissolving 85 gms 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. End point of the titrations were determined by plotting mV against volume of standard Ag NO₃ added. The end point potential was set at + 300 mV.

Experimental : General Procedure :

About 0.5 to 1 gm 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 titration was over.

The chloride content in the samples were calculated from the equation

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

TABLE A-2.1

Retention time of different compounds on FFAP (10% and 3%) column

Sl.No.	Compound	10% FFAP	3% FFAP
		Retention time	Retention time
		min.	min.
1.	Trimethyl urea	1.6	0.9
2.	MIC-trimer	3.95	2.0
3.	Dimethyl urea	4.96	2.55
4.	Dione	10.48	4.79
5.	Trimethyl biuret	12.61	5.80
6.	Dimethyl cyanuric acid	32.28	12.68
7.	Internal standard Dibutyl phthalate		8.15

(Tetramethyl biuret is co-eluting with dimethyl urea tetra MBU separates out on a Carbo wax 20 M TPA. However, this column has not been used for the complete analysis)

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.	Trimethyl urea	1.42
2.	Dimethyl urea	1.78
3.	MIC Trimer	5.55
4.	Tetra methyl biuret	6.04
5.	Trimethyl biuret	6.66
6.	1,3-Dimethyl isocyanurate	8.32
7.	Dione	10.80

TABLE A-2.3

*Reliability test using internal standard
Internal Standard 'Dibutyl Phthalate'*

No.	Compound	Concentration in mg/10 ml	
		Taken	Obtained
1.	TMB	24.4	23.9
2.	DMI	40.8	40.1
3.	MICT	193.1	185.6
4.	DMU	26.6	23.9

TABLE A-2.4

*Reliability test by changing the volume injected
(Internal standard: Dibutyl phthalate)*

No.	Compound	Volume injected (in μ l)	Wt. in mgms	
			Taken	Obtained
1.	DMU	0.4	26.6	-
		0.8	-	27.2
2.	Dione	1.0	15.4	-
		2.0	-	15.7
3.	DMI	1.0	19.5	-
		3.0	-	19.3

TABLE A-2.5

Reliability Test

Compound	gm/100 ml					
	Taken	Found	Taken	Found	Taken	Found
TMU	0.263	0.2766	0.453	0.432	0.656	0.626
MICT	1.465	1.5425	2.446	2.269	3.34	3.183
DMU	0.0715	0.0753	0.134	0.1282	0.201	0.203
Dione	0.2089	0.2198	0.36	0.3384	0.497	0.474
TMBU	0.3312	0.3485	0.596	0.563	0.82	0.789
DMI			1.09	1.041	1.5	1.53

Synthesis of standard compounds

1. 1,3,5-Trimethylisocyanurate (MICT)

Ref: Bloodworth and Davies, J.Chem.Soc. 6558 (1965)

To a solution of dichloromethane (100 ml) and stannic chloride (0.5 g) methyl isocyanate (22 g) was added at 0-5°C in 0.5 hr. The reaction mixture was stirred under ice cold condi-

tion for 5 hrs. The precipitated MICT was filtered and was recrystallized from hot benzene. Yield 17 g.m.p. 175°C (lit. reported 175°C).

2. 1,3-Dimethyl isocyanurate (DMI)

Ref: Kolonko et al., J. Org. Chem. 44(22), 3769 (1979)

A mixture of potassium isocyanate (2.0 g)

and methyl isocyanate (5.7 g) in DMF (100 ml) was allowed to react for 24 hr at 75°C. The DMF was removed by distillation over steam bath to yield a solid mass as residue. It was stirred in water (50 ml) and filtered to remove 1,3,5-trimethyl isocyanurate (MICT). The filtrate was acidified with conc. HCl. The precipitated isocyanuric acid was filtered and was recrystallized from little charcoal and hot toluene to furnish pure colourless crystals of 1,3-dimethyl isocyanuric acid. Yield 2.2 g.m.p. 222-223°C. (lit. report 223°C).

3. 1,3,5-Trimethyl biuret (TMB)

Ref: Heinrich Blitz, Chem. Ber 56B, 1914-26 (1923).

A mixture of sym N,N-dimethyl urea (3g) and methyl isocyanate (3 g) was heated in a S-S-bomb at 100°C for 2 hrs. Afterwards the unreacted methyl isocynate was evaporated and the residue was recrystallized from hot benzene. Yield 1.5 g.m.p. 126°C. (lit. reported 126°C).

4. 1,1,3-Trimethyl urea (TMU)

Ref: School and Holdmann, Ann. 345, 376 (1907)

To a solution of pet. ether (125 ml) and dimethylamine (4.5 g) methyl isocyanate (5.7 g) was added at 0-5°C in 0.5 hr. A colourless solid separated immediately. The reaction mixture was stirred for 5 hrs. Afterwards excess dimethylamine in pet. ether (10 ml 0.8 N)

was added to the reaction mixture and stirred for 0.5 hr. The solution was found to be alkaline (pH 8). The crystalline TMU was filtered, washed with pet. ether, dried under vac. at room temperature. Yield 9.5 g, m.p. 74°C (lit. reported 74-75°C).

5. 1,1,3,5-Trimethyl biuret (TRMB)

A mixture of 1,1,3-trimethyl urea (1.03 g) and methyl isocyanate (1.6 g) was heated in a S.S. reactor at 100°C for 3 hrs. The excess unreacted methyl isocyanate was evaporated. The residue left was analysed by G.C. and G.C./m.s. and was found to be a mixture of DMU, TMU, TRMB AND TMB. The mixture contained about 40% of TRMB which could not be separated and purified.

6. 1,3,5-Trimethyl-1,3,5-triazine-2,4(1H, 3H)-dione (Dione)

Ref: Etienne and Bonte, Bull. Soc. Chem. Fr. 1419 (1975).

To a solution of 1,3,5-trimethyl biuret (2 g) in carbon tetrachloride (5 ml) methylal (2.4 g) and conc. sulphuric acid (6 g) was added. The reaction mixture was stirred at room temperature for 24 hrs. Next day the solvent was evaporated and the residue was diluted with water (20 ml). The reaction mixture was extracted with chloroform (50 ml). The chloroform layer was dried and distilled. The residue when crystallized by benzene and pet. ether (60-80°C) gave colourless crystals. Yield 1.2 g.m.p. 93°C. (lit. reported 95°C).

Samples from VIIth Batch Received on 11/10/85 SAMPLES RECEIVED FROM VIIth Batch

- | | |
|-------------------------------------|--|
| 1. Process water sample dt. 8/10/85 | (No. CBI/CIU/3/3/84/302 dt. 12/1/86. |
| 2. Lake water sample (Red Bottle) | 1. One sample of caustic lye from the tank in UCL Bhopal as per verbal clarification received from Dr. Asad Ali Khan. This was required by Dr. O.G.B. Nambiar. |
| 3. Lake water sample (Blue Bottle). | 2. Five metallic plates from Tank No. E 611. |

Annexure 2.2

SAMPLES FROM 1ST BATCH

Received on 21/3/85.

Sr.No.	Sample	Code	Date
1.	Core sample MIC tank E-610 Safety valve nozzle	A-1	13.2.85
2.	Core sample MIC Tank E-610 Valve nozzle	A-2	13.2.85
3.	Core sample MIC Tank-610 Safety Valve Nozzle	A-3	13.2.85
4.	Core sample MIC tank-610 Safety Valve Nozzle	A-4	13.2.85
5.	Core sample MIC tank-610 process vent Nozzle	B-1	13.2.85
6.	Core sample MIC tank-610 process vent Nozzle	B-2	13.2.85
7.	Core sample MIC tank-610 process vent Nozzle	B-3	13.2.85
8.	Core sample MIC tank-610 process vent Nozzle	B-4	13.2.85
9.	Nozzle B, N2/outlet/inlet outside of core pipe	B-5	
10.	Core sample from MIC tank E-610 Thermowell nozzle	D-1	13.2.85
11.	Core sample from MIC tank E-610 Thermowell nozzle	D-2	13.2.85
12.	Core sample from MIC Tank E-610 Thermowell nozzle	D-3	13.2.85
13.	Core sample from MIC Tank E-610 Thermowell nozzle	D-4	13.2.85
14.	Core sample MIC Tank E-610 Safety Valve nozzle bottom	I-1	13.2.85

1	2	3	4
15.	Core sample MIC Tank E-610 Safety Valve nozzle middle	I-2	13.2.85
16.	Core sample MIC Tank E-610 Safety Valve nozzle top	I-3	13.2.85
17.	Sample from Dip tube bottom piece tank-610	F-1	13.2.85
18.	Sample from dip tube bottom piece tank-610	F-2	13.2.85
19.	Sample from dip tube bottom piece tank-610	F-3	13.2.85
20.	Sample from dip tube bottom piece tank-610	F-4	13.2.85
21.	Sample from level indicator Dip Tube outside MIC Tank 610		13.2.85
22.	Solids from R/DS/S and D/S Spool		19.12.84 5.20pm
23.	Solids from E-610 R/D U/S spool piece	3	19.12.84 5.50pm
24.	Solid from R/D U/S iso valve D/S side	4	19.12.84 5.50pm
25.	Solid from R/D, D/S Spool piece	5	19.12.84 5.40pm
26.	R/D D/s Spool piece and flange side solids E-610 tank	7	19.12.84 6.30pm
27.	Sample from RVVH dead end bleeder towards 200TR Shed (20 ml)	11	13.2.85 4.00pm
28.	Sample of liquid from PSV downstream bleeder of dryer	9	13.2.85 6.00pm
29.	Side stream cooler PSV D/S Bleeder sample 2 pc.		13.2.85 6.00pm
30.	Sample from RVVH drain bleeder on Desuperheat on 2nd level		13.2.85 6.00pm
31.	Top core section MIC tank E-610	-	
32.	Mid core section MIC tank E-610	-	
33.	Bottom core section MIC tank E-610	-	
34.	Solid from E-610 Thermowell	-	20.12.84 3.00pm
35.	Liquid Sample collected from MIC Tank 610 PSV D/S Valve D/S line RVVH	-	13.3.85 10.25
37.	RVVH Bleeder above decanter after opening RGC PSV D/S valve	-	14.2.85 16.30hrs

1	2	3	4
38.	Solid from MIC Tank 610 Process vent Nozzle spool piece		13.2.85
39.	Solid samples 1) D/S side off Blow off DMV 2) D/S end U/s of Common N ₂ make up line to tank - 610		13.2.85
40.	PSV & D/S bleeder of phos. vapouriser E-101		14.2.85 5.00pm
41.	Solid samples D/s pipeline between D/S isolation valve and Blow off DMV		13.2.85
42.	MIC Transfer Recirculation inlet line to MIC Tank E 610 dropped piece		4.3.85 16.00hrs
43.	Sample No.1 'Anode' White powder sample near manhole MIC Tank 610	I	9.3.85
44.	Sample collected near dished end towards MIC Structure Tank 610 (ANODE) (Soil Sample around anode at above mentioned place).	N-2	9.3.85 17.00hrs
45.	Sample from Phos. Vapouriser Safety Valve D/S bleeder		13.2.85 6.00
46.	VGS Caustic	3	5.12.85 18.00hrs
47.	VGS Caustic	1	5.12.84 18.00hrs

SAMPLES FROM IIInd BATCH

Received on 11/4/85.

Sr.No.	Sample	Code	Date	
1.	Sodium hydroxide 1N (approx).	V-1	6.4.85	
2.	2nd from bottom from E-610	V-2	6.4.85	6.35 pm
3.	3rd from bottom from E-610	V-3	6.4.85	6.30 pm
4.	Top layer from E-610	V-4	6.4.85	6.30 pm
5.	Bottom MO57 from E-610	X-1	6.4.85	6.00 pm
6.	2nd from bottom from E-610	X-2	6.4.85	6.00 pm
7.	3rd from bottom from E-610	X-3	6.4.85	6.00 pm
8.	Top layer from E-610	X-4	6.4.85	6.00 pm
9.	Dip tube E-610 Tank	DTI	7.4.85	4.00 pm
10.	Dip tube middle portion E-610	DT2	7.4.85	4.00 pm
11.	Dip tube near bottom	DT3	7.4.85	4.00 pm
12.	Solids on Tank wall	WS3	6.4.85	
13.	E-610 (Manhole from bottom of manhole tank)	MH-1	7.4.85	4.00 pm
14.		MHRV	7.4.85	4.00 pm
15.	E-610	E-1	8.4.85	5.00 pm
16.	E-610	8A-1	8.4.85	5.35 pm
17.	E-610	H-1	8.4.85	3.30 pm
18.	E-610	H-2	8.4.85	3.30 pm
19.	E-610	H-3	8.4.85	3.30 pm
20.	E-610	H-4	8.4.85	3.50 pm
21.	E-610	M-1	8.4.85	1.10 pm
22.	E-610	M-2	8.4.85	1.10 pm
23.	E-610	M-3	8.4.85	1.10 pm
24.	E-610	M-4	8.4.85	1.10 pm
25.	610	9-Z-1	9.4.85	1.40 pm
26.	610	9-Z-2	9.4.85	1.30 pm

SAMPLES FROM IIIRD BATCH

Sr.No.	Sample	-	Code	Date
1.	Top farthest away from manhole. Stainless steel piece cut from the tank 610			
2.	Stainless steel piece cut from Tank - 610			
3.	Stainless steel piece cut from Tank - 610 numbered as 3			
4.	Stainless steel piece cut from Tank - 610, numbered as 4			
5.	E-610 from dished head away from manhole circular piece.			
6.	MIC storage tank E-610, MIC vapour sample collected from blow off line P-1 point		20.12.84	10.1
7.	2 MIC storage Tank E-610 MIC Vapour sample collected from blow off line point.		20.12.84	10.
8.	Cut tube sample 1, E-610		Sample-1	
9.	Cut tube sample 2, E-610		Sample-2	
10.	Cut tube sample 3, E-610		Sample-3	
11.	Cut tube sample 4, E-610		Sample-4	
12.	Cut tube sample 5, E-610		Sample-5	
13.	Cut tube sample 6, E-610		Sample-6	
14.	MIC Samples from High Court from Tank E-611 No.1		Sample-1	
15.	- do - No.2		Sample-2	
16.	- do - No.3		Sample-3	
17.	- do - No.4		Sample-4	
18.	MIC Samples from High Court from Tank E-611 No.5		Sample-5	
19.	MIC Sample from chilled line No.1		Sample -1	
20.	- do - No.2		Sample-2	
21.	- do - No.3		Sample-3	
22.	MIC Sample CBI No. 1		Sample-1	
23.	MIC Sample CBI No.2		Sample-2	

SAMPLES FROM IVTH BATCH

Received on 9/6/85.

Sr.No.	Sample Description	Code	Date
1.	Sample No.1 30/5 RVVH-PVH Spool piece -		30-5-85
2.	Sample No.4 Solid from RVVH-PVH line		30-5-85
3.	Sample No.5 RVVH-PVH Line solid sample		
4.	Sample No.9 (Sr.No.5) PVH liquid		30-5-85
5.	Sample No.8 of Sr. No.5		
6.	Sample No. 10 PVH solid sample before NRV dt.30/5		30-5-85
7.	Sample No.11 PVH Solid sample before NRV		30-5-85
8.	Sample No.16, Solid from RVVH Ist level dead end towards 200 TR		31-5-85
9.	Sample No.17, solid from RVVH Ist level dead end towards 200 TR)		31-5-85
10.	Sample No.20, Sr.No.8 RVVH liquid from bleeder on 2nd level B.F. towards sevrin		31-5-85
11.	Sample No.21, Sr.No.8 RVVH liquid from bleeder on IInd level B.F. towards Sevin dt. 31-5-85		31-5-85
12.	Sample No.24, Solid from RVVH IInd level dead end towards sevin unit 12.40 hrs.		31-5-85
13.	Sample No.25 Sample from RVVH IInd level dead end towards sevin unit 12.40 hrs.		31-5-85
14.	Sample No.27 Solid from (4") RVVH line Flange at B.L. 14-50 hrs. solids.		
15.	Sample No.28 Solids from RVVH 4" B.L. Slip blind flange, 15.00 hrs. line solids		31-5-85
16.	Sample No.31 RVVH VGS line bleeder liquid		31-5-85
17.	Sample No.32 RVVH VGS line bleeder liquid dt 31/5		31-5-85
18.	Sample No.33 Liquid sample from PVH dead end towards 200 TR		
19.	TARCOLE Sample collected from the half Lower portion of the MIC tank 610 from where water was out from below. At 15.50 hrs. dt. 8-3-85 Sample of charcoal drawn on 8-3-85		8-3-85
20.	Water found around Tank E-610 collected on 8-3-85.		
21.	Five bottles containing samples marked to as 7/SST/B, E-1 and F and 7/MRS/D and		
25.	E drawn on 7-5-85.		7-5-85

SAMPLES FROM VTH BATCH

Received on 29/6/85

Sr.No.	Sample Description	Date
1.	15/6 RVVH-IIInd level bleeder towards 200 TR liq. Sample No.2	15.6.85
2.	17/6/VGS Drain sample before taking fresh caustic No.3	17.6.85
3.	14/6/VGS Caustic sample before transfer to spent caustic tank/No.3	14.6.85
4.	14/6 Caustic Sample before transfer to spent caustic tank No.4	14.6.85
5.	15/6/PVH-IIInd level 4" x 3" Reducer liq. Sample No.4	15.6.85
6.	17/6/VGS Drain sample before taking fresh caustic No.4	17.6.85
7.	15/6 RVVH IIInd level bleeder towards Sevin liq. Sample No.6	15.6.85
8.	15/6 RVVH-Ist level bleeder towards Sevin liq. Sample No.8.	15.6.85

3. A PLAUSIBLE CHEMISTRY OF THE EVENT

In order to gain some understanding of the complex chemistry of the reactions that occurred in tank 610 and the various plausible routes by which the products found could have been formed, some sixty odd laboratory experiments are given in Table A-3.1.

The reactions were carried out in S.S. bombs at specified temperatures and predetermined times, cooled to 0°C or less and the product extracted, first with acetone, and then with water. The residue from the acetone extract was submitted to direct GLC analysis. Both—an OV-210 + OV-17 stationary phase on chromosorb column which shows TRMB as a clear separate peak and an FFAP on chromosorb column were used for analysis. Details of instrumental conditions and methods of standardization and peak matching are given in the chapter on Analysis. In most cases the total residue from the acetone extract did not elute completely from the GLC columns due to presence of some quantities of amine hydrochlorides, other polar materials and small quantities of polymeric substances. Therefore, the percentages of the various product components reported in Table A-3.1 do not add up to hundred. They represent the percentages of these components present in the total acetone extract for that particular experiment.

Both acetone and water extracts were tested for chloride ions.

It became clear at an early stage of experimentation that a combination of MIC containing chloroform and small quantities of water, when heated above 200°C in a closed S.S. reactor gave essentially all the products found in tank 610, though not in the same proportion. Also, it was not necessary to add ferric chloride or other ionic metal catalysts to promote trimerisation of MIC. Obviously, sufficient metal ion concentration for catalysis was generated by corrosion of S.S. under the reaction conditions used. It is also likely that other known catalysts such as tertiary amines (trimethylamine, TMA) and isocyanic

acid anion formed in the reaction could have promoted the trimerization reaction.

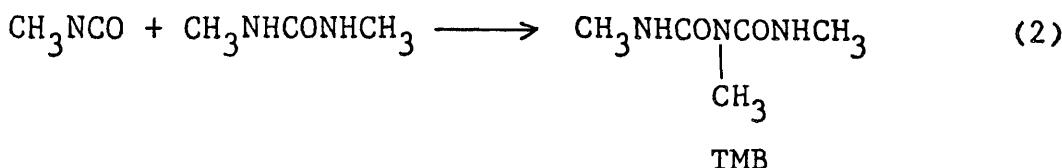
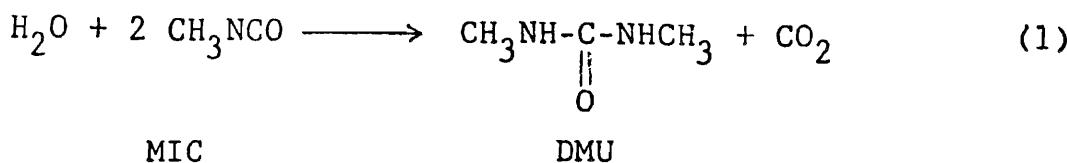
In the above laboratory reactions, even though most of the products found in tank 610 could be identified, one exception was tetramethylbiuret (TRMB) traces of which have been found in the residue in tank 610 but not in the laboratory products. This has been attributed mainly to the differences in the rates of various reactions occurring in the laboratory S.S. bomb as compared to those in tank 610. Thus, since, TRMB is formed by the reaction of trimethylurea (TMU) with MIC, sufficient quantities of the latter in monomeric un-trimerized form should still be available at the high temperatures (above 200°C) at which TMU is formed. Apparently this was the situation in Tank 610 during the event. However, in the laboratory experiments, the rate of trimerization of MIC must have been higher so that by the time TMU is formed above 200°C, not much monomeric MIC remained to react with it and form TRMB. Indeed, planned laboratory experiments in which TMU was included in the reactants gave detectable quantities of TRMB.

All the experiments listed in Table A-3.1 have been carefully planned to gain maximum insight into the reaction in Tank 610. The philosophy has been to 'get maximum information with minimum experimentation'.

The important deductions from the foregoing experiments can be summarised as follows.

3.1 Reaction with water

In the MIC-chloroform-water system, water reacts with 2 moles of MIC to form dimethylurea (DMU) and carbondioxide (Eq. 1). In an environment of excess MIC, the DMU formed begins to react with MIC to give trimethylbiuret (TMB) (Eq. 2).



These reactions are essentially complete between 50° to 100°C. Thus, small quantities of water get scavenged by excess MIC generating one equivalent mole of TMB and CO₂.

3.2 Chloride ion

Chloroform present in MIC appears to be the main source of high Cl⁻ ion content in the residue. However, mechanism of formation by hydrolysis with water is most unlikely since no water would be expected to remain in excess MIC at temperatures at which chloroform is known to react with water.

The small quantities of phosgene, methylcarbamoyl chloride (MCC) and dimethyl allophanyl chloride (DMAC) present in MIC would also contribute equivalent amounts of Cl⁻ ion.

3.3 Trimethylbiuret (TMB)

The TMB formed is quite stable thermally up to temperatures close to 220°C. Thus, the reaction of MIC + CHCl₃ + H₂O at 190°C for 40

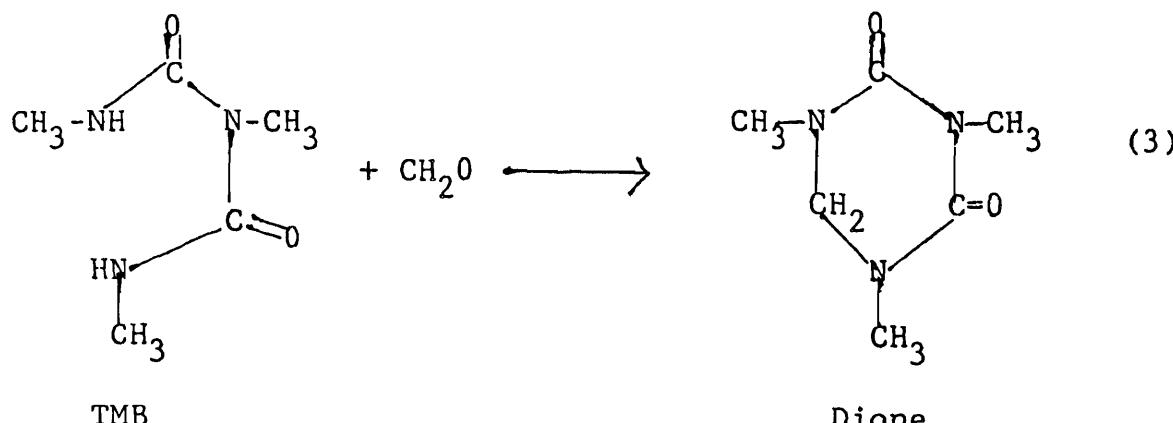
min. (Expt. No. 44 in Table) gave mainly TMB and MIC trimer (MICT) along with a small quantity of DMU. The TMB was approximately equivalent to the water taken. No DMI was detected and only a trace of dione was seen.

At 200°C and above, the thermal fragmentation and other reactions of TMB begin to occur and products found in Tank 610 can be detected. Thus, the above reaction when conducted at 200°C (Expt. No. 18) and especially at 215° - 220°C (Expt. No. 45), produces TMU, DMI and Dione in addition to MICT and TMB. As the reaction temperature is raised further to 250°C (Expt. Nos 33 and 36) the quantities of TMU, DMI and Dione increase and TMB decreases.

Thus, TMB is an important intermediate and appears to play a crucial role in the conversion of MIC to products formed in Tank 610.

3.4 Dione

The dione is readily formed by reaction of TMB with formaldehyde or its equivalent as shown in Eq. 3.

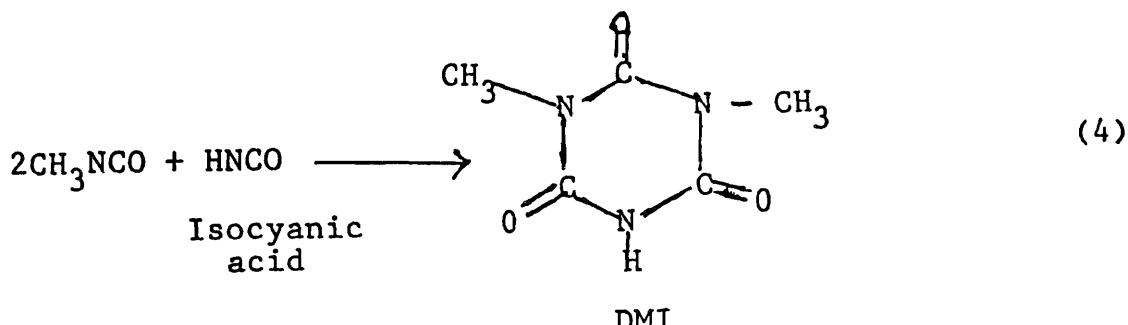


It appears fairly certain that the methylene (-CH₂-) group of dione is derived from the C-atom of chloroform (CHCl₃). The actual reaction is probably dichloromethane (CH₂Cl₂) which is known to be formed from CHCl₃ by disproportionation or reduction. Thus, when TMB was heated with either chloroform (Expt. No. 28) or dichloromethane (Expt. No. 54) to 250°C, dione was formed. However, heating TMB alone (Expt. No. 29) gave no dione although the other products were formed.

The experimentation also indicates that the formation of dione begins only around 200°C or so. Percentage of dione comparable to that found in residue of tank 610 was present only in reactions run at 250°C.

3.5 Dimethylisocyanurate (DMI)

DMI was the second most abundant product found in tank 610. It is known to be readily formed by the reaction of MIC with isocyanic acid or its salts (Eq. 4).

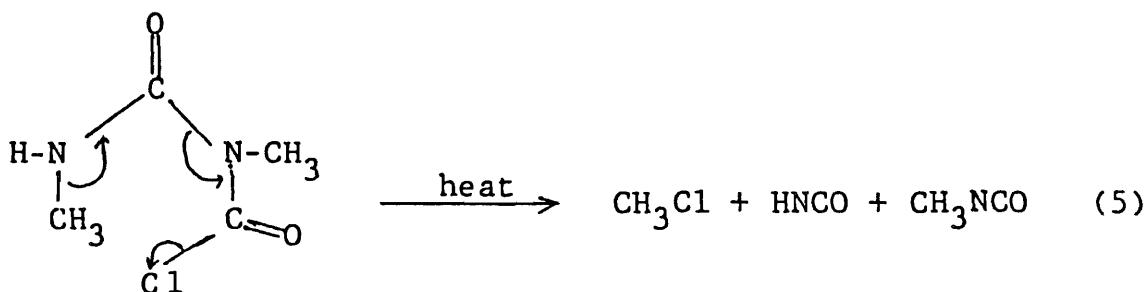


Since structurally DMI is a demethylation product of MICT which was the most abundant component found in the tank residue, experiments were conducted (Expt. Nos. 1 to 4, 9, 21, 30 and 34) to see if MICT could be induced to undergo a demethylation reaction in the presence of suitable substrates. However, even up to 280°C to 300°C, MICT was found to be quite stable to monomethylamine hydrochloride (MMA.HCl) or chloroform with or without water. Even traces of DMI could not be detected

in the product.

Therefore, DMI must have formed by the reaction shown in Eq. 4. Formation of HNCO in a large excess of MIC would readily give DMI. What are the plausible modes of formation of HNCO?

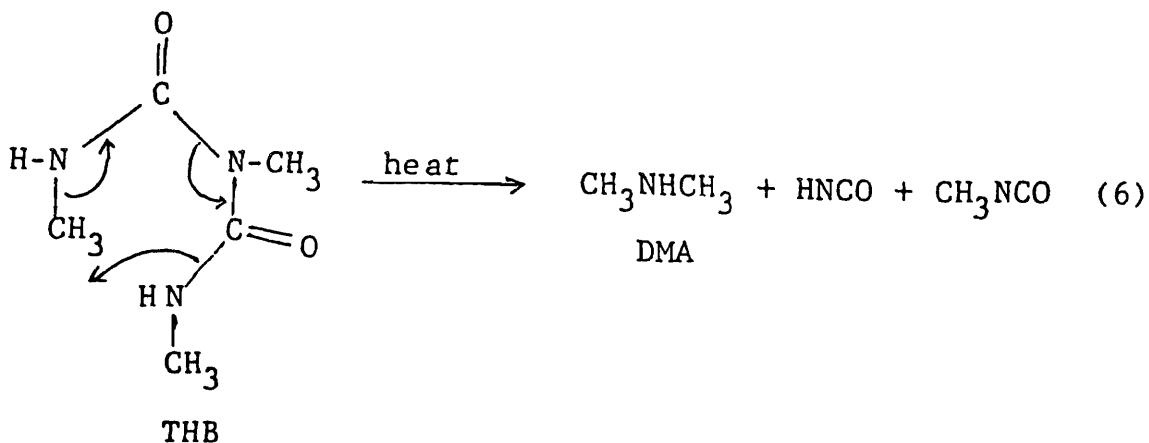
The UCC scientists (UCC report, p. 34) based on their own work, suggest the thermal decomposition of dimethylallophanyl chloride (DMAC) shown in Eq. 5:



Even though this thermal degradation reaction is quite plausible, proceeding through a cyclic six-membered transition state, the quantities of DMAC estimated to be present in MIC were quite small and therefore could not account for all the DMI found in the tank

residue.

A more plausible explanation of the formation of HNCO would be the thermal decomposition of TMB. This reaction and its mechanism is depicted in Eq. 6:

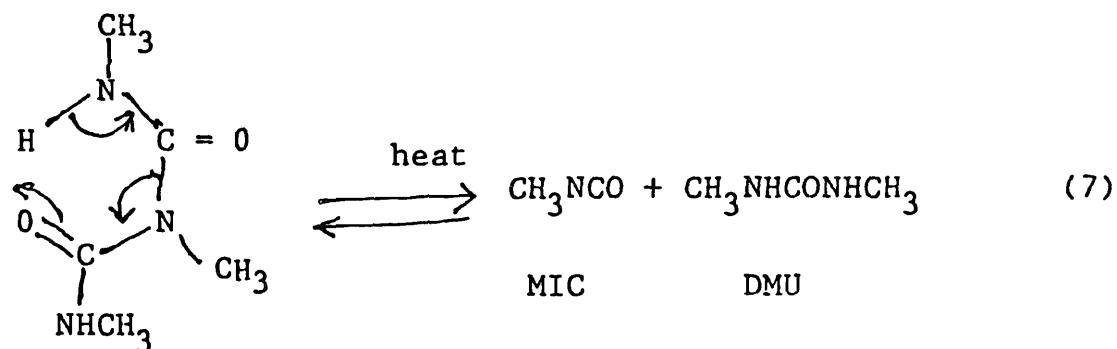


This reaction is analogous to the fragmentation of DMAC shown in Eq. 5 and can satisfactorily account for the quantities of DMI formed.

As an experimental support for the reaction depicted in Eq. 6, pure TMB, on heating to 250°C for 45 min. (Expt. No. 29), gave about 4% DMI in addition to the major products,

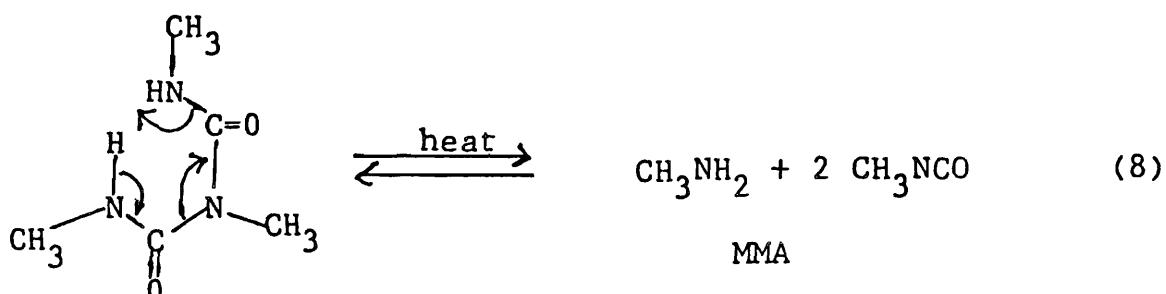
DMU and MICT.

Even though Eq. 6 depicts a mode of thermal decomposition of TMB to give HNCO, the major thermal fragmentation route of TMB would be into its congeners DMU and MIC, shown in Eq. 7. This is the reverse of formation of TMB from MIC and DMU and is an equilibrium reaction:



The equilibrium would shift to the right if MIC were to be removed by an irreversible trimerization reaction. This accounts for the

major products, DMU and MICT, mentioned above in Expt. No. 29.



A further possible mode of thermal fragmentation of TMB is shown in Eq. 8. This also is an equilibrium reaction and shows the possibility of formation of MMA. All the above

three modes of fragmentation of TMB shown in (6), (7) and (8) are thermally allowed electrocyclic processes proceeding through energetically favourable six-membered transition states.

3.6 Dimethylamine (DMA) and Trimethylamine (TMA)

An interesting feature of reaction (6) is that it also offers an explanation for the formation of dimethylamine (DMA) which has been found in the tank residue in the form of DMA hydrochloride, TMU (DMA + MIC) and TRMB (TMU + MIC).

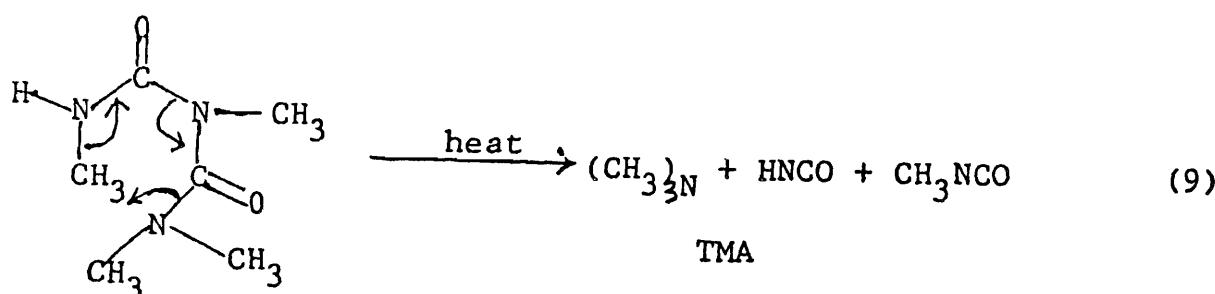
An explanation for the formation of DMA and TMA has been advanced by UCC scientists based on the known disproportionation of MMA. HCl at high temperatures to ammonium chloride and di, tri, and tetramethyl ammonium chlorides. One difficulty with acceptance of this hypothesis is that sizeable quantities of ammonium chloride should also have been present in the tank residue which does not appear to be the case.

Formation of TMA can also be explained through the thermal fragmentation of TRMB shown in Eq. 9 below. This reaction would be analogous to the fragmentation of TMB shown in Eq. 6.

Both DMA and TMA can thus be formed by the thermal cracking of TMB and TRMB respectively.

3.7 Tetramethylbiuret (TRMB)

A further mode of formation of HNCO could be the thermal fragmentation of TRMB shown in Eq. 9. This reaction also offers a route for the formation of TMA which has been found in significant amounts in the tank residue.



3.8 Comments

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.

A finer focussing of the gross chemical picture would be possible only by conducting detailed simulation experiments with control and measurement of reaction parameters like temperature and pressure and more detailed analyses including that of all gaseous products. These have not yet been done.

TABLE A-3.1
Laboratory Experiments with MIC & 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	2	3	4	5	6	7	7
1.	MICT (2.00g), CHCl ₃ (9.09g)	200	120	-	-	MICT (100)	-
2.	MICT (1.30g), CHCl ₃ (3.00g)	200	120	-	-	MICT (100)	-
3.	MICT (0.41g), CH ₃ NH ₃ Cl (0.14g)	200	120	-	-	MICT (100)	-
4.	MICT (0.43g), CH ₃ NH ₃ Cl (0.29g) DMU (0.48g)	200	120	-	-	MICT + DMU (qualitative)	-
5.	MICT (0.52g), NH ₄ Cl (0.23g)	200	120	-	-	MICT (100)	-
6.	DMU (2.20g), urea (3.00g)	200-230	300	-	-	DMI (1) + unknowns	-
7.	Methylcarbamoyl chloride (MCC)+ Dimethyl Allophanyl chloride (DMAC) (0.50g)+ Aq NH ₃ 5ml	27	30	-	-	MICT, DMU, TMB (qualitative)	-
8.	MCC + DMAC (2.35g) + MeNH ₂ (excess) is solvent CH ₂ 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 MeNH ₂ in CH ₂ Cl ₂	27	30	-	-	MICT, DMU, TMB (qualitative)	-

1	2	3	4	5	6	7	8
10.	MICT (4.7g), CHCl ₃ (0.22g), H ₂ O(0.1g), HCl 20% (0.05g)	200	120	-	-	MICT (100)	-
11.	MIC (3.0g), CHCl ₃ (0.150g), H ₂ 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 ₂ O (0.1g)	Mixture temp went up from 23° to 28°, constant for 15 min. at 28°and started decreasing	-	-	-	Not analysed	-
13.	CHCl ₃ (4.5g), H ₂ O (4.0g)	200	120	-	-	CHCl ₃ , CH ₂ Cl ₂ (qualitative)	HCOOH detected
14.	MIC (3.2g), CHCl ₃ (0.225g), H ₂ O (0.1g)	200	15	2.65	-	DMU (1.13), TMB (53.6) MICT(45), Dione (0.5)	Cl ions - HCOOH- 0.3%
15.	MIC (3.4g), CHCl ₃ (0.35g), H ₂ O (0.1g)	240	45	2.31	1.23	MICT (84), TMB(2.0) Dione (1)	-
16.	MIC (2.5g), FeCl ₃ (0.005g)	Temp rose from 23 to 29° in 5 min and then came down to 27°	-	-	-	Not analysed	

1	2	3	4	5	6	7	8
		Rise in temp	Time				
17.	MIC (2.5g), FeCl ₃ (0.04g), H ₂ 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 ₃ (4.5g), H ₂ O(4.0g)	200	120	-	-	CHCl ₃ , CH ₂ Cl ₂ (qualitative)	HCOOH estimated (0.3)
19.	MIC (3.1g), CHCl ₃ (0.22g) H ₂ 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 (1.5g), CHCl ₃ (0.22g), H ₂ O (0.1g)	200	40	2.65	0.37	CHCl ₃ (0.1), CH ₂ Cl ₂ (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 ₃ (0.15g), H ₂ O (0.1g), HCl (trace)	245	45	2.84	0.1	MICT (100)	0.0126
23.	TMB (0.66g), CHCl ₃ (0.075g) H ₂ 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)	

	1	2	3	4	5	6	7	8
25.	DMU (4.00g), MIC (4.8g) (Prepn of TMB)		120	120	6.8g (cryst from benzene)		TMB (100)	-
26.	MIC (6.8g), CHCl ₃ + 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(93), TMB(2) DM1(3.2), Dione (0.8)	
28.	TMB(0.93g), MIC (3.5g), CHCl ₃ (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 ₃ (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)	-
31.	MICT(0.450g) + CH ₃ NH ₃ Cl(0.150g)	280-300	120	0.41	-		MICT (100)	-
32.	MIC (3.0g) + DMU(1.05g) CHCl ₃ (0.225g)	250	45	3.125	0.68		TMU(3.5),DMU(26), (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 ₃ (0.225g) H ₂ 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

1	2	3	4	5	6	7	8
35.	MICT (0.55g) + CHCl ₃ (1.5g)	280	45	0.63	-	MICT (100)	-
36.	MIC(4.5g) + DMU(1.05g) + CHCl ₃ (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 ₃ (0.3g) + H ₂ 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 ₃ (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 ₃ (0.225g)	280-300	45	4.250	0.056	DMU(18), TMU(0.75), MICT(46), TMB(10), DMI(3) Dione(2)	0.006
41.	MIC (3.4g) + DMU (1.02g) + CH ₂ CL ₂ (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 ₃ (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 ₃ (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 ₃ (0.225g) + H ₂ O (0.1g)	100	40	1.09	0.02	DMU(7.4), MICT(5), TMB (83.5)	0.001

1	2	3	4	5	6	7	8
45.	MIC(3.5g) + CHCl ₃ (0.225g) + H ₂ O (0.1g)	190	40	2.64	0.02	DMU(3), MICT(70), TMB(36) Dione (traces)	0.005
46.	MIC(3.5g) + CHCl ₃ (0.225g) + H ₂ 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 ₃ (0.3g)	220	40	2.50	-	TMU(64), DMU(13), Tet MU(Present)	nil
48.	MIC(3.2g) + CHCl ₃ (0.45g), H ₂ 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
49.	MIC(3.4g) + DMU (1.04g) CHCl ₃ (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 ₃ (0.6g) H ₂ 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 ₃ (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 ₂ O (0.2g)	20-29	48	1.02	-	MICT(1), TMB(52.3) DMU(49.4)	
53.	DMU(1.55) + CHCl ₃ (0.3g)	220	60	1.33	0.04	DMU(96.9), TMB(2.02)	0.025
54.	TMB(0.208g) + CH ₂ Cl ₂ (0.15g)	220	60	0.197	0.019	DMU(39.3), TMB(50, MICT, DMI & Dione not seen	Nil

4. WAS CYANIDE PRESENT IN LEAKED MIC?

According to the medical personnel attending on the victims of MIC ingestion at Bhopal, many of the patients showed apparent signs of cyanide poisoning, especially in their positive response to treatment with sodium thiosulphate, an antidote given in cyanide poisoning. As a result, speculation grew in all quarters as to whether the MIC emitted during the event contained hydrogen cyanide, and, if so, in what proportions.

On the face of it, it appeared unlikely that MIC emanating from tank 610 would contain appreciable amounts of HCN since the temperatures in E-610 were unlikely to have crossed 300°C. The published literature on the thermal decomposition of MIC to HCN describes experiments only at 450° - 500°C and proposes a free radical mechanism for such decomposition. However, since the speculation and controversy started hotting up, it became necessary to carry out a few laboratory experiments to check this point. Also, scientists at another laboratory in India (designated Lab X) announced that they had obtained appreciable amounts of cyanide from thermolysis of MIC even at 300°C.

4.1 Pyrolysis of MIC and analysis of cyanide

The following 3 samples of MIC were subjected to pyrolysis and the products analysed for cyanide ion.

- i) MIC from Bhopal E-611
- ii) MIC prepared at Lab-X

- iii) Commercial laboratory reagent grade MIC (Fluka, purity 98%)

Initially, the samples were pyrolysed at 300°C. Later, further experiments were carried out at 350°C, 400°C, 450°C and 500°C. All these experiments were done in sealed pyrex glass ampoules which were later cooled and broken in 0.1 N sodium hydroxide and analysed for CN⁻ ions by the following 3 methods:

- a) Titrimetric method - Ref: Standard methods for examination of water and waste water; 14th Ed. 1975, p. 369-370. American Public Health Association, USA.
- b) Colorimetric methods - Ref: Ibid., p. 370-372.
- c) Cyanide ion selective electrode method - Ref: Details attached in Appendix 4A.

Detailed analytical procedures are given in Appendix 4A.

4.1.1 Pyrolysis of MIC at 300°C

The pyrolysis at 300°C of the following MIC samples was studied:

- i) Scientists at Lab-X synthesized MIC from acetyl chloride and sodium azide according to the following equations:



Purity - 99.9% checked by GLC

Colour - colourless

ii) MIC from Tank E-611, Bhopal

Purity - 99.5% containing chloroform about 0.3%.

Colour - Yellowish

The following experiments were done:

- a) The pyrolysed MIC in sealed ampoule obtained from Lab-X (pyrolysis was done at Lab-X at 250°C) was dissolved in aqueous sodium hydroxide according to procedure described earlier and solution analysed for CN⁻ ion.
- b) MIC (70 microlitres, Lab-X) was taken in a glass ampoule, fused and was heated to 300°C for 1/2 hr, cooled and the content was taken in aqueous sodium hydroxide (25 ml; 0.1N).
- c) MIC (100 microlitres, Lab-X) was taken in a glass ampoule, sealed and heated to 300°C for 1/2 hr, cooled and the content was taken in aqueous sodium hydroxide (25 ml; 0.1N).
- d) MIC (104 microlitres, E-611) was similarly processed as in (b) and (c).
- e) MIC (100 microlitres, E-611) was mixed with acetylchloride (3 microlitres) in an ampoule and the ampoule was sealed and processed as in (b) and (c).
- f) MIC (60 microlitres, Lab-X) was mixed with chloroform (3 microlitres) in an ampoule and the ampoule was sealed and then processed as in (b) and (c).
- g) MIC (25 microlitres, E-611) was also taken in aqueous sodium hydroxide (25 ml; 0.1N).
- h) MIC (25 microlitres, Lab-X) was directly taken in aqueous sodium hydroxide (25 ml; 0.1N).

The results of the above experiments are described in Table 4.1.1.

Observations

Based on the results given in Table No. 4.1.1, the following observations can be made:

i) MIC samples obtained from LAB-X gave substantial amounts of hydrogen cyanide on pyrolysis at 300°C.

ii) MIC samples from Bhopal Tank E-611 gave no HCN (practically nil) at 300°C.

iii) The obvious difference between the two MIC samples was that E-611 contained small quantities of chloroform which possibly acted as a free radical inhibitor during thermal cracking of MIC to HCN.

Therefore, a small quantity of chloroform was added to Lab-X MIC and thermolysed at 300°C. No HCN (or almost nil) was found (see expt. 'f', Table. 4.1.1), thus confirming that chloroform acted as an inhibitor.

iv) To see if small quantity of acetyl chloride impurity (the starting material for Lab-X MIC) could have acted as a promoter, 3% of the same was added to E-611 MIC and pyrolysed. No HCN was formed.

v) Regarding the level of accuracy in the estimation of CN⁻, there was reasonably good agreement between the 2 methods of silver nitrate and colorimetry. However, the ion selective electrode method sometimes gave widely divergent values. Perhaps, some interference by other products of MIC thermolysis was responsible.

4.1.2 Pyrolysis of MIC at higher temperatures

Since the Bhopal E-611 sample of MIC did not give any HCN on thermolysis at 300°C, it was subjected to higher temperatures of 350°, 400°, 450°, and 500°C.

Together with the E-611 MIC another sample of commercial MIC (laboratory reagent grade, Fluka, purity 98%) was also subjected to thermolysis at the same temperatures specified above. The results of these pyrolysis experiments are given in Table 4.1.2 and 4.1.2 (a).

Observations

i) Bhopal E-611 MIC begins to give appreciable quantities of HCN only at 450°C. Approximately 1% HCN was formed at

this temperature. At 400°C only about 0.067% HCN was detected. The experiment at 500°C unfortunately could not be completed as the ampoule exploded.

- ii) In contrast to the Bhopal MIC sample the commercial laboratory reagent grade MIC (Fluka) did not give any appreciable CN⁻ even upto 500°C. Obviously, same strong inhibitor must be present in this commercial sample.

4.1.3 Pyrolysis experiments on derivatives of MIC found in E-610

Since MIC sample from E-611 gave negligible quantities of HCN on pyrolysis upto 400°C, it was of interest to see whether the solid derivatives of MIC found in E-610 gave any HCN on pyrolysis.

With this object in view 5 derivatives of

MIC were initially subjected to pyrolysis at 300°C for 1/2 hr. Results are given in Table No. 4.1.3.

Since no HCN was observable at 300°C the same solid derivatives were again pyrolysed at 450°C for 1/2 hr. The results are tabulated in Table No. 4.1.3(a).

Observations

- i) None of the derivative gave HCN even at 450°C. However the pyrolysis product of DMI when analysed by Ion Selective Electrode method gave CN⁻ of about 1.5%. However, when the same sample was analysed by the Silver Nitrate and Colorimetric methods no CN⁻ was detectable. The values reported in the fourth place of decimal could actually be due to experimental error.

Table 4.1.1

PYROLYSIS OF MIC AT 300°C - ANALYSIS OF CYANIDE

Sample No.	Sample matrix	Analysis of Hydrogen cyanide					
		Silver nitrate method		Colorimetric method		Ion selective electrode	
		mg.	%	mg.	%	mg.	%
a.	Lab-X MIC 100	0.577	0.58	0.504	0.50	1.870	1.87
b.	Lab-X MIC 70	7.740	11.06	8.625	12.30	20.00	28.00
c.	Lab-X MIC 100	7.889	7.89	7.563	7.60	18.00	18.00
d.	E-611 MIC 104	-Not detected-		-Not detected-		0.05	0.45
e.	E-611 MIC 100 + 3 Acetyl chloride	-Not detected-		0.002	0.002	Nil	Nil
f.	Lab-X MIC 60 + 3 CHCl ₃	-Not detected		0.0040	0.007	Nil	Nil
g.	E-611 MIC +25 ml of 0.1002N NaOH	-Not detected		-Not detected-		Nil	Nil
h.	Lab-X MIC 25 + 25 ml of 0.1002N NaOH	-Not detected-		0.0005	0.002	Nil	Nil

e 1 : Colorimetric readings were recorded on "HITACHI-330 UV-VIS-NIR spectrophotometer"

e 2 : Ion selective electrode readings were taken on Digital high impedance mv

e 3 : All pyrolysis experiments were carried out 300° C

Table 4.1.2

THE PYROLYSIS OF BHOPAL E 611 MIC AT 350°-450° C

S.No.	Sample matrix	Temp. °C	Time min.	Cyanide analysis					
				Silver nitrate method		Spectrophotometric (colorimetric method)		Ion selective electrode methc	
				mg	%	mg	%	mg	%
1.	0.100 g	350	30	- Not detected -		0.0012	0.0012	- Not detected -	
2.	0.100 g	400	30	- Not detected -		0.0668	0.0670	0.09	0.09
3.	0.120 g	450	30	1.40	<u>1.17</u>	0.00118	<u>0.99</u>	- Results not reproducible	
4.	0.120 g	500	30	- Ampule exploded at 500° C -					

Table 4.1.2(a)

PYROLYSIS OF LABORATORY REAGENT MIC AT 300°-500° C

S.No.	Sample matrix	Temp. °C	Time min	Cyanide analysis		Ion selective electrode method %
				Cotorimetric method %		
1.	MIC (0.0100 g)	300	40	Nil		Nil
2.	MIC (0.100 g) + CHCl ₃ (0.100 g)	300	40	Nil		Nil
3.	MIC (0.100 g)	350	40	Nil		Nil
4.	MIC (0.100 g)	400	40	Nil		Nil
5.	MIC (0.100 g)	450-500	40	0.007		0.005

Table 4.1.3

PYROLYSIS OF SOLID DERIVATIVES OF MIC AT 300°C FOR 30 MIN.

S.No.	Sample matrix (wt. taken)	<u>Cyanide analysis</u>			
		Colorimetric method		Ion selective electrode metho d	
		mg	%	mg	%
1.	DMI (0.18 g)	0.0016	0.0009	0.0018	0.001
2.	TMB (0.112 g)	0.0011	0.0010	0.0120	0.010
3.	MICT (0.113g)	-Not detected-		-Not detected-	
4.	DMU (0.163 g)	0.0008	0.0005	-Not detected-	
5.	Dione (0.057 g)	0.0005	0.0008	-Not detected-	

Table 4.1.3.(a)

PYROLYSIS OF SOLID DERIVATIVES OF MIC AT 450°C FOR 30 MIN.

S.No.	Sample matrix	<u>Cyanide analysis</u>				
		Silver nitrate method	Colorimetric method	Ion selective method		
			0.00087	0.0008	1.50	1.50
1.	DMI (0.106 g)	-Not detected-	0.00087	0.0008	1.50	1.50
2.	TMB (0.048 g)	-Not detected-	-Not detected-	-	0.06	0.12
3.	MICT (0.071 g)	-Not detected-	0.00190	0.0026	Nil	
4.	DMU (0.049 g)	-Not detected-	0.00120	0.0025	Nil	
5.	Dione (0.030 g)	-Not detected-	0.00060	0.0020	Nil	

ANALYTICAL PROCEDURES

Estimation of Cyanide

The HCN formed by pyrolyses of MIC in sealed ampoules was absorbed by breaking the ampoules in an alkali solution of known strength. The resulting alkali metal cyanide was then estimated. Two methods were standardised and practised for the estimation of alkali metal cyanides so formed.

1. Titrimetric method

Cyanide was titrated against a solution of AgNO_3 of known strength using three different indicator reagents depending upon the nature and colour of alkali metal cyanide solutions. They are -

- (A) Potassium iodide
- (B) Diphenylcarbazide
- (C) Paradimethylaminobenzalrhodanine

Procedure - A

Potassium iodide method

To about 25 ml of cyanide containing solution, 75 ml of water and 5 ml of 6N-ammonia solution was added. To this was added 2 ml of 10% ICl solution. This mixture was then titrated with standard AgNO_3 solution. The end point was persistence of yellow silver iodide and a permanent turbidity.

Procedure - B

Diphenyl carbazide method

In this procedure the cyanide solution was titrated with standard silver nitrate solution using 2 to 3 drops of diphenylcarbazide indicator solution (containing 0.18 g of indicator in 100 ml of alcohol). The end point was a permanent violet colour.

Procedure - C

Paradimethyl aminobenzalrhodanine indicator

To a known volume of cyanide solution, 10 ml of 1N-sodium hydroxide solution and 0.5 ml indicator solution (which was prepared by dissolving 20 mg of indicator in 100 ml of acetone) was added. It was titrated with standard silver nitrate solution till colour of the solution changed from a canary yellow to a salmon hue.

While carrying out titrations by any of these methods care was taken to prepare standard solutions of cyanide with concentrations similar to the ones found in the test solutions in order to compare the end points in more precise manner and thereby increasing accuracy of the results.

The Argentometric titration methods were useful to detect cyanide upto a level of 1 mg/lit. of CN^- depending upon colour and clarity of the alkali metal cyanide solutions under investigation.

2. Colorimetric method

Te

The alkali metal cyanide solutions containing cyanide, below the detectable limits of Argentometric titration methods were subjected to spectrophotometric analysis. The method selected for this purpose used following reagents -

- a) Barbituric acid
- b) Chloramine - T
- c) Pyridine
- d) Sodium dihydrogen phosphate
- e) Sodium hydroxide
- f) Concentrated HCl

At a pH less than 8 (which is adjusted by NaH_2PO_4) the CN^- in the alkaline solution of alkali metal cyanide is converted to cyanogen-chloride, (CNCI) by chloramine-T. This (CNCI) reacts with Pyridine-Barbituric acid reagent to produce a dye. The absorbance of this aqueous solution is then measured at 578 nm.

Preparation of solutions

- (a) Chloramine - T - 1g in 100 ml of water
- (b) Sodium dihydrogen phosphate- (1 m) - 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in one litre of water.
- (c) Sodium hydroxide - (0.25N) Dissolve 10 g of NaOH in one lit of water.
- (d) Pyridine-Barbituric acid reagent.

15g of Barbituric acid was taken into 250 ml volumetric flask and just enough water was added to wash sides of the flask and to wet the barbituric acid. To this 75 ml of pyridine was added. To this 15 ml conc. HCl was added and allowed to cool to room temperature. It was then diluted upto the mark and was shaken well.

Procedure

A suitable volume of test solution was taken and diluted to 20 ml with 0.25N NaOH. This portion was placed in a 50 ml volumetric flask.

15 ml of phosphate buffer was added and mixed thoroughly. To this solution 2 ml chloramine-T solution was added and swirled to mix. To this 5 ml pyridine barbituric acid solution was added and again swirled to mix. It was diluted to the mark with water and mixed well. It was kept for 8 min. for colour

development. Absorbance of developed colour was recorded at 578 nm within 15 min from the time at which the pyridine barbituric acid reagent was added. A calibration curve was slotted by using series of standard known concentration cyanide solutions of suitable range and the concentration of cyanide in test solution was found from the standard curves.

Ion-selective electrode

Solutions. Standard cyanide solution 0.5 gm of sodium cyanide was dissolved in 0.1N Sodium hydroxide. Solution was standardised by titrating against standard silver nitrate potentiometrically. A cyanide ion selective electrode coupled with a reference electrode was used for the titration.

Equipments. Digital high impedance mv meter, CN electrode (anion) and a single junction reference electrode.

Calibration curve

Standard CN solutions were prepared by serial dilution of stock solution. Measurements were carried out by introducing CN electrode and reference electrode in respective solutions. mv readings were under stirred conditions. Readings for the standard solutions are given below.

Conc. ppm	mv Read
468	260
46.8	195
4.68	195
0.46	85

Calibration curve was prepared by plotting CN conc. (100 axis) against mv readings.

PART II

**5. MODELLING AND COMPUTER SIMULATION
OF BHOPAL ACCIDENT**

PART II

5. Modelling and Computer simulation of Bhopal accident

5.1. GENERAL PHILOSOPHY OF MODELLING

The main results of the modelling and simulation efforts of the MIC leakage from the tank 610 are presented in this report. For reasons of brevity the details such as the physico-chemical data, chemistry of the various possible reactions, the analytical tools used and results of the analysis of the residue from the tank presented in Part I have been omitted here. For reasons of completeness, however, the essential points from Part I have been highlighted as and when required.

The model has been developed in three different phases. The first stage begins with the entry of water which reacts with the stored MIC and leads to the evolution of CO₂ with accompanying rise in temperature of the liquid due to the exothermicity of the reaction. The pressure in the tank builds up due to the generation of CO₂ and MIC vapours and eventually the gas starts leaking out. The stage when the safety valve opens marks the end of the first phase and the beginning of the second phase. The model in the first phase restricts the extent of reaction. However, the evolution of gas during the first phase causes considerable extent of mixing within the tank and the storage tank now resembles a well stirred reactor. The second phase of modelling recognises this feature and models the system behaviour appropriately.

It is appreciated that water in the system is a limiting reactant and during the course of events gets totally consumed. The end of water-MIC reaction therefore marks the end of the second phase. During the third and the final stage of modelling the MIC-water reaction is of less importance. The trimerisation reaction, however, still continues and mainly contributes to the rise in the temperature.

It will be noted that while the first phase

models the system behaviour as a batch reactor, during the second and the third phases the presence of leakage of gas implies representation of the system as a semi-continuous reactor. The loss of material through the tank depletes its contents and proper accounting of it is necessary for model computations. In addition one needs to characterise the several reactions that go on within the tank in terms of their rates and exothermicity. While the physico-chemical and thermodynamic data for these reactions are available or can be generated with desired levels of accuracy, the information on the kinetics or the individual rates of reaction of the several processes is not readily available. The present report derives this information from the set of laboratory scale experiments reported in the Union Carbide document.

Before we begin with a rigorous development of the model, it is helpful to obtain an order of magnitude estimate of the extent of products and their distribution reported from the analysis of the tank. It is noted that the tank contained a residue of approximately 12.5 tonnes with almost two-thirds of it in the form of a trimerised product. The analysis therefore reveals that the trimerization of MIC constitutes a major reaction that proceeded in the tank. Among other products that have been noticed the distribution suggests that most of them can be accounted due to the reaction of MIC with monomethylamine (MMA) - a reactant which itself is a product of MIC-water reaction. The analysis thus gives a clue to the three main reactions which must have proceeded within the tank. It is thus anticipated that the spate of events begins with the reaction of MIC with water which produces CO₂ and MMA. MMA in turn starts reacting with MIC forming other products. Simultaneously MIC undergoes trimerization the rate of which is decided by the extent of availability of the catalytic species FeCl₃.

In addition, based on the analysis, vapours that left the tank can be estimated to be around 28 tons. The tank before the accident has been reported to be nearly two-thirds filled with MIC, which presumably contained a little higher proportion of chloroform than usual. The present report assumes that the tank had about 8% chloroform contamination. Based on the material balance considerations presented in the Part I, we also assume that about 450 litres of water entered the tank. These values have been used for quantitative evaluation of the model.

In order that we can proceed with our model building effort, we need kinetic rate data on various reactions that occurred. Unfortunately, as mentioned earlier, no such data are readily available. As regards the main stoichiometric reaction between water and MIC, laboratory scale experiments have been undertaken by Union Carbide with a limited but systematic variation of the pertinent parameters(3). These data will be used by us in the absence of any other data.

5.2 ESTIMATION OF MODEL PARAMETERS

2.1 Analysis of the rate data

Based on the analysis of the residue in the tank it is clear that the three main reactions that proceeded in the tank are the MIC-water reaction, MIC-MMA reaction and the MIC trimerisation reaction. The laboratory scale experimental data on MIC-water and MIC-trimerisation reactions in the presence of varying strengths of FeCl_3 concentration in solution have been reported in the Union Carbide document and have been analysed here to extract the quantitative information regarding the rates of these processes.

The laboratory scale experiments on MIC-water reaction are carried out in a well stirred round-bottom container and the experimental data are reported by noting the amount of gas (CO_2) evolved as a function of time. The two sets of experiments reported differ in the initial composition of mixture and the data are reproduced here in Figure 1. It is obvious from the reported data that the reaction is exothermic and entails a certain rise in temperature as marked along the curves. The system containing a 100:10 volumetric ratio of MIC-water is more vigorous with sharper rise in temperature as compared to the system containing 100:5 proportion of MIC-water. In the laboratory scale

experiments, as reported here, the rise in temperature of the contents has, however, been limited ($220\text{-}32^\circ\text{C}$) and as such these data have been fitted by using a polynomial expression of fifth degree

$$r_{\text{CO}_2} = a + bt + ct^2 + dt^3 + et^4 \quad (1)$$

The coefficients a-e have been obtained for the best fit as $a = 8240$, $b = -9510$, $c = 4930$, $d = -1010$ and $e = 71.1$. The estimated values of the amount of gas evolved per unit time as obtained by using equation (1) have been plotted in Figure 1. The experimental data and the predictions from equation (1) can be seen to agree within one percent accuracy.

It is of interest to note that the temperature of the reaction mixture varies with time and has been recorded for certain values of the measured time along the curve. This information can be utilised to derive the temperature sensitivity of this reaction. For this purpose the rate of CO_2 formation is described by equation (1) has been separated into its temperature and concentration dependent forms as

$$r_{\text{CO}_2} = r(T) f(c) \quad (2)$$

where the temperature dependent part can be expressed as

$$r(T) = r(T_0) \exp \left[\frac{E}{R} \frac{(T - 293)}{(293T)} \right] \quad (3)$$

This procedure yields the activation energy of this particular reactor step as $E = 30 \text{ Kcal/mole}$. In all the subsequent analysis, the MIC-water reaction has been expressed in the form of equation (1) with activation energy as estimated above.

The experimental data on trimerization of MIC in the presence of different extents of ferric chloride have been similarly analysed. The experimental data have been reproduced here in Figure 2 and the typical curve for 66 ppm FeCl_3

has been fitted using the polynomial to obtain

$$r_{\text{trimer}} = 0.01808 + 0.02282 t + 0.0000142 t^2 - 0.000007088 t^3 \quad (4)$$

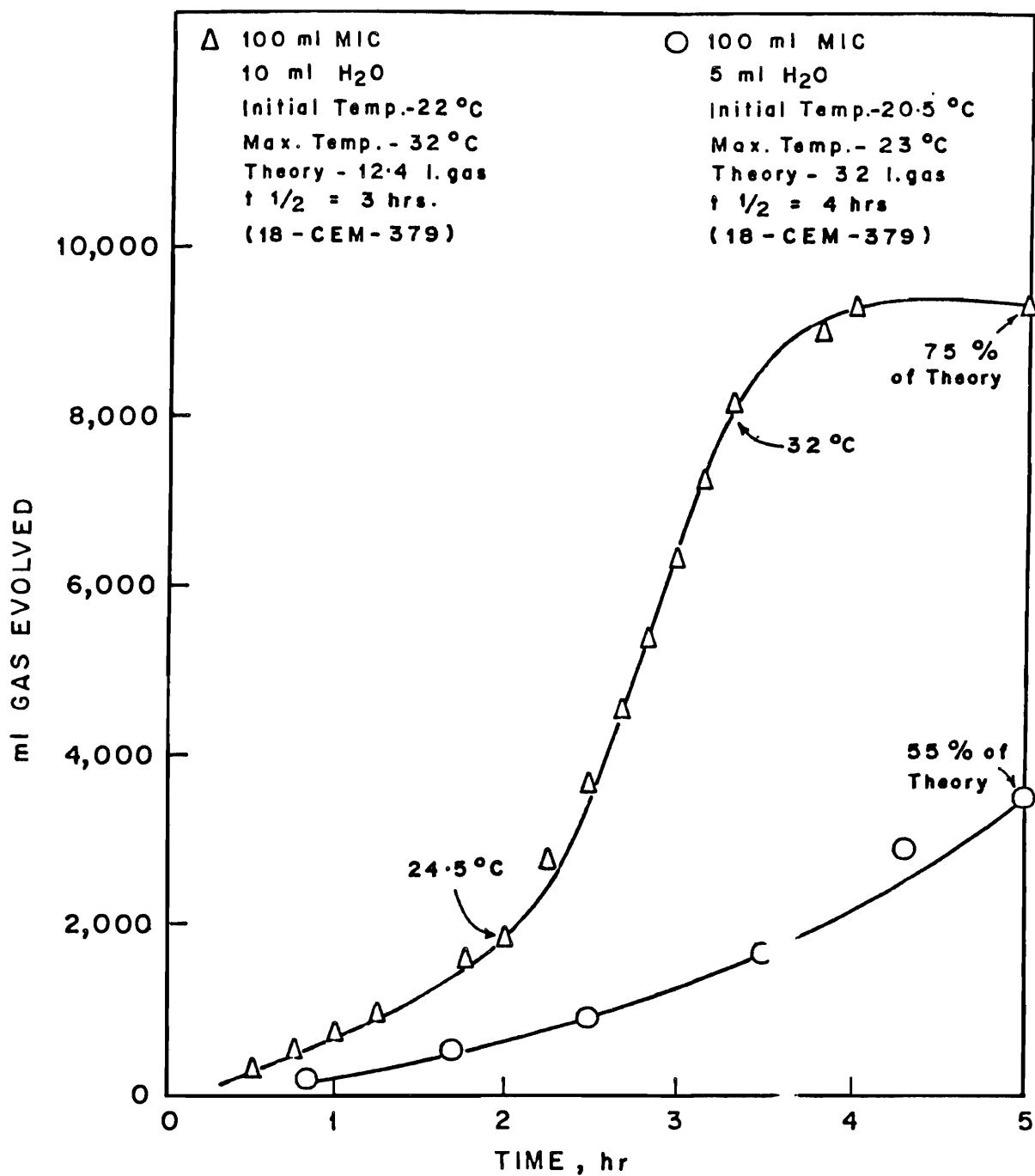


Fig. 1: Amount of gas evolved due to the reaction of water and MIC (Union Carbide Data (3))

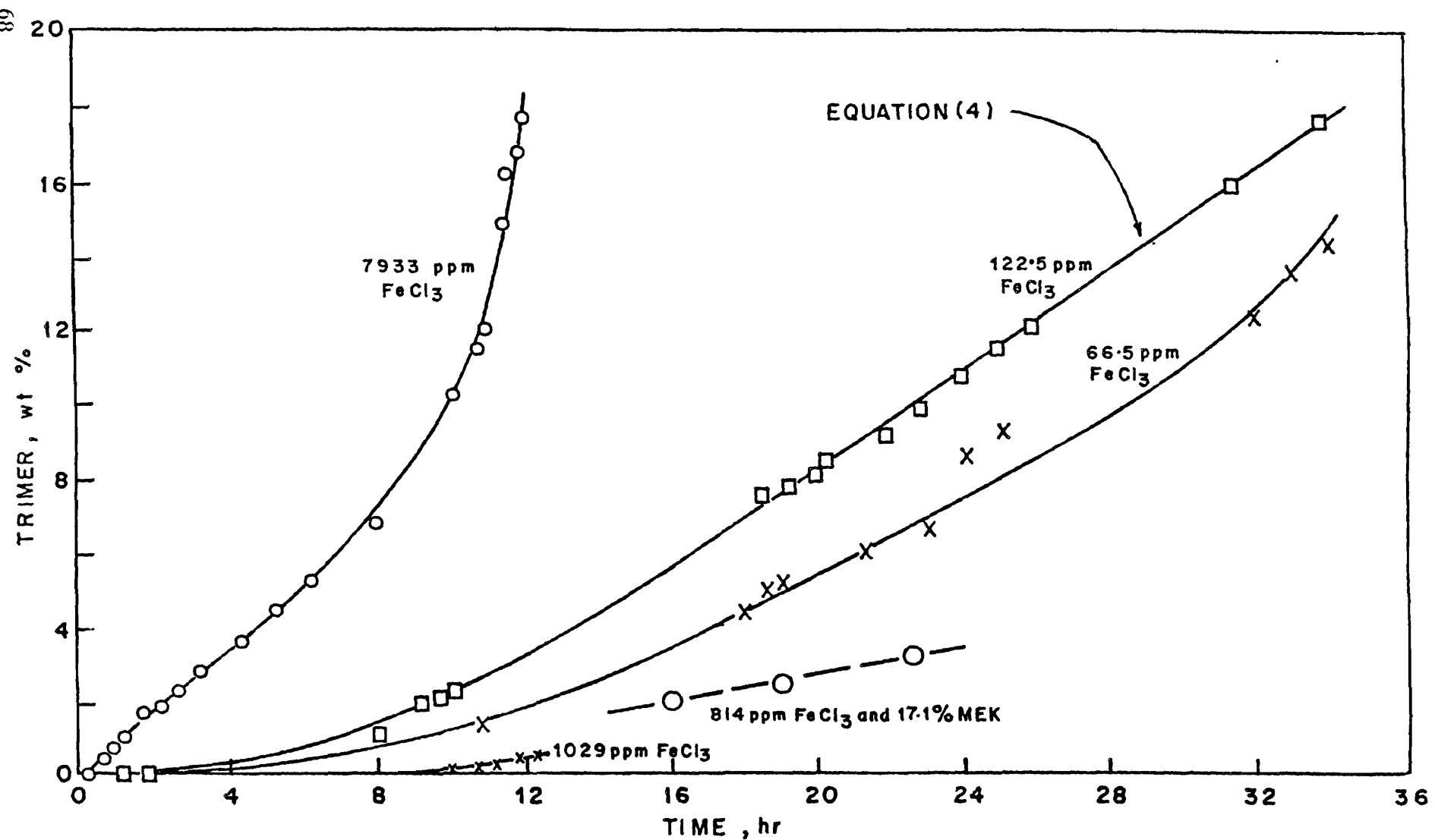


Fig. 2: Rate of ferric chloride catalyzed trimerization of methyl isocyanate
[Union Carbide Data (3)]

Other curves for different extents of FeCl_3 can be similarly fitted. The one reported here, however, is believed to fall in a range that is close to the FeCl_3 contents analysed from the tank and has been subsequently used in model computation.

No data on MIC-MMA reaction have been reported. It is known, however, that the MIC-MMA reaction is much faster than the MIC-water reaction. It is expected therefore (especially in the presence of large concentration of MIC) that the MMA formed due to the reaction of MIC with water will get quickly consumed and the rate of its reaction with MIC will be dictated by its own availability which is governed by its reaction with water. The nonavailability of MIC-MMA rate data is therefore not a serious handicap.

2.2 Additional data required for model estimations

In the previous section we have summarised the basic information regarding the rates of the important processes. In addition, for the purpose of model building, we require information regarding the leakage rates etc. from the tank. The present section summarises this information for use in the subsequent sections.

Data on common physical and thermophysical properties such as densities and specific heats of the liquid reactants and products are readily available in standard references. We additionally need information regarding the heats of reaction. These have been estimated by using the heats of formation and other thermodynamic data. The procedures used for estimation have been summarised in Appendix-I.

Among other properties of the reactant mixture, the one of immediate concern to us here relates to the pertinent vapour pressure-temperature relationship. Based on the analysis and identification of chemical species present in the tank, it is reasonable to expect MIC and chloroform to predominantly contribute to the vapour pressure exerted and it is important to establish the vapour pressure-temperature curve for this systems quantitatively. In addition water-MIC reaction leads to the generation of CO_2 , which will also contribute to the total pressure in the tank.

The individual vapour pressure-temperature data for the MIC and chloroform reported in the

literature (1,2) and can be summarised in the form of following functional relationship for MIC

$$\ln p_{\text{vpr}} = 10.135656 - \frac{10.425246}{T_r} - 4.94905 \cdot \frac{\ln T_r}{0.28959 T_r^6} \quad (5)$$

where p_{vpr} refers to the reduced vapour pressure of MIC at temperature $T^\circ\text{K}$ and is defined as p_{vp}/p_c where p_{vp} is the required vapour pressure in atmosphere and p_c the critical vapour pressure of MIC, reported to be 55 atm. The reduced temperature T_r is likewise defined as T/T_c and the critical temperature of MIC is 491°K . Equation (5) has been fitted to the experimental vapour pressure-temperature data for MIC and can be assumed to be valid over the entire range from room temperature to critical temperature.

The vapour pressure-temperature data for chloroform have been correlated by using the simple relation

$$\ln P_{\text{vp}} = 1.669856 - \frac{3566.933}{T} \quad (6)$$

where p_{vp} is in atm and T is $^\circ\text{K}$.

In order to estimate the vapour pressure of the mixture we invoke the assumption of ideal mixture and write the total pressure as a summation of the constituent parts as

$$P = (p_{\text{vp}})_1 x_1 + (p_{\text{vp}})_2 x_2 \quad (7)$$

where P refers to the total pressure, $(p_{\text{vp}})_1$ and $(p_{\text{vp}})_2$ to vapour pressures of the MIC and chloroform, and x_1 and x_2 to the mole fractions of MIC and chloroform in liquid at temperature $T^\circ\text{K}$. The gas phase mole fractions of the two components are obviously related to the corresponding liquid phase mole fractions as

$$\frac{y_1}{y} = \frac{(p_{\text{vp}})_1 x_1}{P} \quad \text{and} \quad \frac{y_2}{z} = \frac{(p_{\text{vp}})_2 x_2}{P}$$

These equations will be used for the estimation of the quantities of MIC and chloroform present in the vapour form.

2.3 Calculation of leakage rates

The information available on the leakage capacity of the safety valve is somewhat uncertain. The available data documents (3) estimate the leakage rate MIC from the tank at 40 psig to be around 10,000 pounds/hr. Even here, the estimate is based on the assumption of single phase flow and complications due to the two-phase nature of the system are ignored. In the present analysis we have accepted the basic leakage rate as estimated for the single phase flow and modified it to take into account the variations in the pressure and temperature in the tank. It is of interest to note that both these parameters are changing with time, the leakage term is also therefore a variable and is duly accounted for in the model. As far as the varia-

tions of flow rate through the vent valve is concerned, we assume that it increases as square-root of pressure in the tank. The effect of temperature is little more involved, in that the temperature affects the Reynolds number of the escaping fluid due to the variation of densities and viscosities and the Reynolds number in turn affects the coefficients of discharge. The leakage term is therefore appended properly to take care of such variations and the coefficient of discharge is evaluated from the generalised $C_d \cdot R_e$ relationship (4).

In an alternative method, one can rely on the recent experimental investigations of two-phase flow in connection with vent sizing exercises (5). The analysis of experiments leads to the following empirical correlation, which can be used for calculating the discharge rates:

$$A = \frac{m_0 q}{G \left[\left(\frac{V}{m_0} - \frac{T_s}{T_m} \frac{dp}{dt} \right)^{1/2} + \left(\frac{C_p \Delta T}{p} \right)^{1/2} \right]^2}, \text{ mks units} \quad (8)$$

where A is the vent area, m_0 is the total charge in the vessel (approximately 40 tons, depleting with time), V is the vessel volume (approximately 60,000 litres), G is the mass flux (quantity to be estimated), C_p is the liquid specific heat, T_s the temperature at which the valve opens (estimated to be approximately 72°C as seen from the results derived of model at the end of phase I), T_m is the maximum temperature reached in the system at time t , dp/dt is the rate of variation of pressure with temperature and q is the average heat generation rate. As would be noticed, except for the vent area and volume of the vessel, other parameters in this equation are time dependent. The mass flux is also therefore time dependent.

The literature data on two-phase systems also indicate that the two-phase critical flow rate G can be accurately estimated using the relation

$$G = \frac{dp}{dt} (T/C_p)^{1/2} \quad (9)$$

while the average heat generation rate q obeys the relation

$$\bar{q} = \frac{1}{2} C_p \frac{dt}{dt} + \frac{dT}{dt} \quad (10)$$

where the quantities in square bracket refer to the self heat rates of the set temperature and maximum temperature in the system. The advantage of relations given by equations (8) to (10) is obvious in that one does not require any explicit information regarding the kinetics of the system. In the present calculations both the alternatives have been employed and they seem to yield results which agree with each other reasonably well.

5.3 A MODEL FORMULATION

3.1 Overall balance

The accident tank was nearly two thirds filled with MIC. It is estimated that it contained about 8% chloroform. The weights of the individual

components have thus been estimated as 38 tons of MIC and 3.04 tons of chloroform. In terms of their molar quantities these correspond to nearly 6.66×10^5 moles of MIC mixed with 2.54×10^4 moles of chloroform. This mixture in the tank received about 450 litres of water (2.5×10^4 moles) that is assumed to set in the MIC-water reaction. The stoichiometry of MIC-water reaction suggests that eventually one would end up with 2.5×10^4 moles of MMA and equal quantity of CO₂ that would leave the system. The MMA formed however reacts with MIC and again basing the calculations on the reaction stoichiometry suggests that one would end up with 2.5×10^4 moles of MMA based product. A possible hypothesis that can be made is that ignoring other reactions such as trimerization, we would have about 6.16×10^5 moles of MIC left. The product analysis reveals a large (nearly two-thirds) of total residue as trimer. For the total residue estimated at 15.2 tons, this amounts to the consumption of about 1.8×10^5 moles of MIC in the trimerization reaction. We have thus about 4.36×10^5 moles of MIC not accounted due to the reaction, which must have left the tank. In addition the chloroform in the system amounting to 2.54×10^4 moles has also left the tank. The estimated leakage thus gives a figure of nearly 24 tons of material leaving the tank that checks well with the accepted reports.

In the model developed here this overall balance will help in identifying the important stages during the progress of the reaction. We have now been able to assign approximate values to the quantity of MIC that reaction with water, the rate of consumption of which is governed by its kinetics discussed earlier. By maintaining

a balance on this quantity we are able to identify the time at which the water gets totally consumed. The model in the subsequent stages then neglects this reaction. Likewise we have used a counter on the quantities of MIC consumed due to its reaction with MMA and trimerization. The information is necessary for proper description of the model in different stages of the reaction mixture. With this background information we now turn to the model development.

Phase 1 Model

The mathematical model describing the events during this phase takes into account the reaction of MIC with water along with the associated heat effects. It is argued that due to the density differences of MIC and water the latter will float on the surface. This is a conservative estimate and any contamination of MIC with the chloroform present would further increase the density difference. The model thus envisages a local reaction of MIC with water at the interface, the extent of which increases due to the stirring action of the generated bubbles of CO₂. The heat of reaction that is released causes the temperature of the reaction mass to increase. Part of this heat will be removed by the volatile reactants, which will be vaporising and carbon dioxide will be generated due to the reaction. This will exert a pressure in the tank since the free space available is limited.

The stage of events discussed above can be expressed in terms of conservation equations for mass and heat. For the batch mode of operation (as is the case during this phase) the equations take the following form

$$\frac{dCO_2}{dt} = r_{CO_2} \exp \left[\frac{E - \left\{ \frac{(T+273) - 293}{293(T+273)} \right\} V_{cor}}{R} \right] \quad (11)$$

$$-\frac{dMIC}{dt} = r_{CO_2} + br_{MMA} \quad (12)$$

$$\frac{dT}{dt} = \frac{1}{V \rho C_p} r_{CO_2} (-\Delta H_1) + br_{MMA} (-\Delta H_2) - \lambda \quad (13)$$

where λ is heat loss due to vaporisation of volatiles.

Equation (11) describes the amount of CO₂ generated due to reaction. It should be noted that r_1 represents the rate of CO₂ generation measured in the units of litres of gas evolved per unit time from a 100 ml volume of MIC. The factor V_{cor} is therefore incorporated to convert it into proper units and that the actual volume of the reacting MIC could be taken into account. The extent of MIC reacted due to water and the product MMA is described by equation (12). The factor b is introduced in this equation to take care of the reactivity of MMA. In the present case we assume b value to be of the order of unity. The last equation describing the temperature variation takes into account the loss in heat due to the vaporization of the volatile materials such as MIC and chloroform. The functional relations used to describe the various rates and other parameters in these equations appear in the programme listing that is appended at the end of this report.

The set of equations have been numerically integrated to obtain the amount of CO₂ evolved as a function of time (see Figure 3), the amount of MIC consumed at various stages during the reaction, and the temperature of the reactive medium. The vapour pressure-temperature relations presented earlier have now been used to obtain the amounts of MIC and chloroform in the free space and the pressure exerted due to

these vapours and the carbondioxide gas. The integration is continued until the time the system reaches a pressure of 40 psi where the valve is assumed to open allowing the system to discharge.

It is noted that the safety valve has an enormous capacity to leak out the gases and the system pressure therefore suddenly falls when the valve opens. The temperature of the system, however, remains relatively unchanged. This has important implications in that the liquid now starts suddenly boiling which along with the generated CO₂ creates sufficient turbulence to spread the reaction to larger volumes. The reaction that was restricted in the beginning to floating layer now spreads over to a larger volume. The system quickly reaches the threshold pressure conditions and the valve opens. The model described here now ceases to represent the situation realistically and additional considerations such as the extent of reaction volume and loss due to leakage need to be incorporated to describe the real situation. The results of the first phase description are presented in the form of computer output at the end of this report.

Phase 2 Model

As discussed earlier, the model during this phase should describe the semi-continuous nature of the system due to the continued outflow of material from the tank. The governing equations during this phase are:

$$\frac{dCO_2}{dy} = r_{CO_2} (\alpha_{V_c}) - L \quad (14)$$

$$\frac{-d(MIC)}{dt} = r_{CO_2} (\alpha_{V_c}) + r_{MMA} (\alpha_{V_c}) + 3r_{tri} (\alpha_{V_t}) - leak \quad (15)$$

$$\frac{dT}{dt} = \frac{1}{VPC} \left[r_{CO_2} (-\Delta H_1) + br_{MMA} (-\Delta H_2) + 3r_{tri} (-\Delta H_3) - \lambda \right] \quad (16)$$

where L is the leak; αV_i and αV_t are the volume corrections of CO₂ and trimer, respectively.

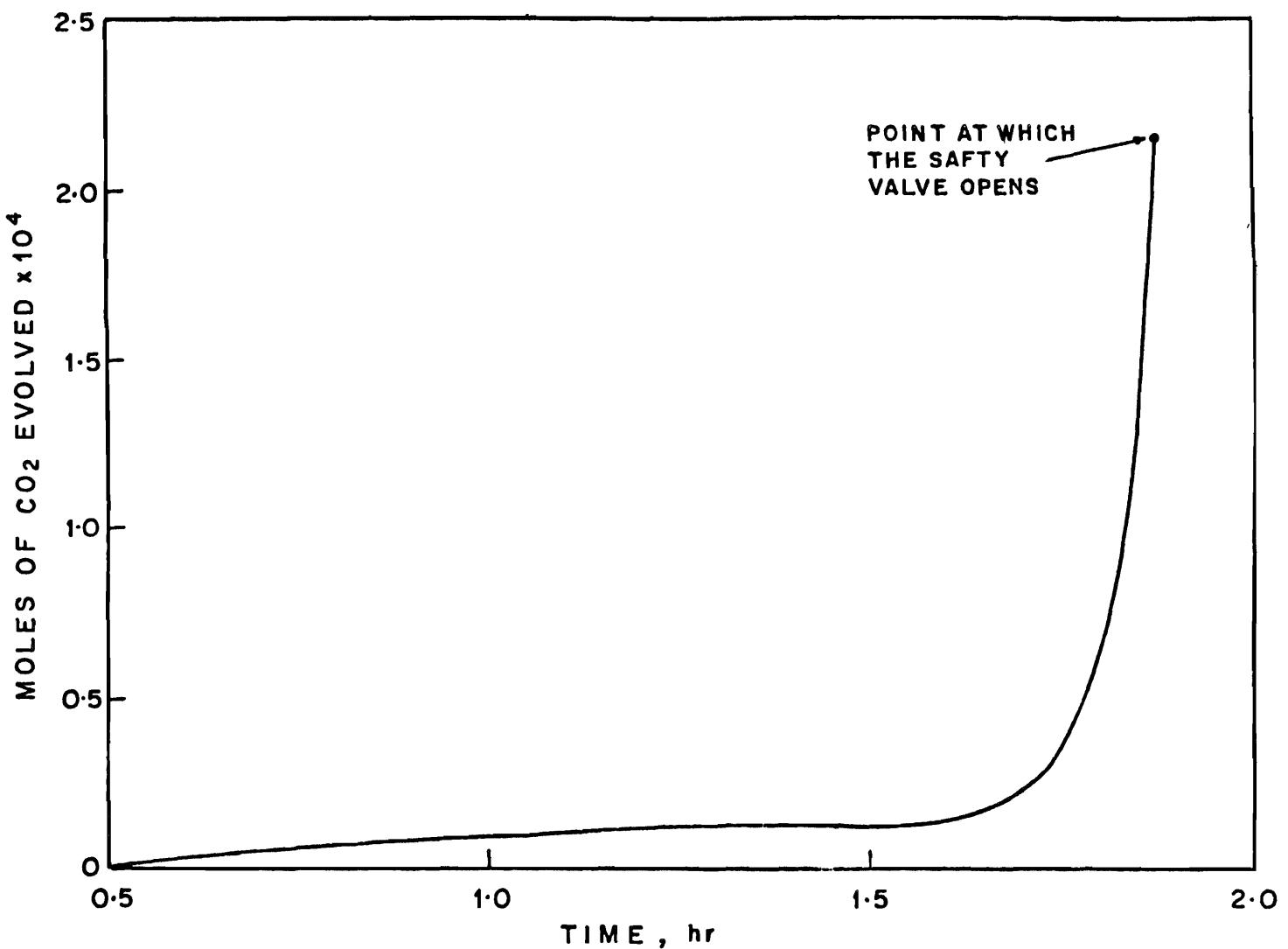


Fig.3: Model predictions on generation of CO₂ as a function of time

The model as described here has two distinctive features. As would be noted the model now takes into account the additional trimerization reaction. It may be appreciated that the large extent of mixing caused due to bubbling of generated CO₂ stirs up the reactant mass dispersing the potential catalysts such as FeCl₃ (assumed to be present due to corrosion of the tank occurring over a long period of time) uniformly through the mixture. As is known, excessive heat liberation contributes to the rise in the temperature of the liquid. The volume correction factors associated with the rate terms in equations (14) and (15) take into account the extent of reaction volume, where the individual reaction proceeds and also converts the rates into proper units.

The set of equations (14)-(16) have been numerically integrated subject to the appropriate initial conditions that are derived from the analysis of the first phase. This enables one to estimate the moles of CO₂, amount of MIC consumed due to each one of the reactions, the temperature and the amount of material lost through the vent. It is possible in these calculations to keep an account of the amount of MIC consumed due to the individual reactions and its loss through the vent. The instantaneous temperature of the reactive medium has been used to

calculate the extent of volatiles and the pressure exerted due to them in the system. The numerical procedure adopted will be clear from the form of the computer output at the end of this report.

As would be noticed, the water being the limiting component, it gets consumed during the course of the reaction. The MIC-MMA reaction being faster than the MIC-water reaction also comes to an end. It should be noted, however, that the reactions between MIC and other MMA based products and the trimerization reaction continues. The model during the second phase now becomes invalid and we have to move over to the next phase to take care of the subsequent events.

Phase 3 Model

It is assumed that during this phase the MIC-water and MIC-MMA reaction can be neglected. The only predominant reaction during this phase is therefore the trimerization. Other reactions such as those leading to MIC reactions with other MMA based products also continue. We assume them to be negligibly small in extent. We feel that these can be incorporated, if desired, by using some effective rate expression. The model during this phase can thus be described as

$$\frac{-d(\text{MIC})}{dt} = -3r_{\text{trim}} \alpha_{v_t} - L \quad (17)$$

$$\frac{dT}{dt} = \frac{1}{V \rho C_p} \left[r_{\text{trim}} \left(-\frac{\Delta H}{3} \right) - \lambda \right] \quad (18)$$

The results of the numerical integration during this phase are also presented as computer outputs at the end of this report.

highlight the main findings of the results of the present model.

5.4 IMPORTANT RESULTS OF THE ANALYSIS

It should be noted that models in phase 1 to phase 3 follow in succession and time parameters appearing in these models run continuously. This is essential since calculations pertaining to parameters such as the various rate functions, the contributions of the leak terms and heat loss and generation terms are based on the absolute value of the time parameter. The functional relations for all these parameters are listed in the programme listing. We shall now

In phase 1 the major contribution to the build-up of pressure in the system seems to have been caused due to the generation of CO₂. During this phase, it may be recollect that the reaction begins in localised zones the extent of which is arbitrarily chosen by assigning values to the parameter V_{cor}. Several numerical runs with different values of this parameter were execut-

ed to obtain the right range. It appears from these experiments that the system requires a period of about one and half hour to reach the threshold conditions when the safety valve opens. The reaction medium during this time is raised to a temperature of about 72°C and the gas leakage starts.

During the second phase, large extent of reaction begins all over the volume of the liquid mass causing a steep rise in pressure and temperature of the system. The excessive rates of generation of CO₂ and large extent of the volatiles in the gas phase contribute to the sudden pressure rise in the system which is negated only to a small extent by the leak. The loss of the material and to a certain extent the consumption of reactants, enhances the free board volume in the system which further helps to

keep a check on the rising pressure. As it appears from the computed results, even so, the pressure in the system rises to about 200 psi with temperature in the range of 180°C.

The elimination of water and MMA reaction during the course of events also removes the source of heat from the system and the only available source for maintaining the temperature and therefore the pressure in the system now becomes trimerization. During this phase trimerization proceeds for a substantial length of time and helps to maintain the temperature and pressure at around 200°C and 200 psi, respectively. Eventually over a period of time the entire material gets ejected out of the tank. There is no heat source in the system now and the pressure in the tank falls in relation to the leakage rate in the tank. The pressure profile in the tank as calculated in this model is shown in Figure 4.

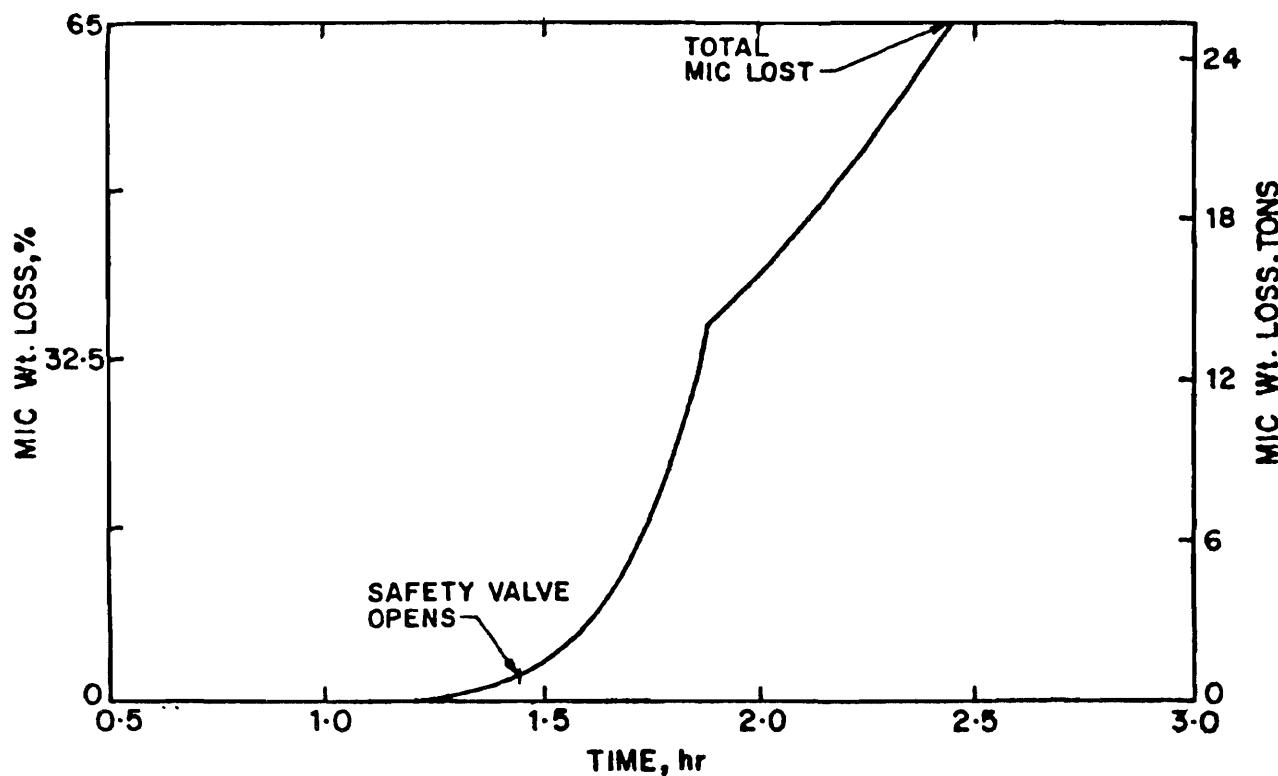


FIGURE 4 : MODEL PREDICTIONS ON LOSS OF MIC FROM THE ACCIDENT TANK

Fig. 4: Model predictions on loss of MIC from the accident tank

The present model seems to be qualitatively and (and in some cases quantitatively) consistent with description of the events that is documented in general reports. It also establishes useful bounds on the ranges of temperatures and pressures that might have been reached during the event in the accident tank. It is worthwhile recalling here that the mechanical and metallurgical testing of the tank material indicated that the tank was not subjected to pressures exceeding 200 psi and temperatures exceeding 250°C. These limits are consistent with model calculation. In addition, the model predicts a loss of about 28 tons of material from the tank (Figure 5). The extent of trimer formed also corresponds to the amounts determined from the residue analysis.

In view of the general agreement of the predicted results with the actual observations in the tank, the following stages can be envisaged. The initial pressure build up in the tank was due to the evolution of CO₂ in the first phase. The vigorous reaction during the second phase caused a sudden increase in pressure and the temp-

erature rose due to the adiabatic conditions in a highly exothermic reaction. This continued until the water got exhausted. Subsequently the temperature was sustained by trimerisation reaction alone and the rest of the MIC was vented off.

As per the present model, the trimerization reaction has played a significant role in causing the subsequent leakage. It is interesting to conjecture as to what would have happened if such rapid trimerisation had not occurred. In other words, we can predict as to what would have happened if the contamination due to FeCl₃ (presumably due to the prior corrosion of the tank) did not exist. The model results for this case can be computed. The predictions are shown in Figure 6. As can be seen, the pressure build up is not sustained. Also the total MIC leakage is comparatively smaller. The main damage, therefore, seems to have been caused by the prior corrosive of the tank, which makes FeCl₃ catalyst available for the reaction and made it possible to reach an almost autocatalytic like catastrophic state.

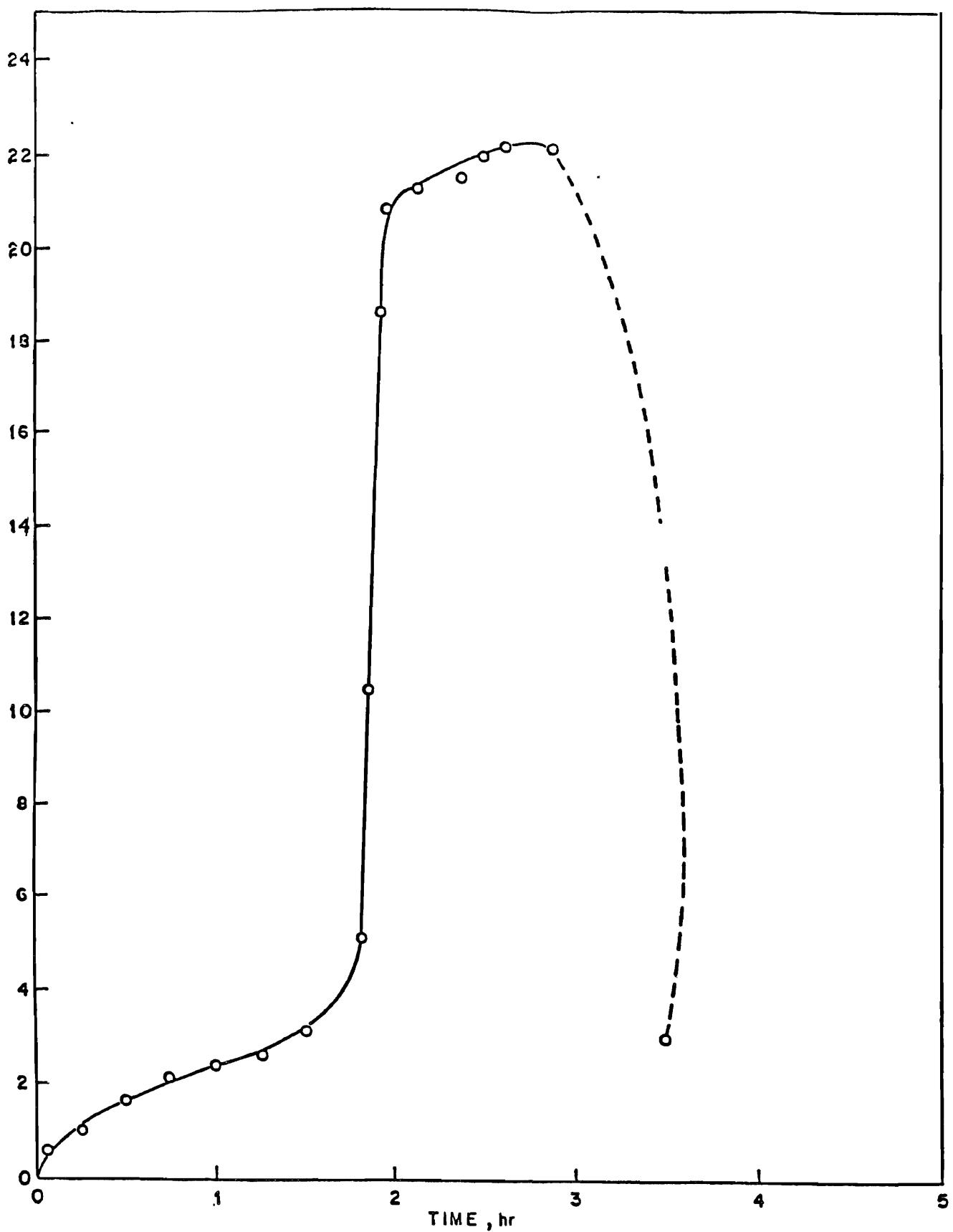
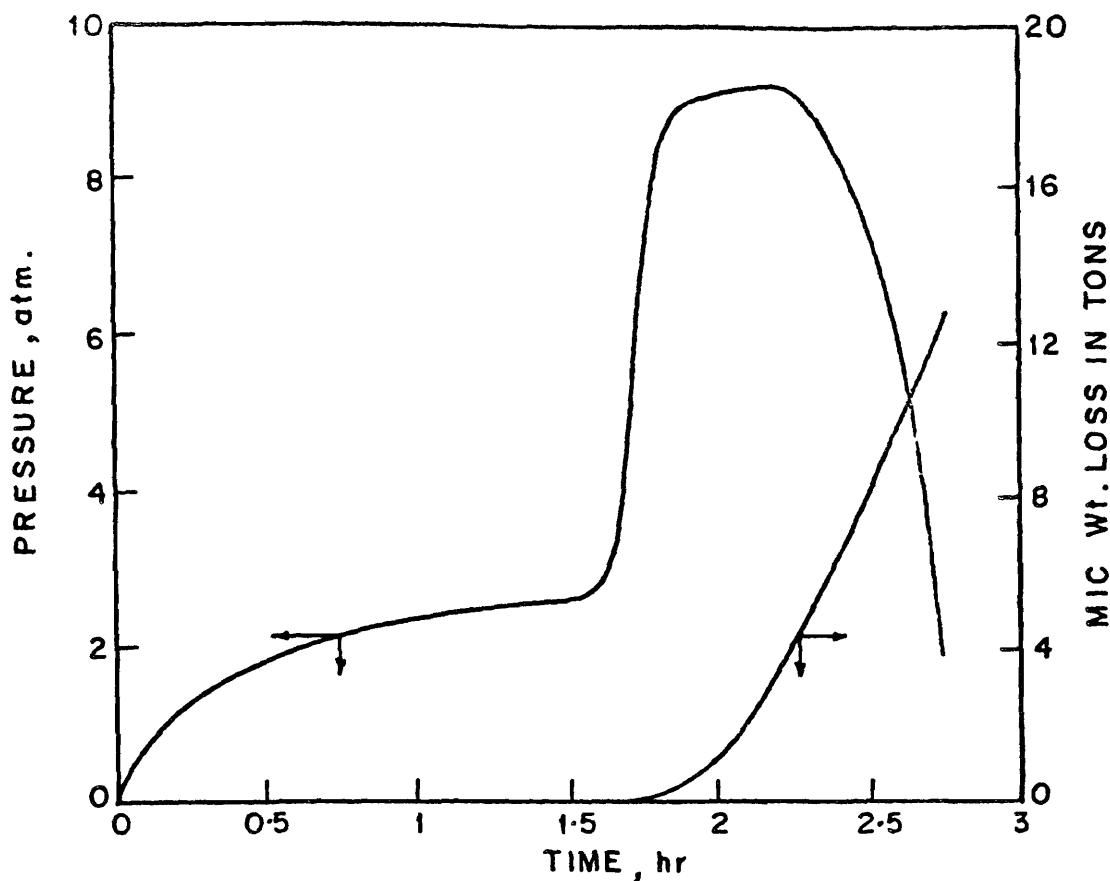


Fig. 5: Model predictions on pressure development in the tank during the accident.



*Fig. 6: Model predictions on MIC loss and pressure buildup
(in the absence of trimerization)*

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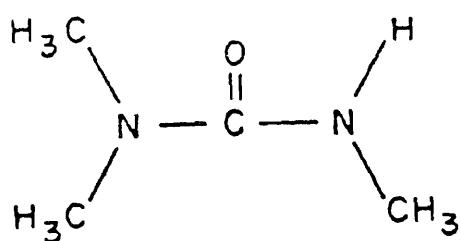
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APPENDIX - I

Thermodynamic Data

1.	Heat of trimerization of MIC	=	300 kcal/kg
2.	Heat of vaporization of MIC	=	137 kcal/kg
3.	Heat of formation of MIC	=	13.7 kcal/gmole
4.	Specific heat of MIC	=	0.5 kcal/kg°C
5.	Heat of formation of methyl amine (gas) ¹	=	-6.7 kcal/gmole
6.	Heat of formation of water (liquid)	=	-68.3 kcal/gmole
7.	Heat of formation of CO ₂ (gas) ¹	=	-94.05 kcal/gmole
8.	Heat of formation of HCl (gas) ¹	=	-22.06 kcal/gmole
9.	Heat of formation of HCNO ²	=	-36.4 kcal/gmole
10.	Heat of formation of Dimethyl urea ³	=	-25.04 kcal/gmole
11.	Heat of formation of Trimethyl urea ³	=	-29.82 kcal/gmole
12.	Heat of formation of DMI ³	=	-68.02 kcal/gmole
13.	Heat of formation of Trimethyl biurate ³	=	-47.83 kcal/gmole
14.	Heat of formation of Dione ³	=	-30.51 kcal/gmole
15.	Heat of formation of Dimethyl Amine ³	=	-7.03 kcal/gmole
16.	Heat of formation of Trimethyl Amine ³	=	-11.81 kcal/gmole
17.	Heat of formation of CH ₂ Cl ₂	=	-13.39 kcal/gmole

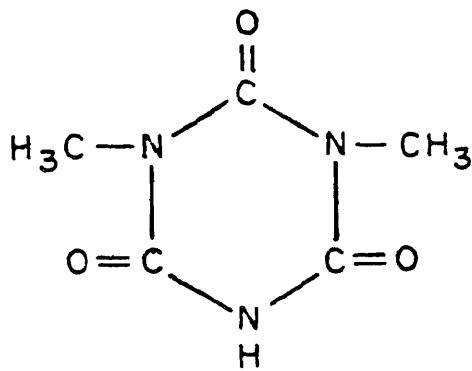
Calculation of Heat of Formation of
Trimethyl urea



<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	3	-10.25	-30.75
C = O	1	-31.48	-31.48
N	1	18.94	18.94
N ₄	1	13.47	13.47
		<hr/>	<hr/>
	Total	-21.82	

Heat of formation of trimethyl urea =
-29.82 kcal/gmole

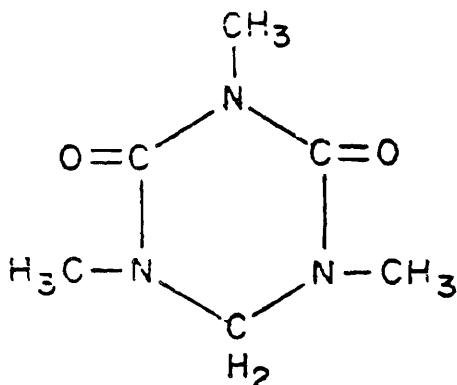
Calculation of Heat of Formation of DMI



<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	2	-10.25	-20.50
C = O	3	-31.48	-94.44
N-	2	19.21	38.42
(Aromatic)			
NH	1	8.5	8.50
(Aromatic)			
	Total	-68.02	

Heat of formation of DMI = -68.02 kcal/gmole

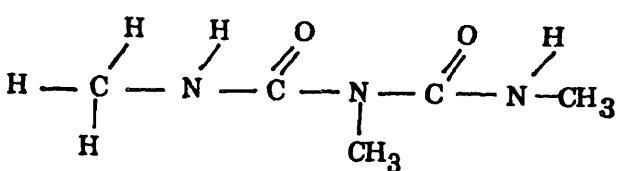
Calculation of Heat of Formation of Dione



<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	3	-10.25	-30.75
C = O	2	-31.48	-62.96
CH ₂	1	5.57	5.57
N-	3	19.21	57.63
(Ring)			
	Total	-30.51	

Heat of formation of Dione = - 30.51 kcal/gmole

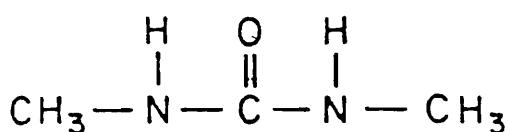
Calculation of Heat of Formation of
Trimethyl Biurate



<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	3	-10.25	-30.75
C	2	-31.48	-62.96
NH	2	13.47	26.94
N-	1	18.94	18.94
	Total	-47.83	

Heat of formation of Trimethyl-Biurate =
- 47.83 kcal/gmole

**Calculation of Heat of formation of
Dimethyl urea**

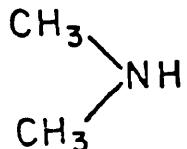


<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	2	-10.25	-20.50
C = O	1	-31.48	-31.48
NH	2	13.47	26.94

		Total	- 25.04

Heat of formation of Dimethyl urea =
- 25.04 kcal/gmole

**Calculation of Heat of formation of
Dimethyl amine**

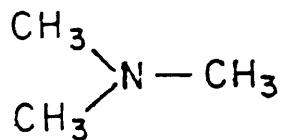


<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	2	-10.25	-20.50
NH	1	13.47	13.47

		Total	- 7.03

Heat of formation of Dimethyl Amine =
- 7.03 kcal/gmole

**Calculation of Heat of formation of
Trimethyl amine**



<u>Group</u>	<u>No.</u>	<u>Contribution/Group</u>	<u>Total</u>
-CH ₃	3	-10.25	-30.75
N-	1	18.94	18.94

		Total	-11.81

Heat of formation of Trimethyl amine =
- 11.81 kcal/gmole

Calculation of Heat of Formation of CH₂Cl₂

Methane Group	-17.89
First Chlorine	0.0
Second Chlorine	4.5

	-13.39 kcal/gmole

POSSIBLE REACTIONS OCCURRED IN THE ACCIDENT TANK

1. $\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	$\rightarrow \text{CH}_3\text{NH}_2 + \text{CO}_2,$	$\Delta H_R = -59.11 \text{ kcal/gmole}$
2. $\text{CH}_3\text{NH}_2 + \text{MIO}$	$\rightarrow \text{DMU}$	$\Delta H_R = -156.1 \text{ kcal/gmole}$
3. DMU	$\rightarrow \text{DMA} + \text{HCNO}$	$\Delta H_R = 106.4 \text{ kcal/gmole}$
4. HCNO + MIC	$\rightarrow \text{DMI}$	$\Delta H_R = -40.89 \text{ kcal/gmole}$
5. DMA + MIC	$\rightarrow \text{TMU}$	$\Delta H_R = -156.47 \text{ kcal/gmole}$
6. DMU + MIC	$\rightarrow \text{Trimethyl Biurate}$	$\Delta H_R = -183.10 \text{ kcal/gmole}$
7. TMU	$\rightarrow \text{TMA} + \text{HNCO}$	$\Delta H_R = 101.6 \text{ kcal/gmole}$
8. 3MIC	$\rightarrow \text{MIC Trimer}$	$\Delta H_R = -300 \text{ kcal/gmole}$
9. DMU + $\text{CH}_2\text{Cl}_2 + \text{MIC}$	$\rightarrow \text{Dione} + 2\text{HCl}$	$\Delta H_R = -107.1 \text{ kcal/gmole}$
10. MIC + TMA + HCl	$\rightarrow \text{TETR-MA - HNCO}$	$\Delta H_R = -27.5 \text{ kcal/gmole}$

APPENDIX II

Energy Balance Calculations

The total heat liberated can be calculated as

$$Q = \sum_{n=1}^{10} R_n \Delta H_n$$

where R_n = Amount (gmoles) of reactant n consumed/total amount reacted

ΔH_n = Heat liberated/gmole

$$Q = 5466.497 \times 10^3 \text{ kcal}$$

Initial quantity of MIC = 40909 kg.

Residue = 15200 kg.

This implies that amount of MIC escaped = 29012 kg.

Therefore we calculate heat liberated = Sensible heating + evaporation + heating of residue
 giving $5466.497 \times 10^3 = 40909 \times 0.5 \times (T_p - 20) + 25709 \times 123.88 + 15200 \times 0.5 (T - T_p)$
 leading to the conclusion that final temperature $T = 149^\circ\text{C}$

Similarly the final temperature can be calculated for various vaporization temperatures.

Vaporization temperature, T, $^\circ\text{C}$	Final temperature, T, $^\circ\text{C}$
40	198.8
50	173.59
60	156.67

APPENDIX III

COMPUTER PROGRAMME LISTING

```
C
C      PHASE2.FTN
C
REAL NMIC,NCHCL,NC02
DIMENSION Y(3),F(3),S(3),P(3),Y0(3),Z(5)
COMMON X0,B,RHO,CF,DH1,DH2,DH3,E1BR,E2BR,AF,RF,RFTRIM,VARCO2,VARTRM
COMMON ALEAK.,RCO2T,AALeak,RMMA,RTRIM,Y1MIC,Y1CHCL,ALEAK3,TOTP,CD
CHARACTER FN*15
TYPE *, 'File name to store the results: ?'
ACCEPT 17,FN
17 FORMAT(A15)
TYPE *, 'Step size(H),TLMT : ?'
ACCEPT *,H,TLMT
C      H = 0.005, RFC02 = RF
RF = 0.58
Y0(3) = 60.0
CD = 1.75
C      VARCO2 IS THE VOLUME CORRECTION FOR THE CO2 PRODUCTION
C      VARTRM IS THE VOLUME CORRECTION FOR THE TRIMERISATION REACTION
C      500LIT. OF WATER
VARCO2 = 1.75E02
VARTRM = 1.05E05
N7 = 10
B=1.0
C      RF IS THE REDUCTION FACTOR FOR THE CO2 PRODUCTION
C      B IS THE MULTIPLE FOR THE MMA REACTION
C      RFTRIM IS THE REDUCTION FACTOR FOR THE TRIMERISATION REACTION
RFTRIM=1.0
C      Open the file for storing
OPEN(UNIT=2,FILE=FN,STATUS='NEW')
WRITE(2,*) 'RF= ',RF,'CD= ',CD
C      Input parameter values here. N is the no. of equations to be solved
N = 3
NS = 1
Y0(1)=649.818/5.0E03
Y0(2)=6.655E05
YCHCL3 = Y0(2)*57.0*0.06/119.5
AF=3.0
RCMT = 500.0
E1BR = 15.0
E2BR = 20.0
RHO =1.2
CF = 0.5
DH1 = 18.25E03
DH2 = 18.25E03
DH3 = 300.0*57.0
R0= 1.45
```

```

TYPE *, 'Initial guess values are:
TYPE *, 'Y0(1)=' , Y0(1), 'Y0(2)=' , Y0(2), 'Y0(3)=' , Y0(3), 'TIME=' , R0
WRITE(2,*)
'Initial guess values are:
WRITE(2,*)
'Y0(1)=' , Y0(1), 'Y0(2)=' , Y0(2), 'Y0(3)=' , Y0(3), 'TIME=' , R0
WRITE(2,*)
'B=' , B, 'RFCO2=' , RF, 'VARCO2=' , VARCO2, 'VARTRIM=' , VARTRM
WRITE(2,*)
'X0,CO2MOL,Y(2),Y(3),PCO2,TOTP,AP,ALEAK,RCO2T,AVOL,RCMT1
1,RCMT,SRMMA,Y1MIC,Y1CHCL,YCHCL3,XCHCL3'
Y(1) = Y0(1)
Y(2) = Y0(2)
Y(3) = Y0(3)
F(1) = Y(1)
F(2) = Y(2)
F(3) = Y(3)
GOTO 140
25   X0 = R0
      F(1) = EQN1(Y)
      F(2) = EQN2(Y)
      F(3) = EQN3(Y)
140   DO 10 J = 1,N
      S(J) = Y(J)
      P(J) = F(J)
      Y(J) = S(J)+0.5*H*F(J)
10    CONTINUE
      X0 = R0+H/2.0
      F(1) = EQN1(Y)
      F(2) = EQN2(Y)
      F(3) = EQN3(Y)
      DO 20 J = 1,N
      P(J) = P(J)+2.0*F(J)
      Y(J) = S(J)+0.5*H*F(J)
20    CONTINUE
      F(1) = EQN1(Y)
      F(2) = EQN2(Y)
      F(3) = EQN3(Y)
      DO 30 J = 1,N
      P(J) = P(J)+2.0*F(J)
      Y(J) = S(J)+H*F(J)
30    CONTINUE
      X0 = R0+H
      F(1) = EQN1(Y)
      F(2) = EQN2(Y)
      F(3) = EQN3(Y)
      DO 40 J = 1,N
      Y(J) = S(J)+(P(J)+F(J))*H/6.0
40    CONTINUE
      NS = NS+1
      N10 = MOD(NS,N7)
C      AALEAK IS THE CUMULATIVE OF ALEAK
C      ALEAK IS THE LEAK (VAPORS + ENTRAINMENT) IN 0.005HRS. (STEP SIZE)
C      AVOL IS THE THE AVAILABLE VOLUME FOR THE VAPORS
C      PCO2 IS THE PRESSURE DUE TO CO2 (ATM.)
C      VPR IS THE VAPOR PRESSURE DUE TO MIC (ATM.)
      AALEAK = ( ALEAK*0.005+57.0/(1.2*1000.0))+AALEAK
      AVOL=20000.+ (RCO2T*VARCO2/1000.)*(57./1.2)+AALEAK

```

```

AP1 = Y(1)*(0.082*(Y(3)+273.)/AVOL)
PCO2 =AP1
TR = (Y(3)+273.)/(491.0)
PVPR = 10.135656-(10.425246/TR)-(4.94905*ALOG(TR))+0.28959*(TR**6.
C THE FACTOR 0.5 APPEARS AS A CORRECTION FOR VAPOR PRESS. DATA
PVPR = EXP(PVPR)
PVP = PVPR*55.
PCHCL3 = EXP(10.669856-(3566.933/(Y(3)+273.)))
SRMMA=SRMMA+RMMA
SRTRIM = SRTRIM+RTRIM
YCHCL3=YCHCL3-Y1CHCL
X1MIC = Y(2)/(Y(2)+YCHCL3+SRMMA+SRTRIM)
XCHCL3 = YCHCL3/(Y(2)+YCHCL3+SRMMA+SRTRIM)
TOTP = ( PVP*X1MIC ) + ( PCHCL3*XCHCL3 ) + ( PCO2 )
C AP IS THE TOTAL PRESSURE (ATM.)
Y1MIC = PVP*X1MIC*AVOL/(0.082*(Y(3)+273.0))
Y1CHCL = PCHCL3*XCHCL3*AVOL/(0.082*(Y(3)+273.0))
CO2MOL=Y(1)
C CALCULATION OF PRESSURE BY BISECTION METHOD
NMIC = Y1MIC
NCHCL = Y1CHCL
NCO2 = Y(1)
AKG = (NMIC*57.0)+(NCHCL*119.5)+(NCO2*44.0)
SMINUS = 8000.0*(NMIC+NCHCL+NCO2)*1000.0*0.003/AKG
SMINUS=SMINUS*CD*(Y(3)+273.)/273.
RMOLES = (NMIC+NCHCL+NCO2)-S0RT(TOTP/3.0)*SMINUS
AP = RMOLES*(0.082*(Y(3)+273.))/AVOL
TYPE*, 'AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS :'
IF (N10.EQ.0) THEN
WRITE(2,*) 'AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS :'
WRITE(2,*) AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS
ENDIF
TYPE *,AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS
RCMT IS THE REACTED AMOUNT OF MIC (MOLES)
C RCMT = Y(2)-Y(C)-AALEAK*1.2/57.0
RCMT1 = RCMT+((RCO2T+RMMA)*VARCO2)
RCMT = RCMT1+(3.0*RTRIM*VARTRIM)
TYPE *,X0,CO2MOL,Y(2),Y(3),PCO2,TOTP,AP,AALEAK,RCO2T,AVOL,RCMT1
1,RCMT,SRMMA,Y1MIC,Y1CHCL,YCHCL3,XCHCL3
IF (N10.EQ.0) THEN
WRITE(2,*) X0,CO2MOL,Y(2),Y(3),PCO2,TOTP,AP,AALEAK,RCO2T,AVOL,RCMT1
1,RCMT,SRMMA,Y1MIC,Y1CHCL,YCHCL3,XCHCL3
WRITE(2,*) ****
1*****
ENDIF
TYPE*, ****
1***'
ENDIF
TYPE*, ****
1***'
112 RO = X0
C TLMT is the upper limit of time T
IF (RCMT1 .GT. 50000.0) THEN
GO TO 55
ENDIF
IF (X0.GT.TLMT) GOTO 55
GOTO 25

```

```

55    CONTINUE
      WRITE(2,*) 'AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS :
      WRITE(2,*) AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS
      WRITE(2,*) X0,CO2MOL,Y(2),Y(3),PCO2,TOTP,AP,ALEAK,RCO2T,AVOL,RCMT1
      1,RCMT,SRMMA,Y1MIC,Y1CHCL,YCHCL3,XCHCL3
      WRITE(2,*) '*****'
      1*****
      CLOSE (2)
      END

```

C
C

Function #1

```

FUNCTION EQN1(Y)
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RFTRIM,VARCO2,VARTRM
COMMON ALEAK,RCO2T,ALEAK,RHMMA,RTRIM,Y1MIC,Y1CHCL,ALEAK3,TOTP,CD
E1 = EXP(E1BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R1TO = 0.824E04-(2.0*0.951E04*X0)+(3.0*0.493E04*X0**2.0)
R1TO = R1TO-(4.0*0.101E04*X0**3.0)+(5.0*0.711E02*X0**4.0)
VCOR=(273.*TOTP-1.E-03)/(22.4*(Y(3)+273.))
RCO2T = R1TO+E1*VCOR*RF
ALEAK2 = 8000.0+SQRT(TOTP/3.0)*Y(1)*((273.+Y(3))/273.)*CD
ALEAK1 = (Y1MIC*57.0/1000.0)+(Y(1)*44.0/1000.0)+(Y1CHCL*119.5/1000.0
ALEAK2 = ALEAK2/ALEAK1
EQN1 = RCO2T*VARCO2-ALEAK2
IF (EQN1.LT.0.0) THEN
   EQN1 = 0.0
ENDIF
RETURN
END

```

C
C

Function #2

```

FUNCTION EQN2(Y)
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RFTRIM,VARCO2,VARTRM
COMMON ALEAK,RCO2T,ALEAK,RHMMA,RTRIM,Y1MIC,Y1CHCL,ALEAK3,TOTP,CD
E1 = EXP(E1BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
E2 = EXP(E2BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R1TO = 0.824E04-(2.0*0.951E04*X0)+(3.0*0.493E04*X0**2.0)
R1TO = R1TO-(4.0*0.101E04*X0**3.0)+(5.0*0.711E02*X0**4.0)
VCOR=(273.*TOTP-1.E-03)/(22.4*(Y(3)+273.))
RCO2T = R1TO+E1*VCOR*RF
RCTO = 0.1608E-01+(2.0*10*0.05282)+(3.0*10**2.0*0.4425E-04)
RCTO = RCTO-(4.0*10**3.0*0.7088E-05)
RTRIM = RCTO*E2*RFTRIM/57.0
RMMA=E1*(R1TO+273.*TOTP+1E-03/(22.4*(Y(3)+273.)))-RF
ALEAK = 8000.0+SQRT(TOTP/3.0)*Y1MIC*(Y(3)+273.)/273.*CD
ALEAK1 = (Y1MIC*57.0/1000.0)+(Y(1)*44.0/1000.0)+(Y1CHCL*119.5/1000.0
ALEAK2 = ALEAK/ALEAK1

```

```

ALEAF = (4./3.)*ALEAF/ALEAF1
C15 = -(RC02T+B*RMMA)*VARCO2 -3.* RTRIM*VARTRM - ALEAF
EDN2 = C15
RETURN
END

C
C      Function #3
C
FUNCTION EDN3(Y)
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RFTRIM,VARCO2,VARTRM
COMMON ALEAF,RC02T,ALEAF1,RMMA,FTRIM,7MIC,Y1CHCL,ALEAK3,TOTP,CD
E1 = EXP(E1ER+((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R1TO = 0.824E04-(2.0*0.951E04*X0)+(3.0*0.493E04*X0**2.0)
R1TO = R1TO-(4.0*0.101E04*X0**3.0)+(5.0*0.711E02*X0**4.0)
VCOR=(273.+TOTP*1.E-03)/(22.4*(Y(3)+273.))
RC02T = R1TO+E1*VCOR+RF
E2 = EXP(E2ER*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R2TO = 0.1808E-01+(2.0*X0*0.62282)+(3.0*X0**2.0*0.1425E-04)
R2TO = R2TO-(4.0*X0**3.0*0.7086E-05)
RTRIM = R2TO*E2*RFTRIM/57.0
RMMA=E1*(R1TO+273.+TOTP*1E-03)/(22.4*(Y(3)+273.))*RF
C1 = 1.0/(RHO*CP)
C5=RC02T*DH1/47.5
C6=RMMA*DH2/47.5
C7=RTRIM*DHS/47.5
EDN3 = C1*(C5+B*C6+C.0*C7)
RETURN
END

C
C      PHASE1.FTN
C
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RMMA
CHARACTER FN*15
TYPE *, 'File name to store the results:?'*
ACCEPT 17,FN
17 FORMAT(A15)
TYPE *, 'Step size(H),TLMT :?'
ACCEPT *,H,TLMT
TYPE *, 'RFC02,B :?'
ACCEPT *,RF,B
C      Write counter
TYPE *, 'Write counter :?'
ACCEPT *,N7
C      H = 0.005
C      B = 1.0
C      RFC02 = RF
C      RF = 0.58
C      Open the file for storing

```

```

OPEN(UNIT=2,FILE=FN,STATUS='NEW')
C Input parameter values here. N is the no. of equations to be solved
N = 3
NS = 1
Y0(1)=0.0
Y0(2)=4.00-(4.*57.*0.08/119.5)
Y0(3)=20.
YCHCL3=(4.*57.*0.08/119.5)
AP=0.0
E1BR = 15.0
E2BR = 20.0
RHO = 0.8
CP = 0.5
DH1 = 18.25E03
DH2 = 18.25E03
DH3 = 300.0*57.0
R0=0.0
TYPE *, 'Initial guess values are:'
TYPE *, 'Y0(1)=' , Y0(1), 'Y0(2)=' , Y0(2), 'Y0(3)=' , Y0(3), 'TIME=' , R0
WRITE(2,*)'Initial guess values are:'
WRITE(2,*)'Y0(1)=' , Y0(1), 'Y0(2)=' , Y0(2), 'Y0(3)=' , Y0(3), 'TIME=' , R0
WRITE(2,*)'B=' , B, 'RFC02=' , RF
WRITE(2,*)'X0,C02MOL,Y(2),Y(3),PC02,AP,SRMMA,AMLMIC,AMCHCL'
C R0 = 0.0
Y(1) = Y0(1)
Y(2) = Y0(2)
Y(3) = Y0(3)
F(1) = Y(1)
F(2) = Y(2)
F(3) = Y(3)
GOTO 140
25 X0 = R0
F(1) = EQN1(Y)
F(2) = EQN2(Y)
F(3) = EQN3(Y)
140 DO 10 J = 1,N
S(J) = Y(J)
P(J) = F(J)
Y(J) = S(J)+0.5*H*F(J)
10 CONTINUE
X0 = R0+H/2.0
F(1) = EQN1(Y)
F(2) = EQN2(Y)
F(3) = EQN3(Y)
DO 20 J = 1,N
P(J) = P(J)+2.0*F(J)
Y(J) = S(J)+0.5*H*F(J)
20 CONTINUE
F(1) = EQN1(Y)
F(2) = EQN2(Y)
F(3) = EQN3(Y)
DO 30 J = 1,N
P(J) = P(J)+2.0*F(J)
Y(J) = S(J)+H*F(J)

```

```

30    CONTINUE
      X0 = R0+H
      F(1) = EQN1(Y)
      F(2) = EQN2(Y)
      F(3) = EQN3(Y)
      DO 40 J = 1,N
      Y(J) = S(J)+(P(J)+F(J))*H/6.0
40    CONTINUE
      NS = NS+1
      N10 = MOD(NS,N7)
      AVOL=20000.+((Y(1)*5.0E03/1000.)*(57./0.6)
      AP1 = Y(1)*5.0E03*(0.062*(Y(3)+273.)/AVOL)
      PC02 = AP1
      TR = (Y(3)+273.)/(491.0)
      PVPR = 10.135656-(10.425246/TR)-(4.94905*ALOG(TR))+0.28959*(TR**6.0)
      PVPR = EXP(PVPR)
C     TYPE*, 'TR=', TR, 'PVPR=', PVPR
      PVP = PVPR+55.
      PCHCL3 = EXP(10.669856-(3566.933/(Y(3)+273.)))
      SRMMA=RMMMA+SRMMA
      YCHCL3=YCHCL3-AY2
      X1MIC = Y(2)/(Y(2)+YCHCL3+SRMMA)
      XCHCL3 = YCHCL3/(Y(2)+YCHCL3+SRMMA)
      TOTP = PVP*X1MIC + PCHCL3*XCHCL3
C     TYPE *, 'PCHCL3,X1MIC,XCHCL3,YCHCL3'
C     TYPE *, PCHCL3, X1MIC, XCHCL3, YCHCL3
      AY1=PVP *X1MIC /TOTP
      AY2 = PCHCL3*XCHCL3/TOTP
C     AP IS THE TOTAL PRESSURE (ATM.)
      AP =(2.0/14.7)+ PC02 +TOTP
      AMLMIC=AY1
      AMCHCL =AY2
C     RCMT IS THE REACTED AMOUNT OF MIC (MOLES)
      AP =(2.0/14.7)+ PC02 +TOTP
      CO2MOL=Y(1)*5.E03
      TYPE 232,X0,CO2MOL,Y(2),Y(3),PC02,AP,SRMMA,AMLMIC,AMCHCL
      IF (N10.EQ.0) THEN
      WRITE(2,232)X0,CO2MOL,Y(2),Y(3),PC02,AP,SRMMA,AMLMIC,AMCHCL
      ENDIF
232    FORMAT(1X,F5.3,1X,F7.2,1X,F5.2,1X,F6.2,1X,F5.2,1X,F5.2,1X,
      C F8.3,1X,F5.2,1X,E16.7)
112    RO = X0
C     TLMT is the upper limit of time T
      IF (X0.GT.TLMT) GOTO 55
      GO TO 25
55    CONTINUE
      CLOSE (2)
      END
C

```

```

C      Function #1
C
C      FUNCTION EDN1(Y)
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RMMA
E1 = EXP(E1BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R1TO = 0.824E04-(2.0*0.951E04*X0)+(3.0*0.493E04*X0**2.0)
R1TO = R1TO-(4.0*0.101E04*X0**3.0)+(5.0*0.711E02*X0**4.0)
VCOR=(273.*AP*1.E-03)/(22.4*(Y(3)+273.))
RC02T = R1TO*E1*VCOR*RF
EON1 = RC02T
RETURN
END

C      Function #2
C
C      FUNCTION EDN2(Y)
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RMMA
E1 = EXP(E1BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
E2 = EXP(E2BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R1TO = 0.824E04-(2.0*0.951E04*X0)+(3.0*0.493E04*X0**2.0)
R1TO = R1TO-(4.0*0.101E04*X0**3.0)+(5.0*0.711E02*X0**4.0)
VCOR=(273.*AP*1.E-03)/(22.4*(Y(3)+273.))
RC02T = R1TO*E1*VCOR*RF
RMMA=E1*(R1TO*273.*AP*1E-03/(22.4*(Y(3)+273.)))*RF
C15 = -(RC02T+B*RMMA)
EQN2 = C15
RETURN
END

C      Function #3
C
C      FUNCTION EQN3(Y)
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RMMA
E1 = EXP(E1BR*((Y(3)+273.)-293.0)/(293.0*(Y(3)+273.)))
R1TO = 0.824E04-(2.0*0.951E04*X0)+(3.0*0.493E04*X0**2.0)
R1TO = R1TO-(4.0*0.101E04*X0**3.0)+(5.0*0.711E02*X0**4.0)
VCOR=(273.*AP*1.E-03)/(22.4*(Y(3)+273.))
RC02T = R1TO*E1*VCOR*RF
RMMA=E1*(R1TO*273.*AP*1E-03)/(22.4*(Y(3)+273.))*RF
C1 = 1.0/(RHO*CP)
C5=RC02T*D1/100.
C6=RMMA*D2/100.
EQN3 = C1*(C5+B*C6)
RETURN
END

```

```

C
C      THIS IS PHASE III
C
REAL NMIC
DIMENSION Y(3),F(3),S(3),P(3),Y0(3)
COMMON XO,B,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RFTRIM,VARCOZ,VARTRM
COMMON Y1MIC,ALEAK',RCOIT,AALEAK',TOTP,RTRIM,RDH3,CD
CHARACTER FN*15
TYPE *, 'File name to store the results: ?'
ACCEPT 17,FN
17 FORMAT(A15)
TYPE *, 'TLMT : ?'
ACCEPT *,TLMT
RDH3 = 1.2
RFTRIM = 1.0
CD = 1.75
RCMT1=500.
H=0.005
VARTRM=1.05E05
Y1MIC = 21232.
AINVOL =31002.94
AALEAK=11075.49
AINP =18.727
C      Open the file for storing
OPEN(UNIT=2,FILE=FN,STATUS='NEW')
C      Input parameter values here. N is the no. of equations to be solved
N = 2
NS = 1
Y0(1)=4.33175E05
Y0(2)=169.8378
AP=AIP
E2BR = 20.0
RHO =1.2
CP = 0.5
DH3 = 300.0*57.0
R0=1.87500
TYPE *, 'Initial guess values are:'
TYPE *, 'Y0(1)=' ,Y0(1) , 'Y0(2)=' ,Y0(2) , 'TIME=' ,R0
WRITE(2,*) 'Initial guess values are:'
WRITE(2,*) 'Y0(1)=' ,Y0(1) , 'Y0(2)=' ,Y0(2) , 'TIME=' ,R0 , 'Y1MIC
1=' ,Y1MIC
WRITE(2,*) 'VARTRIM=' ,VARTRM , 'RDH3=' ,RDH3
WRITE(2,*) 'RFTRIM=' ,RFTRIM , 'CD=' ,CD
WRITE(2,*) 'XO,Y(1),Y(2),AP,TOTP,Y1MIC,AALEAK,AVDL,RCMT1'
Y(1) = Y0(1)
Y(2) = Y0(2)
F(1) = Y(1)
F(2) = Y(2)
GOTO 140
25   XO = R0
F(1) = EDN1(Y)
F(2) = EDN2(Y)
140   DO 10 J = 1,N
S(J) = Y(J)
P(J) = F(J)
Y(J) = S(J)+0.5*H*F(J)

```

```

10    CONTINUE
      X0 = R0+H/2.0
      F(1) = EDN1(Y)
      F(2) = EDN2(Y)
      DO 20 J = 1,N
      P(J) = P(J)+2.0*F(J)
      Y(J) = S(J)+0.5*H*F(J)
20    CONTINUE
      F(1) = EDN1(Y)
      F(2) = EDN2(Y)
      DO 30 J = 1,N
      P(J) = P(J)+2.0*F(J)
      Y(J) = S(J)+H*F(J)
30    CONTINUE
      X0 = R0+H
      F(1) = EDN1(Y)
      F(2) = EDN2(Y)
      DO 40 J = 1,N
      Y(J) = S(J)+(P(J)+F(J))>H/6.0
40    CONTINUE
      NS = NS+1
      AALEAK = ALEAK*0.005*57.0/(1.2*1000.0)+AALEAK
      AVOL=AINVOL+ AALEAK
      TR=(Y(2)+273.)/(491.)
      PVPR=10.135656-(10.425246/TR)-(4.94905*ALOG(TR))+0.28959*(TR**6.)
      PVPR=EXP(PVPR)
      PVP=PVPR*55.
      SRTRIM=SRTRIM+RTRIM
      X1MIC=Y(1)/(Y(1)+SRTRIM)
      TOTP=PVP*X1MIC
      Y1MIC=PVP*X1MIC*AVOL/(0.082*(Y(2)+273.))
      NMIC=Y1MIC
      AMG=NMIC*57.
      SMINUS=6000.0*NMIC*1000.*0.005/AMG
      SMINUS=SMINUS*CD*(Y(2)+273.)/273.
      RMOLES=NMIC-SQRT(TOTP/3.)*SMINUS
      AP=RMOLES*(0.082*(Y(2)+273.))/AVOL
      RCMT1=RCMT1+(VARTRM*3.*RTRIM)
      TYPE *,X0,Y(1),Y(2),TOTP,AP,Y1MIC,AALEAK,AVOL,RCMT1
      WRITE(2,*)X0,Y(1),Y(2),TOTP,AP,Y1MIC,AALEAK,AVOL,RCMT1
      TYPE*, '*****'*****'*****'*****'*****'*****'*****'-'
      WRITE(2,*) '*****'*****'*****'*****'*****'*****'*****'-'
112   RO = X0
C     TLMT is the upper limit of time T
      IF (X0.GT.TLMT) GOTO 55
      GOTO 25
55    CONTINUE
      CLOSE (2)
      END
C
      FUNCTION EDN1(Y)
      DIMENSION Y(3)
      COMMON X0,E,RHO,CP,DH1,DH2,DH3,E1BR,E2BR,AP,RF,RFTRIM,VARC02,VARTRM
      COMMON Y1MIC,ALEAK,RC02T,AALEAK,TOTP,RTRIM,RDH3,C0
      E2 = EXP(E2BR*((Y(2)+273.)-293.0)/(293.0*(Y(2)+273.)))

```

```

R2T0 = 0.01808+(2.0*X0+0.02262)+(3.0*X0**2.0*0.1425E-04)
R2T0 = R2T0-(4.0*X0**3.0*0.7088E-05)
RTRIM = R2T0*E2*RFTRIM/57.0
ALEAK = 8000.0*SORT(TDTP/3.0)*Y1MIC*((Y(2)+273.)/273.)*CD
ALEAK1 = (Y1MIC*57.0/1000.0)+(Y(1)*44.0/1000.0)
ALEAK = (4./3.)*ALEAK/ALEAK1
C15 = -3.* RTRIM*VARTRM - ALEAK
EDN1 = C15
RETURN
END

```

Function #3

```

FUNCTION EDN2(Y).
DIMENSION Y(3)
COMMON X0,B,RHO,CP,DH1,DH2,DH3,E1ER,E2ER,AP,RF,RFTRIM,VARCO2,VARTRM
COMMON Y1MIC,ALEAK,RCO2T,RALEAK,TOTF,RTRIM,RDH3,CD
E2 = EXP(ECBR*((Y(2)+273.)-293.0)/(293.0*(Y(2)+273.)))
R2T0 = 0.01808+(2.0*X0+0.02262)+(3.0*X0**2.0*0.1425E-04)
R2T0 = R2T0-(4.0*X0**3.0*0.7088E-05)
RTRIM = R2T0*E2*RFTRIM/57.0
C1 = 1.0/(RHO*CP)
C7=RTRIM*DHT/47.5
EDN2 = (C1*RDH3*C7)
RETURN
END

```

Initial guess values are:

$Y_0(t) = 433175.0$ $Y_0(\Sigma) = 167.8378$ TIME= 1.875000 Y1MIC=

 21232.00
 VARTRIM= 1050000.0 RDHJ= 1.200000
 RFTRIM= 1.000000 CD= 1.750000
 X0,Y(1),Y(2),HP,TOTP,Y1MIC,AHLEN1,AVOL,RCMT1
 1.850000 433533.5 169.9849 25.87384 20.83146
 30017.26 11075.69 42156.63 1087.295

 1.860000 430941.4 170.0119 25.88569 20.85616
 30126.59 11195.34 42281.28 1449.376

 1.850000 424359.0 170.0803 25.91568 20.91869
 30281.23 11509.80 42592.75 9444.657

 2.000000 417624.8 170.1503 25.94675 20.98215
 30440.14 11828.40 42911.40 15583.00

 2.050001 410730.6 170.2216 25.97827 21.04655
 30905.61 12154.69 43237.63 21621.16

 2.100002 403665.2 170.2945 26.01050 21.11196
 31178.02 12488.92 43571.66 26202.32

 2.400009 357143.8 170.7625 26.21613 21.52681
 33112.47 14851.98 45934.92 72084.45

 2.425009 352891.3 170.8038 26.23654 21.56325
 33145.73 14892.50 45970.44 72611.83

 2.450010 346571.4 170.8450 26.25512 21.60001
 33715.65 15097.06 46180.00 76468.61

AP,NMIC,NCHCL,NCO2,RMOLES,SMINUS :
 2.01934e-0000.219 67.95076 0.1241643 1671.062
 1582.553
 1.695000 0.2241643 574018.4 56.14204 2.7068472E-04
 4.312119 2.01934e-0000.451 4369.151 0.1464792 24370.37
 23966.4e-0000.219 3.983370 3500.219 67.95076
 22433.29 3.9253761E-02

 AF,NMIC,NCHCL,NCO2,RMOLES,SMINUS :
 3.102223 4789.620 95.46107 0.3541738 2618.214
 1632.183
 1.745000 0.3041738 547143.1 97.60213 4.1964720E-04
 5.76668 3.102223 5646.305 0.2067707 25648.02
 31987.68 32533.38 5.753980 4763.620 95.46107
 22433.08 3.9772702E-02

 AF,NMIC,NCHCL,NCO2,RMOLES,SMINUS :
 5.235478 7224.558 148.5437 0.6151372 4465.507
 1705.170
 1.795000 0.6151372 514143.2 114.4249 7.1797704E-04
 8.696478 5.235478 7215.770 0.3155771 27013.39
 38440.16 39001.9e-0000.260 6.361260 7224.558 148.5437
 21501.44 4.0140599E-02

 AF,NMIC,NCHCL,NCO2,RMOLES,SMINUS :
 10.50623 12897.25 274.0977 1.246392 9051.900
 1815.334
 1.645000 1.246392 470039.5 142.0210 1.4466435E-03
 15.26398 10.50623 9316.257 0.5524260 29320.66
 45.223.57 46200.11 12.64690 12897.25 274.0977
 19331.41 3.9933130E-02

 AF,NMIC,NCHCL,NCO2,RMOLES,SMINUS :
 18.72703 21232.33 454.8937 2.15e168 16025.50
 1947.335
 1.875000 2.156163 433175.4 169.8376 2.5163473E-03
 25.33566 18.72703 11073.67 0.8723722 31321.94
 50318.42 51204.43 16.96765 21232.33 454.8937
 17522.98 3.6678143E-02

Initial guess values are:
 $\text{Y0(1)} = 0.0000000$ $\text{Y0(2)} = 3.847364$ $\text{Y0(3)} = 20.00000$ TIME=
 0.0000000
 $B = 0.7500000$ RFC02= 0.5800000
 $X0,COCMOL,Y(2),Y(3),FC02,AP,SRMMA,AMLMIC,AMCHCL$
 0.045 22.31 3.84 23.58 0.03 0.60 0.686 0.59 0.6606674E-02
 0.095 47.64 3.83 27.62 0.06 0.63 1.893 1.00 0.1796052E-02
 0.145 70.64 3.83 31.50 0.09 0.65 2.606 1.00 0.4862765E-03
 0.195 91.57 3.82 34.64 0.12 0.69 3.638 1.00 0.1316523E-03
 0.245 110.57 3.81 37.67 0.14 0.72 4.392 1.00 0.3565629E-04
 0.295 127.68 3.81 40.41 0.16 0.75 5.071 1.00 0.9656951E-05
 0.345 142.96 3.80 42.84 0.15 0.78 5.678 1.00 0.2614230E-05
 0.395 150.45 3.80 45.00 0.20 0.81 6.213 1.00 0.7071249E-06
 0.445 168.24 3.79 46.66 0.22 0.84 6.680 1.00 0.1910735E-06
 0.495 178.41 3.79 48.51 0.24 0.86 7.083 1.00 0.5157174E-07
 0.545 187.08 3.79 49.89 0.25 0.88 7.427 1.00 0.1390339E-07
 0.595 194.37 3.78 51.06 0.26 0.90 7.716 1.00 0.3744091E-08
 0.645 200.44 3.78 52.01 0.27 0.91 7.958 1.00 0.1007224E-08
 0.695 205.42 3.78 52.82 0.27 0.93 8.153 1.00 0.2707131E-09
 0.745 209.48 3.78 53.47 0.28 0.94 8.314 1.00 0.7270246E-10
 0.793 212.78 3.78 53.99 0.29 0.94 8.444 1.00 0.1951175E-10
 0.845 215.47 3.78 54.42 0.29 0.95 8.551 1.00 0.5233601E-11
 0.695 217.70 3.77 54.78 0.29 0.96 8.639 1.00 0.1403141E-11
 0.945 219.62 3.77 55.09 0.30 0.96 8.716 1.00 0.3760384E-12
 0.595 221.37 3.77 55.37 0.30 0.97 8.785 1.00 0.1007433E-12
 1.045 223.07 3.77 55.64 0.30 0.97 8.853 1.00 0.2698151E-13
 1.095 224.56 3.77 55.92 0.30 0.97 8.925 1.00 0.7224173E-14
 1.145 226.83 3.77 56.24 0.31 0.98 9.005 1.00 0.1933636E-14
 1.195 229.11 3.77 56.60 0.31 0.99 9.098 1.00 0.5173844E-15
 1.245 231.76 3.77 57.03 0.31 0.99 9.204 1.00 0.1383817E-15
 1.295 234.94 3.77 57.53 0.32 1.00 9.331 1.00 0.3699453E-16
 1.345 238.67 3.77 58.13 0.32 1.01 9.462 1.00 0.9884344E-17
 1.395 243.07 3.77 58.83 0.33 1.02 9.655 1.00 0.2639167E-17
 1.445 248.20 3.76 59.65 0.34 1.04 9.865 1.00 0.7040496E-18
 1.495 254.14 3.76 60.60 0.35 1.05 10.105 1.00 0.1876344E-18

REGIONAL RESEARCH LABORATORY
HYDERABAD

CHEMICAL STUDIES ON MIC
AND
DESIGN AND ENGINEERING OF RRL SCIENTISTS

1986

The report of the Regional Research Laboratory, Hyderabad (RRL—H), gives, in Part I, details of the experimental evidence of chemical transformation which took place in the ill-fated MIC tank. It includes results of experimental simulation of conditions prevailing in the tank during the accident. Predetermined proportions of MIC, chloroform and water were subjected to various conditions and the products identified. Presence of large quantities of carbon dioxide and relatively smaller fractions of trimethyl amine in the gaseous products has proved to be significant in confirming the sequence of reactions postulated earlier by the Report on Scientific Studies on the Factors related to Bhopal Toxic Gas Leakage of December 1985. Similarly, the presence of certain constituents of the residue has re-affirmed the dependence of the reactions on the pressure prevailing in the tank. Part II deals with the efforts of the Design and Engineering group of RRL.

RRL scientists were involved right from the beginning in the investigations and the subsequent safe disposal of MIC during "Operation Faith". Later they visited the UCIL premises in order to carry out various assigned tasks, including sampling of the residue, weighing of the tank, examination of the engineering documents for assessing the adequacy of design and operation of the MIC plant, etc. Various hypotheses proposed to explain the sequence of events prior to the incident were also scrutinized by studying in detail the design specifications of the plant and equipment and the prevailing operating conditions.

RRLH scientists assisted the Central Bureau of Investigation (CBI) and the lawyers by providing clarifications to specific questions raised by them on the design and engineering aspects of the MIC process plant. Some results of the above could also be found in the concluding paragraphs.

PART I: DECOMPOSITION STUDIES ON MIC

c

REPORT OF WORK ON MIC DECOMPOSITION STUDIES

1.0 Background

The scientific studies on the factors related to the Bhopal toxic gas leakage presented in the CSIR report of December (1985), though concise, embodies the results of (i) a chemical study on the tank residue and the reactions of MIC and (ii) an exhaustive analysis of the design features and facilities for the manufacture of MIC, its storage, utilization and disposal at the Bhopal plant. It establishes that a combination of conditions for the occurrence of the mishap already existed in the plant, due to the lack of engineering features commensurate in proportion to the properties of explosive reactivity, ready volatility and high inhalation toxicity of MIC. From the chemical analysis of the tank residue and the chemistry of the formation of products, it has been deduced that (i) the temperature of the tank should have reached 250°C causing the pressure in the tank to rise to around 11.13 kg/cm²g, (ii) there should have been an ingress of at least 500 kg of water initiating the reaction and activating the metal contaminants and (iii) there should have been an intrusion of sodium hydroxide to account for the quantity of sodium present in the tank residue.

While the report undoubtedly demonstrated that there was no formation of hydrogen cyanide during the pyrolysis of MIC or its reaction products, an analysis of the gaseous products was much desired. With this requirement in view, a few experiments have been carried out primarily for gas analysis and simultaneously for the product analysis to see if any further insight into the reaction could be gained.

2.0 Factors considered

Firstly the heats of reactions were taken into consideration. The values for the common reactions of MIC are:

i) Polymerisation : 345 Btu/lb of MIC

- ii) Trimerisation : 540 Btu/lb of MIC
- (iii) Reaction with water : 585 Btu/lb of MIC,
3700 Btu/lb of water

Considering the heat of reaction with water, it may be seen that every kg of water reacting with 6.33 kg of MIC will liberate 2051.28 Kcals of heat sufficient to vapourise 16.59 kg of MIC at ambient temp. and atmospheric pressure. In other words, water added to an extent of 4.36 (W%) in MIC can cause the vapourisation of the entire quantity of MIC taken. If the trimerisation reaction is considered, the heat liberated for every kg of trimer formed is equivalent to the vapourisation of 7.3 kg of MIC. For the reaction involving DMI formation, heat produced by the formation of one kg of DMI will evaporate 2.78 kg of MIC. Though the reaction with water at room temperature is slow, the heat produced accelerates the reaction rapidly. The trimerisation reaction is violent, but has an induction period depending upon the catalyst. The DMI formation takes place only above 200°C. From the December (1985) report, it may be seen that the trimerisation reaction is the major reaction producing the maximum heat, enough to evaporate 50,590 kg of MIC, followed by the reaction with water and the DMI formation (heat equivalent is 8494 kg and 7442.6 kg of MIC respectively). So the water quantity for the reactions under study are taken in the range 3-8 (W%).

The second factor considered was the content of chloroform in the MIC stored in tank 610. December (1985) report shows that chloroform has no influence whatsoever in initiating or accelerating the run away reactions. Chloroform was responsible for the formation of dione which takes place above 200°C and was estimated to be 595 kg from the tank residue analysis. This works out to 5% based on the MIC used up in the reaction (12,087 kg) and 1.45% on the total quantity of MIC present in the tank (41,338 kg). The UCC report of

March (1985) states that the last discharges of MIC from MIC refining still to tank 610 contained chloroform to an extent of 12-16%. Taking this into account, one can arrive at a conclusion that chloroform was present in the MIC in the tank 610 to an extent of 3.608-4.8%. There is no room to assume more than 5% of CHCl_3 content in the MIC of tank 610. So the chloroform concentrations for the experiments were chosen in the range 3 to 6 (W%).

Experiments with different proportions of water and chloroform in the selected ranges were carried out and the data are given in Tables 1-4.

3.0 Preliminary Studies

The GCMS of the commercial sample (Fluka 1977) used in the reactions showed besides MIC, chloroform present as stabilizer and a small amount of dimer which readily reverts to MIC.

The mass spectrum of MIC by liquid inlet system was identical with the above and a fragment ion peak corresponding to m/z 27 (HCN) shows up in both, indicating that MIC fragments to HCN on electron impact.

Pyrolysis of plain MIC at 250°C for 2 hours has carried out in a couple of experiments and the gases collected showed on GCMS, no other components except MIC and the fragment ion peak m/z 27 which was less than 2% in intensity. The peaks at m/z 83 and 85 observed represent CHCl_2^{35+} and $\text{CHCl}^{35}\text{Cl}^{37+}$ arising from the stabilizer. The solid residue showed the presence of only one product, the trimer (MICT) with M⁺ 171 and matching in all respects with an authentic sample of MICT.

Application of GCMS was tried to identify the gaseous products as well as the solids produced in the pyrolysis of MIC with water and with water-chloroform mixtures. Table 1 summarises the experiments carried out and the results obtained. It may be seen that all the major products are identified in the solids formed. But in the case of the gas analysis, only carbon dioxide was identified. Vitiated by the high concentration of carbon dioxide, the presence or absence of other constituents could not be established in GCMS. Therefore, it was decided to use GC for subsequent experiments.

4.0 Pyrolysis Studies

Pyrolysis of MIC in presence of water and water-

chloroform mixtures were carried out in a specially made bomb, with provision for collection of gases after the experiment. The bomb is a stainless steel cylinder closed at one end and fitted at the other end with a screw cap and needle valve which could withstand a pressure of 204 atmospheres. Provision for inserting a thermocouple for measuring the inside temperature was made. The general procedure is to charge the material by volume in the order, MIC - chloroform-water and quickly closed the end securely. Then the cylinder is heated electrically to the desired temperature and maintained at that temperature for two hours. Finally the cylinder is withdrawn from the heater and allowed to cool in a well-ventilated hood. When the inside temperature has fallen to 100°C, gases are collected in an evacuated gas collector tube and taken for gas analysis by GC. The cylinder was allowed to cool to 20°C and the solids removed from the reactor by leaching with methanol. After evaporating methanol, the solids are analysed by GC.

Table 2 gives the experimental conditions and table 3 gives the results of gas analysis. Table 4 gives the composition of products in the acetone extract.

The presence of amine in the gaseous products in the experiment 9 was recognised but the individual identification was not possible due to insufficient quantity of the gas mixture. In experiment 10, the presence of trimethyl amine was confirmed. Other amines are either absent or below the level of detection by the present procedure. Subsequently, in all the rest of the experiments, trimethyl amine was found to be present. One additional peak from experiment 14 to 17, which was found to be neutral by chemical treatment was identified as being due to carbon monoxide.

5.0 Inferences and Discussion

The detection of carbon monoxide in the gaseous products of experiments 14-17 is an important observation. But it is not surprising because of the presence of chloroform and water in the reaction. December (1985) report describes two experiments (13 and 18) on the hydrolysis of chloroform to formic acid by water at 200°C. There are instances in literature that report the formation of formic acid and hydrochloric acid from chloroform and water. Thus formic acid could give rise to carbon monoxide. Alternatively, the origin of carbon monoxide can be traced to the reaction

TABLE 1

No.	MIC (g)	H ₂ O (g)	CHCl ₃ (g)	Temp (°C)	Time(hr)	Gas (M ⁺)	Analysis		Products identified
							Solids (M ⁺)		
1	2.5	-	-	245-250	2	27,57	171		MICT
2	2.9	-	-	240-250	2	27,57 83,85	171		MICT
3	2.9	3	-	245-250	1	44 (CO ₂)	171,88, 140,156		MICT DMU DMI
4	2.9	0.9	-	240-250	1	CO ₂	171,88, 134,157		MICT DMU DMI
5	4.24	0.56	0.1	245-260	2	CO ₂	171,88, 140,157		MICT DMU DHI DIONE
6	4.24	0.56	0.1	235-245	2	CO ₂	171,88, 102,157		MICT DMU TMU DMI DIONE
7	4.24	0.56	0.1	240-246	2	CO ₂	171,88 102,157		"
8	3.26	0.12	0.326	260-274	2	CO ₂	By GC		MICT DMU TMU DIONE TMB DMI

TABLE 2

MIC pyrolysis experimental conditions

SNo.	Expt. No.	MIC,g (% w/w)	H ₂ O,g (% w/w)	CHCl ₃ ,g (% w/w)	Total wt.5	Inside temp.°C	Time hrs
1	9	3.26 (87.97)	0.12 (3.24)	0.326 (8.79)	3.706	270-75	2
2	10	3.868 (96.5)	0.14 (3.5)	Nil	4.008	296-300	2
3	11	3.868 (94.10)	0.24 (5.84)	Nil	4.108	295-300	2
4	12	3.868 (91.92)	0.34 (8.08)	Nil	4.208	250-255	2
5	13	3.868 (93.70)	0.14 (3.39)	0.12 (2.91)	4.128	250-260	2
6	14	3.868 (91.05)	0.14 (3.30)	0.24 (5.65)	4.248	255-260	2
7	15A	3.868 (91.48)	0.24 (5.68)	0.12 (2.84)	4.228	250-260	2
8	15B	3.868 (91.48)	0.24 (5.68)	0.12 (2.84)	4.228	250-260	2
9	16	3.868 (86.96)	0.34 (7.64)	0.24 (5.4)	4.448	250-260	2
10	17	4.220	0.18	0.60	5.00	250-260	2

TABLE 3
Gas Analysis of MIC Decomposition products
(Qualitative)

Sample	No.of peaks	Identification	Remarks
Expt 9	2	Amines?	Individual identification could not be done
Expt 10	1	Amine MMA nor DMA	The peak was identified as TMA by GC/Ms
Expt 11	1	TMA	Comparison with aq.solution of TMA was done.
Expt 12	2	TMA (minor) Acetone (major)	Acetone is from solvent used
Expt 13	2	TMA (major) Acetone (minor)	Poor concentration of the sample.
Expt 14	3	Not identified TMA Acetone (Tr)	GC/MS was carried out. But only one peak corresponding to TMA was obtained concentration was also poor.
Expt 15	3	Not identified	Peak (1) was found to be neutral by chemical treatment and the presence of CO ₂ was detected by IR also. HCN is ruled out.
Expt 16	3	Not identified TMA Acetone (Tr)	Peak no.(1) disappeared after 4 days. CO is suspected at this stage.
Expt 15 B	2	CO TMA	(1) was confirmed by comparison with pure CO and later by GC analysis of gas in the coal division (Mr Salvapathi).
Expt 17	2	CO TMA	Peak (1) was confirmed by comparison with pure CO and later by Mr Salvapathi.

GC conditions:

Column: 12' 1/8" SS column, 3% Carbowax 2% KOH coated on chromosorb WAW.

Column temp: 30°C, Injector temp: 100°C, Detector (FID) temp: 100°C

Carrier gas (N₂) flow: 6-8 ml/mt.

TABLE 4
Quantitative GC analysis of-acetone soluble residues from MIC decomposition products

Sample	TMU	DMU	MICT	DIONE	TMB	DMI	Remarks
Expt 9	*P	3.1	64.2	2.9	Tr	P	
Expt 10	P	6.0	55.0	*Tr	TR	Tr	
Expt 11	P	9.2	58.2	Tr	Tr	Tr	
Expt 12	P	55.5	30.8	Tr	Tr	Tr	*Tr = less than 0.1%
Expt 13	P	17.5	65.4	1.4	0.5	P	*P = 1-2%
Expt 14	P	13.5	53.6	3.2	0.5	P	
Expt 15	2.2	27.2	32.8	1.4	0.3	0.6	
Expt 16	0.5	6.2	80.0	0.8	Tr	0.2	
Expt 17	1.1	5.4	43.0	2.2	Tr	3.6	

Conditions:

Column: 4' 1/8" SS column, 10% DEGS coated on chromosorb W.AW

Column temp: 190°C, Injector temp: 220°C, Detector (FID) temp: 220°C

Carrier gas (N₂) flow: 50-60 ml/mt.

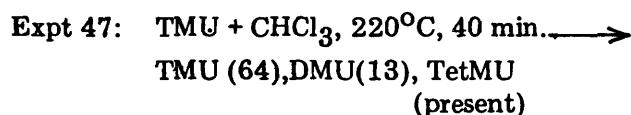
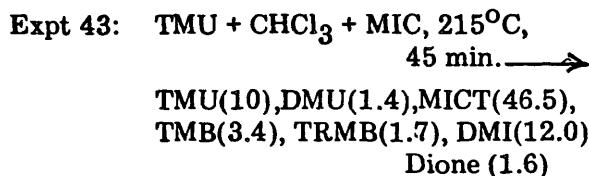
Method: external standard

Remarks:

1. The samples when made into acetone solution still contains insoluble particles.
2. Some polymers are suspected to be present and they do not come out of column under the operating conditions.

of formic acid with MIC to form the anhydride which decomposes thermally to carbon monoxide, carbon dioxide and methyl amine. This sequence can be confirmed experimentally. Whatever be the route of formation of carbon monoxide, the source seems to be formic acid and not methyl isocyanate or its reaction products, since carbon monoxide was detectable only in experiments involving chloroform.

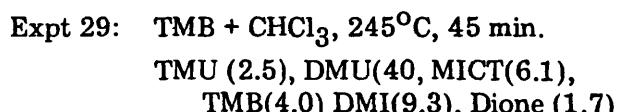
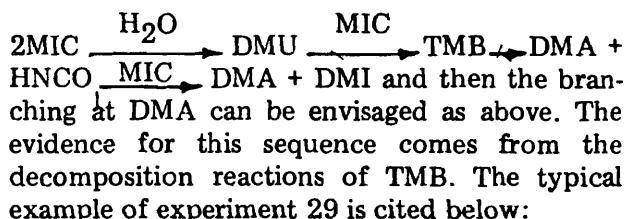
Another significant observation is the detection of trimethyl amine in the gaseous products of all experiments irrespective of whether chloroform is added or not. December (1985) report suggested that the formation of trimethyl amine was associated with the formation of DMI as in Eq. 10 (P. 58) and this was used in the material balance calculations. The current observation justifies this suggestion, since it lends support for the associated formation of trimethyl amine and DMI. Eq. 10 was derived as a continuation of Eq. 7 (P. 58) assuming the intermediacy of trimethyl urea (TMU, Eq. 8, P. 58) and tetramethyl biuret (TRMB, Eq. 9, P. 57). That this approach is rational gets established by the evidence trended by experiments 43 and 47 carried out on TMU. The results are reproduced below:



Expt 47 indicates that chloroform has no role to play in the decomposition of TMU. The reaction is one of exchange of amine groups at high temperatures, as is usual with methylated ureas. The products are obviously DMU and tetramethyl urea. In contrast, the decomposition of TMU in presence of MIC as in Expt 43 produces DMI as the second abundant product and TRMB to an extent of 1.7%. This implies that TRMB is formed as an intermediate only to decompose to TMA, MIC and HNCO which lead to the formation of DMI. The conversion sequence DMA $\xrightarrow{\text{MIC}}$ TMU $\xrightarrow{\text{MIC}}$ TRMB \longrightarrow TMA + HNCO $\xrightarrow{\text{MIC}}$ TMA + DMI gets established by this evidence. Linking this sequence with Eq. 7 (P. 57), one obtains the Eq. 10 which seems to be fairly correct. It is to be noted that HNCO

is formed from TRMB and that TMA is an essential co-product, the identification of which in the present experiments confirms the above reaction sequence.

Similarly the formation of DMA can be reasonably formulated by the sequence



The major product is DMU and it is evident that TMB formed at lower temperatures reverts back at higher temperatures to DMU and MIC, from which MIC undergoes other reactions. The formation of DMI as the next abundant product indicates that a portion of TMB breaks up into DMA, HNCO and MIC from which TMU, TMU based products, DMI and MICT are formed. Thus there is ample ground for concluding that DMA and TMA are formed in the thermal decompositions of MIC reaction products.

The suggestion that the mixture of amine hydrochlorides could arise from the disproportion of methylamine hydrochloride at elevated temperatures as put forward in the UC report of March (1985) is untenable because of the presence of abundant quantities of MIC. Moreover, it is known that methylamine formed even at lower temperatures is quickly fixed up as DMU, the magnitude of the heat of this reaction has been discussed earlier in this report.

Having arrived at a logical sequence of major reactions, a material balance was worked out and presented in Annexure 1. TMU formation was taken as per the present scheme which is different from that adopted by the report of December (1985). Despite this change, the material balance remains to be the same.

Analysis of the acetone soluble residues by GC (Table 4) shows the usual trends such as (i) the formation of more DMU and less MICT with increasing quantities of water and (ii) the formation of more dione with more chloroform. The poor formation of DMI is intriguing, but it suggests that pressure has to be considered as an important parameter. In experiment 14, the reactant concentration is held close to the ratio arrived at by the material balance calcula-

tions. A comparison of the results (weight percentage of products) with the composition of tank residue is provided below:

	MIC	H ₂ O	CHCl ₃	TMU	DMU	MICT	Dione	TMB	DMI
Expt 14	91.05%	3.30%	5.65%	1.2	13.5	53.6	3.2	0.5	1.2
Mat.Bal	91.62%	3.88%	4.5%	1.52	1.29	55.71	3.13	0.94	21.42

It may be noted that except for the differences in the DMU and DMI concentrations, all others are fairly agreeing. Taking into account that the tank residues are likely to have formed at a pressure of 11-13 kg/cm²g and 250°C, the discrepancy noted suggests that the reactions of MIC are influenced by pressure. A rough calculation on this basis shows that the pressure of the reaction in experiment 14 should be around 1.25 kg/cm²g which is just one tenth of the pressure experienced by the tank 610. Expt 17 was a repetition of experiment 8 of the article in J. Org. Chem., 51, 3781 (1986) to appreciate the replication of the results. A comparison of the area percentages of the products is given below, as weight percentages are not quoted in the paper.

	MIC	H ₂ O	CHCl ₃	TMU	DMU	MICT	Dione	TMB	DMI
Expt 17	84.4%	3.6%	12.00%	3.1	10.5	74.1	6.2	-	5.1
Expt 8 (J.Org.Chem.)	84.4%	3.6%	12.00%	5.3	2.1	51.4	2.6	1.4	17.3

The estimated pressure in experiment 8 is around 2.04 kg/cm²g which is twice the pressure in experiment 14. Here again, it is seen that DMU and DMI are the substances that exhibit large differences. The inference that the pressure of 1.25 kg/cm²g in experiment 17 and the pressure of 2.04 kg/cm²g in experiment 8 (J. Org. Chem.) bear a relationship for the respective formation of DMI suggests that a systematic study of the influence of pressure on this reaction has to be done to achieve the replication of the chemistry of the products formed in the tank 610.

Summary

1. Experiments with different proportions of water and chloroform in the selected ranges 3-8% for water and 3-6% for chloroform were carried out at 250°C and gases collected were analysed.
2. Besides large amounts of carbon dioxide, trimethyl amine was identified in all experiments irrespective of whether chloroform was added or not.
3. The identification of trimethyl amine helped to confirm the reaction sequences. DMA and TMA have been postulated to arise from the decomposition of the reaction products of MIC.
4. The identification of carbon monoxide in experiments involving chloroform showed that it might have formed through formic acid.
5. The analysis of the acetone soluble residues suggested the possible dependence of the reactions on the pressure of the reaction.
6. Acetone insolubles were found to contain unidentified long chain polymeric materials.

Personnel involved in the work

1. Dr. A.V. Rama Rao
2. Dr. R.V. Venkataraman
3. Dr. M Panduranga Rao
4. Dr. P. Shanthan Rao
5. Dr. M. Vairamani
6. Dr. R. Srinivas
7. Mr. G.K. Viswanadha Rao
8. Mr. K. Radhakrishnan
9. Mr. M. Eshwar Rao

Annexure I

Material balance

1. MMA	$\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	MMA + CO_2	(1)
4.17	4.17	4.17	4.17
2. TMA 7.17	$7\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	2DMI + TMA + CO_2	(2)
	50.19	7.17	14.34
TMU 1.87	$5\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	DMI + TMU + CO_2	(3)
DMI 17.04	9.35	1.87	1.87
DMA 5.47	$4\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	DVI + DMA + CO_2	(4)
	3.32	0.83	0.83
	$2\text{CH}_3\text{NCO} + 2\text{H}_2\text{O}$	DMA + NH_3 + 2CO_2	(5)
	9.28	9.28	4.64
3. DIONE 2.49	$3\text{MIC} + \text{H}_2\text{O} + 2\text{CHCl}_3$	DIONE + $2\text{HCl} + \text{CO}_2 + \text{CCl}_4$	(6)
	4.47	2.49	4.98
4. DMU 1.83	$2\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	DMU + CO_2	(7)
	3.66	1.83	1.83
5. TM3 0.81	$3\text{CH}_3\text{NCO} + \text{H}_2\text{O}$	TMB + CO_2	(8)
	2.43	0.81	0.81
6. MICT	$3\text{CH}_3\text{NCO}$	MICT	(9)
	122.16	40.72	

- Same as in report of December, 1985.

PART II: DESIGN AND ENGINEERING EFFORT OF RRLH SCIENTISTS

DESIGN AND ENGINEERING EFFORTS

Introduction - Why RRLH was called to UCIL

The Regional Research Laboratory, Hyderabad, (RRLH) is the only institution of CSIR which deals with process design and engineering of chemical process plants. As such the DGSIR, called upon RRLH scientists to associate themselves very closely with the operation at Union Carbide India Limited (UCIL), Agricultural Products Division, Bhopal.

RRL(H) is also the only institute in CSIR which has developed a process for the manufacture of phosgene, a very toxic chemical used in the manufacture of intermediates including methyl isocyanate (MIC), and toluene diisocyanate. Scientists at RRLH have designed, fabricated, installed and operated a pilot plant for making 120 Kg of phosgene per day. The process was successfully demonstrated to Hindustan Organic Chemicals, a public sector undertaking, and hence RRLH had acquired considerable experience in safety/handling of toxic materials at sufficiently larger scale.

RRLH has, over a period of several years, designed and commissioned industrial plants for the manufacture of pesticides based on the process know-how developed by the laboratory. This activity involves design of systems for receiving, handling and storage of toxic and inflammable materials. Process design and instrumentation, of all hazardous operations forms a part of this activity. Consequently, the scientists at RRLH are very well aware of this standard procedures to be adopted in investigating any hazard. Incorporation of most appropriate safety devices and safe disposal of toxic and inflammable materials during an unforeseen emergencies is conceived at the design stage at RRLH.

Finally, intensive interaction between the chemists, chemical engineers and mechanical engineers during the development of process technology for agro-chemicals has resulted in a unique orientation of the personnel involvement in various disciplines and a high level of competency.

2. DETAILS OF THE INVOLVEMENT OF RRLH IN UCIL CASE:

2.1 At UCIL Premises:

(Summary of Visit Reports compiled by RRLH scientists after their visits to UCIL, APD plant is enclosed as Appendix I)

1. Scientists from RRLH were among the first to reach UCIL after the incident on 2/3 Dec 1984 resulting in the release of large quantities of MIC. They were associated with many critical assignments which were completed during the first few weeks including the following:
 - a) Assessment of hazard resulting from the presence of approx. 20 tonnes of MIC on UCIL premises.
 - b) Evaluation of methods for stabilising left over MIC for its safe disposal.
 - c) Scrutiny of procedures available, for safe disposal of MIC.
 - d) Inspection of plant and equipment available at UCIL to undertake the operation.
 - e) Evaluation of 'Zero-risk' procedure for the disposal.
 - f) Determination of the quality of MIC vis-a-vis the risk involved in its disposal.
 - g) Preparation for and participation in "Operation Faith".
 - h) Coordination of activities of personnel of various agencies during the operation.
 - i) Technical assessment of the causes of the incident.
 - j) Preliminary checking of designs of critical equipment earmarked for use during "Operation Faith".

2. Subsequent visits were made to UCIL to assist the Scientific Team of the Government of India in sampling the residue in Tank 610 and analysis of residue samples. More details are provided in Appendix II, Section 1.1, and Section 2 where details of the operation are given.
3. Decontamination of MIC structure was one of the most important assignments in which engineers from RRLH were closely involved. Representatives of the Ministry of Chemicals and Fertilizers were advised about the validity and suitability of procedures suggested by UCIL.
4. The Attorney's firm Robin Zelle Larson and Kaplan (RZLK) hired by Government of India in USA deputed their representatives to visit the UCIL plant and get acquainted with MIC plant. Their visit was organised and a get together was arranged for them to meet all the scientists involved in the UCIL case (Please see Appendix II Section 4).

Scientists of RRLH visited RZLK in USA to assist them in preparing technical part of the legal documents. Visit Reports of the scientists may be referred to for further details.

2.2 Outside UCIL

1 Engineering Aspects of UCIL Plant

With the expertise generated as a consequence of design and engineering activities, RRLH scientists were called upon to look closely at the overall design of MIC plant and analyse the reasons for the failure of process instrumentation and control systems. Several discussions were held at RRLH and some of the conclusions drawn up are presented in Appendix III.

It was also possible to draw a comparison between the UCL's own plant at USA and UCIL Bhopal plant based upon the press statements made by UCL. Engineering features and safety aspects of the two units were highlighted in a note filed with CSIR.

A detailed review of the Report compiled by UCL in March 1985 was carried out with respect to the design and engineering.

Similarly the Emergency Procedure prescribed by UCIL and venting system of MIC

tank were critically scrutinized and a separate note on this aspect was submitted to CSIR.

.2 Public Relations & Publicity

CSIR Headquarters was the centre of activities for a number of months after the incident. Technical journals like the Chemical & Engineering News sent their representatives to obtain information on the incident as well as the follow-up action taken. Such visitors had to be taken to various places in India accompanied by Scientists with intimate knowledge of the UCIL case. RRLH Scientists very often performed these tasks.

Very often during the period following the incident, the Senior Scientists of CSIR were asked to present their views in the national and international seminars, symposia. Material required for presentation had been prepared by Scientists of RRLH to suit the requirements of the particular forum without digressing too much and with due regard to the legal aspects of the case.

1. OPERATIONS IN BHOPAL

1.1 Sampling

1.1.1 During the Operation Faith the thermowell nozzle of tank 610 was opened. Arrangements were made for evacuating any volatile and gaseous substances from this nozzle by having a cold trap to condense the material. After ascertaining that no volatile or gaseous products were found at this location, the nozzle was used for withdrawing solid residue samples. These samples were collected by CBI under the guidance of Dr S Varadarajan, Director-General, CSIR. One set of samples was given to UCC team.

1.1.2 The M.P. High court through an order, decided that samples of MIC (tank 611) collected earlier and remnants of tank 610 be analysed by a team of scientists from CSIR in the presence of an independent expert to be nominated by DGSIR. The DGSIR in turn requested Dr. C S P Iyer, Head, Analytical Division, Bhabha Atomic Research Centre, Bombay to provide the expertise. The DGSIR has also nominated Dr N R Ayyangar, Scientist, NCL, Pune, to be in-charge of all analytical work pertaining to the court order.

1.1.3 During the second week of February

1985, a team consisting of the above named scientists and others who were concerned with Operation Faith finalised a sampling procedure and a sampling schedule at Bhopal. Accordingly, it was decided to withdraw residue samples from tank 610 using 5 process/instrumentation nozzles available on the manhole cover representatives of CBI as well as UCIL (as representative of UCC, USA). From each of the 5 sampling nozzles residue samples were drawn and one such set comprising of all 5 samples was handed over to UCIL for UCC. The other set was taken to NCL for investigative analysis.

1.1.4 While the samples of the residue were being collected, it was felt by Dr C S P Iyer as well as others that the material withdrawn in this fashion would not perhaps give a total picture of all the components remaining and the distribution in the entire tank 610. This observation was made as a result of the location of the manhole which is situated at one end of the tank which is 40' long. It was, therefore, decided that a more comprehensive samples from the tank so that any variation of the composition of the residue along the axis as well as laterly can be accounted. The CBI was requested to arrange for excavation of tank 610 as early as possible so that suitable sampling windows can be cut at various locations on the tank for withdrawal of samples.

1.1.5 In the first week of April 1985 Dr C P Iyer, along with other scientists from CSIR and Ministry of Chemicals and Fertilisers, Government of India and Mr L H Baker of UCC gathered at UCIL, Bhopal, to implement the revised sample plan.

1.1.6 Tank 610 was cut open at four locations on the 7 segmented tank as follows:

- i) The dished end at the far end of the tank
- ii) On segments 4 & 6 at the top
- iii) On segments 4 & 4 on the side

1.1.7 Solid residue samples were collected from all the four locations and one set of each was handed over to UCC, UCIL and CSIR. It was discovered during the sampling that the earlier samples (withdrawn in February 1985) might not have been representative as the total depth of the residue was found to be much more throughout the tank.

1.2 Decontamination of MIC Structure

1.2.1 During the month of April 1985, the CBI was asked by the M.P. Government to make arrangements for decontaminating the MIC structure to enable closure of the UCIL premises by 11th July 1985. Although a list of all toxic and hazardous chemicals was prepared as early as in January 1985 and some action was already taken, it was felt that decontamination of process equipment in the MIC structure should be dealt with very carefully. The CBI was, therefore, asked to get a procedure for decontamination of MIC structure from UCIL for examination by the scientists of Ministry of Chemicals and Fertilisers, Government of India and CSIR.

1.2.2 This procedure was thoroughly examined at Bhopal by asking pertinent questions about the relevant procedures. Subsequently some modifications were made to the procedures supplied by UCIL and clearance was given to CBI to start the work.

1.2.3 Representatives of the Ministry of Chemicals and Fertilisers, Government of India, supervised the start-up of operation. The operation was completed successfully eventhough there was leethal MIC related contaminants in the various systems. The plant was subsequently shut down on the 11th July 1985.

2. MIC analysis at Bhopal

2.1 Samples of MIC collected during Operation Faith from tank 611 under the supervision of CBI were analysed during February 1985 at Bhopal by a team of scientists from CSIR. For this purpose, facilities available at UCIL Research Centre were utilised. However, chemists and analysts employed by the Regional Research Laboratory, Bhopal (CSIR) worked under the supervision of Dr N R Ayyangar, Scientist, NCL, Pune, to complete the analysis. Dr C S P Iyer of BARC was also present.

2.2 Trace metal analysis of the non-volatile residue of MIC samples was carried out by Dr N R Ayyangar and Dr C S P Iyer at Defence Metallurgical Research Laboratories, Hyderabad, and Nuclear Fuel complex, Hyderabad.

2.3 The results of all the analysis were compiled and sent to DGSIR.

3. Investigative analysis at NCL, Pune

3.1 The samples of MIC withdrawn by CBI from various locations during the Operation Faith were taken to NCL for complete analysis. The results were passed on to CBI.

3.2 The residue samples withdrawn from tank 610 in February 1985 and April 1985 (referred to in section 1.1) were transferred to NCL for complete analysis. Since the material contains a number of components, some of which are difficult to identify, a comprehensive programme of analytical work has been drawn up. This includes identification of each component by the most modern analytical techniques such as Mass Spectrometry, Infrared Spectrometry, HPLC, Column Chromatography, etc.

3.3 The programme also involves preparation of ultra pure compounds of the required chemical structure in order to identify corresponding molecules available in the residue sample. A team of several senior scientists has been entrusted with this job and the work is in progress.

4. Visits of R,Z,L & K teams

4.1 A team consisting of the following R,Z,L & K Attorneys visited the UCIL plant towards the end of March 1985 in order to gather first hand information on the disaster as well as to get acquainted with the relief measures taken immediately after the disaster.

- i) Mr M V Cireci
- ii) Mr B A Finzen
- iii) Ms R B Walburn
- iv) Ms A Barcelow

4.2 Dr G Thyagarajan, Director, RRL, Hyderabad, Dr P V Krishna, Adviser, Ministry of Chemicals and Fertilisers, Government of India, Dr A A Khan, Scientist, RRL, Hyderabad, accompanied the R,Z,L & K team to Bhopal. Discussions were organised between

the Madhya Pradesh State Government officials of the Medical and Health, Public Administration, Social Service and Law Ministries. R,Z, L & K had an opportunity to get to know the dimensions of the problems of relief operation and the kind of records which are available with M.P. State Government, Subsequently, members of the team proceeded to UCIL plant and spent several hours understanding the sequence of events and the equipment involved in the incident.

4.3 Towards the end of May 1985, a team consisting of Mr B A Finzen and Mr L Zelle visited Bhopal. This time, Dr P V Krishna, Adviser, Ministry of Chemicals and Fertilisers, Dr A A Khan, Scientist, RRL, Hyderabad, accompanied the lawyers to Bhopal. After meeting the state government officials, Mr Zelle and Mr Finzen spent time with the scientific team which was entrusted with the job of neutralising MIC during Operation Faith and the job of follow-up action at Bhopal. The Additional Director, CBI, Mr G Ramachandran as well as Superintendent of Police of CBI in-charge of the investigations at Bhopal, Mr. Murari Lal were also consulted by R, Z, L & K.

4.4 Dr G Thyagarajan, Director, RRL, Hyderabad, had organised a get-together at Hyderabad of all the scientists working on various aspects of Bhopal gas leak disaster. Mr Finzen and Mr Zelle were taken to Hyderabad to discuss all technical matters concerning the disaster with these individuals. The get-together was spread over two days during which intensive discussions were held between the R,Z, L & K team and the scientists on various aspects including the design and operation of MIC plant, safety systems available at UCIL, sequence of events leading upto this incident, the UCIL report on Bhopal incident investigation published in March 1985, the observations made during Operation Faith, the role of various scientists and engineers during Operation Faith, various probable causes of the incident, legal proceedings in US courts etc.

APPENDIX I

**SUMMARY OF VISIT REPORT COMPILED
BY SCIENTISTS OF REGIONAL RESEARCH
LABORATORY, HYDERABAD,
AFTER VISITS TO UNCIL, APD PLANT,
BHOPAL**

Visit Report No.1

Subsequent to the leakage of MIC (Methyl isocyanate) from the Union Carbide Factory at Bhopal, causing unprecedented number of casualties, Dr S Nagabhushan Rao, Mr S Koteswara Rao and Dr A A Khan, Scientists of the Regional Research Laboratory, Hyderabad, were summoned by DGSIR to Bhopal.

Various hypothesis of the possible causes for the incident were examined by the Chemical Group. As a result, several alternatives for the safe disposal of remaining large quantity of MIC were formulated. Carbamoylation with *o*-naphthol appeared to be the most suitable method.

A 'zero-risk' procedure for the operation was evolved. After taking appropriate precautionary measures, approximately 23 tonnes of MIC from the storage tanks and drums was carbamoylated thus rendering UCIL premises devoid of MIC.

Visit Report No.2

1. Core samples of solids (polymer) were withdrawn from five nozzles available on manhole of tank E-610.
2. Spool pieces and control valves on process vent line (PVH) and level indicator probe were removed and inspected. Solids deposited in these lines/valves were collected.
3. Several valves in the relief valve vent header (RVVH) in MIC structure, sealed by CBI, were opened and substantial quantity of water was noticed at 3 locations out of a total of 11.
4. PVH & RVVH were found to be interconnected on the pipe rack behind MIC storage area. PVH was found to be 'slip blinded' in MIC battery limit area.
5. CBI authorized UCIL to make necessary arrangements for lifting and weighing of the

tank E-610 as per the procedure agreed to by DGSIR.

6. Dr C S P Iyer (BARC) and Dr N R Ayyangar (NCL) plan to visit RRL(H) on 21.2.85 to organize and discuss analytical work pertaining to solid samples and also to conduct trace metal analysis (by ICP) at NFC or DMRL.

Visit Report No.3

1. Visual inspection of Tank 610 was carried out after excavation. The Tank appears to have been subjected to high internal pressure which resulted in bulging between stiffening rings.
2. Scrutiny of MIC Quality Control Reports was made to ascertain whether MIC had been withdrawn and utilized between 3.10.84 and 5.12.84 from Tank 610. Analytical data of all MIC samples was collected.
3. MIC samples from Tank 610 Chiller, Tank 610 and 619 were analysed for CBI and report submitted.
4. Discussions were held with CBI in presence of Mr G Ramachandran, Joint Director, CBI. Minutes of meeting are enclosed in Annex.III. The one point which came for discussion and proposed by CSIR Scientists regarding legal implications of conducting the simulation exercise was deleted by CBI (Ann. III A).
5. CBI requested for a brief list of points relating to safety aspects of MIC storage which can be passed on to Interpol for comparing the Institute plant with UCIL. This was prepared and handed over
6. It was observed from data sheets that the pressure in Tank 610 decreased from 20 psig to 2 psig on 21.10.1984 during the second shift. Thereafter this tank remained at 1-2 psig while other two tanks could be maintained at 15-25 psig.

7. A consignment of 44 samples was recovered from CBI custody and 400 of these, consisting of core (residue) material, solid deposits in pipe lines etc, water drained from RVVH, liquid collected from PSV downstream, line on MIC Tank 611 on 13.3.85 etc, were handed over to MG Sane of NCL from taking them Pune. 4 residue samples (Series C) will be taken to RRL, Hyderabad.

Visit Report No.4

1. Five sampling windows measuring approximately 12"x12" square or 12" dia circle were cut open in the SS Tank 610 for withdrawing Core samples in the presence of representatives of UCC, UCIL and CBI.
2. The inside of tank 610 was video filmed through one of the sampling windows.
3. Samples of residue were withdrawn from all the windows and the manhole, identified and sealed in appropriate bottles. Sampling windows were sealed properly afterwards to avoid any ingress of moisture.

Visit Report No. 5

1. Mr Bruce Finzen and Mr. Lawrence Zelle belonging to the Lawyers firm Robin, Zelle, Larson and Kaplan (RZLK), who have been entrusted with the legal aspects of UCIL case by the Government of India, visited the UCIL plant. They were given full description of the events leading upto the Dec'84 incident of MIC. Various technical queries raised by them were also answered.
2. Amounts of chloroform and phosgene present in MIC of Tank 610 were worked out from the data on analysis of plant samples.

Visit Report No.6

1. Decontamination procedures pertaining to MIC structure and proposed by UCIL, were examined with the help of documents available at UCIL. Discussions were also held with UCIL personnel to seek certain clarifications. The decontamination procedures were cleared subject to certain conditions, e.g., complete

and thorough washing of the Vent Gas Scrubber system, draining of PVH and RVVH in presence of CBI and Min. of Chemicals (MCF) Team.

2. Various 'Scenarios' proposed by MCF team which individually or in combination might have resulted in the release of MIC were examined. Among the process areas which came for in-depth discussion were MMA storage area, vapouriser, and pre-heated, pyrolyzer accumulator, caustic back up for VGC, and Off space MIC. In each case engineering documents eg, P & I diagrams etc, were used and the process equipment and piping was inspected at site.

Visit report No.7

1. Metals samples of the wall of Tank 611 were marked, not identified and sealed for further examination.
2. Tank 611 remains in good shape - no distortions were noticed on close examination.
3. Detailed measurements were taken of Tank 610 to determine the extent of deformation of the tank between the stiffening rings and outside.
3. Video film of phosgene filters, 6" RVVH isolation valve near the filters, service drops behind MIC storage area, GBB header, process and instrumentation nozzles of Tank 619 were taken by CBI. MCF team provided the commentary.

Visit Report No.8

1. Tank 610 which was involved in the incident releasing large quantities of MIC, was lifted on a trailer taken to a weighing bridge, weighed and brought back to the position previously occupied by 611.
2. Supervision of the above operation was mainly carried out by engineers from EIL Delhi. Assistance was rendered in coordinating the work between UCIL, CBI and Government of India's scientific team deputed to Bhopal to oversee the operations.

**NAMES OF SCIENTISTS OF
REGIONAL RESEARCH LABORATORY,
HYDERABAD, AND THEIR DATES OF
VISIT TO UCIL, APD, BHOPAL**

S.No.	Name of Visiting Scientists	Date of visit
1.	Dr S Nagabhushan Rao Mr S Koteshwar Rao Dr A A Khan	5-22 Dec.1984
2.	Mr M Anandam Dr A A Khan	10-15 Feb 1985
3.	Mr M Anandam Dr A A Khan	12-15 March 1985
4.	Mr M Anandam Dr A A Khan Dr U T Bhalerao	6-10 Apr 1985
5.	Mr M Anandam Mr M Hasan Dr A A Khan	25-26 May 1985
6.	Mr M Anandam Dr A A Khan	11-15 June 1985
7.	Dr A A Khan	6-8 Jan 1986
8.	Dr A A Khan	24-27 Sept 1986

APPENDIX II

A Note on Developments after Operation Faith

1. Operations at Bhopal
- 1.1 Sampling
- 1.2 Decontamination
2. MIC Analysis at Bhopal
3. Investigative Analysis at NCL, Pune
4. Visit R, Z, L & K teams
5. Medical studies (ICMR, MP Medical colleges)
6. Relief operations (MP Government, Bhopal)
7. Toxicological studies (ITRC)
8. Environmental studies (NEERI)
9. Agricultural studies (IARI)

P.S: Items 1 to 4 are covered in the note.
Rest of the items may have to be got from the various institutions marked in the parenthesis.

APPENDIX III

CONFIDENTIAL (From: Dr. G. Thyagarajan
DRRL-H)

ENGINEERING ASPECTS OF UCIL PLANT

Mechanical Design:

1. Manhole entry is not as per ASME Code. The clearance available through the manhole is less than 300 mm.
2. No insulation is provided for the tank which is supposed to contain MIC at sub-ambient temperature. A 30ton chiller is inadequate for the load. Providing for chilling of MIC without insulating the tank serves no purpose.
3. No provision is made for free/unrestricted access to the inside of the tank for inspection/contingencies.
4. Relief valve vent header of MIC storage should have been separately routed to the vent gas scrubber instead of connecting it to RVVH of the MIC plant.

Vent Relief & Safe Disposal:

1. If the contents of any of the storage tanks are inadvertently contaminated with water, and the contamination is manifested by a rise in temperature or pressure, no backup system has been provided for unloading and safe disposal of the contents.
2. Vent gas scrubber (VGS) can take initially 40 gpm of liquid MIC for first 30 min. and subsequently 9 gpm only when the temperature rises to 70°C. this is equivalent to only 2 tonnes per hour. Hence VGS is not designed to cope with relief valve vent header (RVVH) loads.
3. Transfer of MIC between tanks has to be carried out manually which is a tedious and time consuming operation.
4. Safety relief valve is designed for handling vapour only, whereas during an emergency both liquid and vapour enter the line generating excessive back pressure.

5. VGS is located approx. 350 ft away from the MIC storage area with the intervening pipe line with no vapour-liquid disengagement chamber/vessel.

Maintenance Practice:

1. RVVH is cleaned by purging with water, thereby increasing the possibility of water entering into the MIC storage tanks speedily when PVH is interconnected to RVVH.
2. Removal and replacement of rupture disc is possible only after isolation of the tank. During this period the tank has no safety device on it.
3. No provision is made for cleaning the process pipe connecting downstream of N₂ bleed valve to process vent header (PVH).
4. No provision is made for cleaning the non-return valve on nitrogen inlet line.

Process Instrumentation:

1. The type of level indicating system selected is not suitable for MIC as it gets clogged with solid.
2. The "Pressure high" alarm was not operative. (Please check from records).
3. The PVH nitrogen bleed valve has a narrow aperture (orifice) which is susceptible to clogging by solids.

These comments by consensus of:

Dr Asad Ali Khan
Mr S Koteswara Rao
Mr M Anandam
Dr Nagabhushan Rao
Dr U T Bhalerao, and
Dr G Thyagarajan

Possible causes of the accident	Comment		
A - Ingress of a small amount of water from impure N ₂ - led to destruction of inhibitor phosgene, liberating some chlorides, which caused MIC polymerization.	Possibly, but reaction too slow to have triggered the sudden lift of (incubation time data from lit). If this was the reason, why 611 did not lift off? Pressure data do not favour this.	o Formation of various polymerisation products in the tank.	- All these can be explained.
B - Some HCl liberated together with rust or such Fe particles, generated a polymerisation, release of heat, MIC vapourisation etc.etc.		o Because of high temperature, if the MIC in 610 was off-spec. material containing large % of CHCl ₃ . Then decomposition of CHCl ₃ might have taken place at high temperature giving rise to hydrolysable chlorides.	- CHCl ₃ can be decomposed at high temperature, so explainable.
C - A surge of water entered the tank, and the following occurred:		Concurrent rapid polymerisation of MIC accelerated by Fe, FeCl ₃ , etc.	
<ul style="list-style-type: none"> o MIC-water reaction, forming CH₃NH₂, CO₂, DMU and TMB etc. o Temperature induced rapid polymerisation of MIC itself. o Vapourisation of substantial quantity of MIC and release into the air. 	<ul style="list-style-type: none"> - Well known - Well known - Records show the temperature shot upto not less than 175°C. (trimer sublimes at 175°) 	610 MIC was sufficiently off - spec. to have polymerised, aided by metallic impurities in the tanks.	

By consensus of:

Dr Asad Ali Khan
 Mr M Anandam
 Mr S Koteswara Rao
 Dr Nagabhushan Rao
 Dr U T Bhalerao, and
 Dr G Thyagarajan

Excerpt from Operating Manual, p. 138,
 Nov. 1984

The instruments on MIC Transfer line from MRS condenser liquid outlet and storage tank inlet.....

Temp. diff. between two temp. sensing points is measured. MIC takes 12 to 15 mts. between the two temp. sensing points. Time is ade-

quate for reaction to occur and can be detected in the event of contamination. The instruments have a sensitivity to detect a 1°C temp. This is equivalent to less than a gallon of water per day reacting in 1411 lb/hr MIC stream.

SEQUENCE OF EVENTS TOWARDS THE ACCIDENT

- 22-10-84:- MIC production and filling of tanks 45 t each into 610 and 611.
- 25-11-84:- Sevin production in progress. From 611, to 7x4 t = 28 t drawn leaving 17 t in 611.
- 2-12-84
- 30-11-84:- Problems in pressurising 611
So went back to 610; N₂ lines to 610 are also found blocked. RD of 610 was intact.

Back to 611, copper tubing was connected in N₂ bleeders and tank was pressurised.

Sevin production was continued till accident occurred.
- 2-12-84:- MIC plant was under maintenance
- When did this start? Cleaning of vent header
- Gleaning of VH with water in progress at 10.00 p.m. Statements to be checked. Important.
- Detection of MIC vapour and water at 55-60' level from the VH.
- Presumably people rushed to control room; did not return to the site.
- Pressure readings of 610 at 2220: 2 psig on 2.12.84 2245: 10 psig 0015: 12 psig 0100: Pressure gauge needle stayed up. 0130: Safety valve reseated.
- Shift changes at 2245

22nd Feb. 1985

Hyderabad
G. Thyagarajan

NEGLIGENCE

1. Relief valve vent header and process vent header should *not* have been interconnected. This interconnection increased the possibility of water entering MIC tanks. It is well known that MIC reacts violently with water.
2. Relief valve vent header should *not* have been flooded with water.
3. The 6" CI valve located on RVVH near phosgene vaporiser should have been slip blinded before admitting water through a hose - this is required as per the maintenance manual. This is also essential to avoid water entering the RVVH which is also connected to MIC tanks 610, 611 and 619.
4. Vent gas scrubber and flare were not in operation.
5. Analysis of residue in tank 610 shows presence of large quantities of hydrolyzable chlorides indicating the off-spec. MIC *must* have been charged into this without knowing the consequences.
6. Scrubber and flare should *not* have been taken down for maintenance as long as huge quantity of MIC was stored in tank farm.
7. Detailed hazard management procedures are neither available nor followed to cope with sudden and large releases of MIC stored in tank farm.
8. No effective steps for mitigating the impending disaster were taken although pressure in tank 610 started rising 2-3 hours before MIC release. At 22²⁰ hrs pressure had gone 10 psig (normal pressure = 2 psig). MIC release occurred after 00¹⁵ hr.
9. Civil authorities were not informed of the impending disaster whereby *preventing* them from taking necessary steps between 22²⁰ and 00¹⁵ hours before MIC was actually released.
10. After the disaster appropriate medical treatment could not be provided because no information was made available.
11. There is no monitoring method for knowing whether water has entered or is entering MIC tank.
12. What was the time lag between release of MIC and actual reporting to civil authorities?

G. Thyagarajan
Hyderabad, 22-11-85

NATIONAL AERONAUTICAL LABORATORY
BANGALORE

INVESTIGATION ON THE STAINLESS STEEL PLATES
FROM THE METHYL ISOCYANATE STORAGE
TANKS E-610 AND E-611 OF UNION CARBIDE PLANT
AT BHOPAL

OCTOBER 1986

Following pages contain the Report on investigations on stainless steel plates from MIC storage tanks No. E-610 and E-611 of Union Carbide Plant at Bhopal by NAL. Methods of chemical analysis and metallography using electron microscopy have been employed for these investigations.

The following scientists participated in this investigation .

Dr V. Ramachandran

Dr A.C. Raghuram

Dr R.V. Krishnan

Mr S. Radhakrishnan

Mr R. Rangaraju

Mr M.A. Parameswara

Mr M.A. Venkataswamy

Dr S.R. Rajagopalan

Mrs Bharathi Bai J. Basu

Mr R. Kannan

Help was also received from the staff members of the (1) Regional Sophisticated Instruments Centre, IIT., Madras (2) Department of Chemistry, IIT., Madras and (3) Solid State and Structural Chemistry Unit, IISc., Bangalore, in analysing the deposits on the plates.

**INVESTIGATIONS ON STAINLESS STEEL
PLATES FROM METHYL ISOCYANATE
TANKS NO. E-610 AND E-611 OF
UNION CARBIDE PLANT AT BHOPAL**

INTRODUCTION

Following the accident in December 1984 at the Union Carbide Plant at Bhopal, National Aeronautical Laboratory was requested to carry out metallurgical investigations on samples cut from the stainless steel tanks No.610 and 611 in which methyl isocyanate had been stored prior to the accident. The tank 610 removed from its mound is shown in Fig. 1. It is about 2.5 m in diameter and 12 m long, made of stainless steel plates of 8mm thickness along the straight portion and about 10 mm at the dished ends. Tank 611 is said to be similar to tank 610. Specimens cut from the dished end and also from the barrel at various locations as shown in Fig. 2, were supplied for laboratory examination.

VISUAL EXAMINATION

When tank 610 was removed from its mound, it was found that its external surface had a coating of bitumen with fibre reinforcement. After peeling the coating, the tank surface was examined. There were no signs of corrosion on

the external surface of the tank. There was no evidence of burning or charring of the bitumen coating. The soil sticking to the bitumen was loose and showed no evidence of sintering. These observations suggest that the tank had not been exposed to very high temperatures.

In tank 610, there was a strongly adhering dark deposit on the inner surface of the plate cut from the top of the tank. Colourless crystalline material was also present on this deposit. Fig. 3 shows the appearance of these deposits. The plates cut from the dished end and from the sides of the tank had similar deposits but the amount of crystalline deposits was more and they had slight greenish tinge.

In the samples from tank 611 sent to NAL, there were no such deposits on the inner surface. However, there was a brownish stain at a few locations as shown in Fig. 4.

CHEMICAL ANALYSIS

Chemical analysis of the samples from the plates for the main alloying elements gave the following results:

Tank No.	Sample location (Ref. Fig.2)	% Mn	% Cr	% Ni	% Mo
610	WA (dished end)	0.86	20.24	10.03	Nil
"	WB (barrel)	1.73	20.32	8.7	0.35
611	WA (dished end)	0.67	17.64	11.14	< 0.02
"	WE (barrel)	1.30	17.74	9.86	0.41

It was reported that the dished end was made of 304 stainless steel (composition limits: Mn 2% max, Cr 18-20%, Ni 8-11%) and the barrel made of 316 stainless steel (composition limits: Mn max, Cr 16-18%, Ni 10-14%, Mo 2-3%). If the plates WB and WE (taken from the barrel) are of 316 stainless steel, then the observed molybdenum content in these samples is less than that for material of that specification.

The colourless deposit in tank 610 was found to contain dimethyl urea, trimethyl biuret, trimethyl cyanurate and some hydrolysable chloride. Besides it showed presence of nickel, chromium, iron and traces of calcium and sodium. The tenacious deposit in tank 610 was found to contain C,N,O and chloride.

The plates from tank 611 sent to NAL, shown in Fig. 4, exhibit a few brownish patches. These patches appear to be rust.

SCANNING ELECTRON MICROSCOPY

After removal of the deposit with organic solvents and ultrasonic cleaning, the inner surface of both types of plates from both the tanks was found to be pitted. Fig. 5 to 8 show shallow pits on the inner surface of the plates, taken in a scanning electron microscope.

METALLOGRAPHY

Metallographic examination of the inner surface

as well as the transverse section of the samples was carried out. Fig. 9 and 10 show the microstructures of samples taken from tanks 610 and 611. The inner surface of the plates indicates equiaxed grains with twins characteristic of annealed material. The transverse section of the samples shows a banded structure, as seen in Fig. 9(a), 9(e), 10(a) and 10(e) which is not uncommon in rolled plate material.

DISCUSSION

Metallography of the stainless steel plates from both the tanks reveals only normal microstructure. In such stainless steel, microstructural changes will be perceptible only if the material is exposed to temperatures above 650°C. Further, plates of tank 610 exhibited normal hardness values w/t' no variation along the thickness. This indicates that the inner surface of the plates has not experienced temperatures high enough to soften the material. On the external surface of tank 610 there is no evidence by bitumen burning. Even the soil was loose, without any consolidation or sintering. From these considerations it is concluded that the interior of the tank 610 could not have experienced any temperature higher than about 650°C.

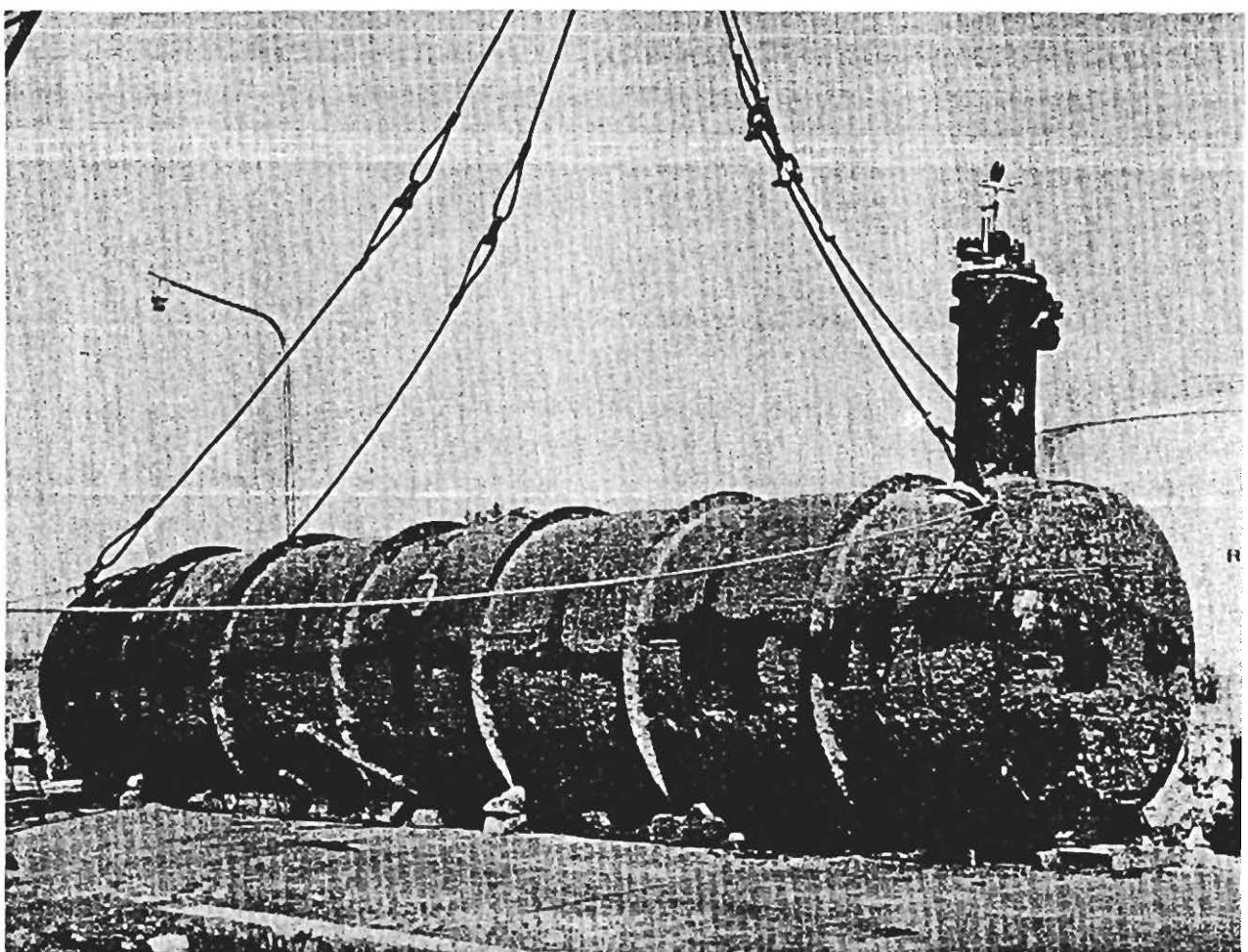


Fig.1: Methyl Isocynate Tank 610

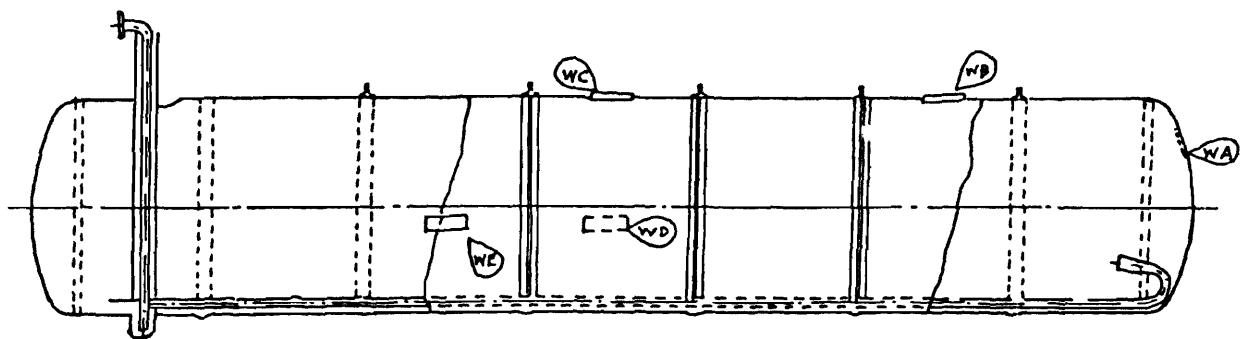


Fig.2: Location of samples removed from tanks 610 and 611 for laboratory examination.

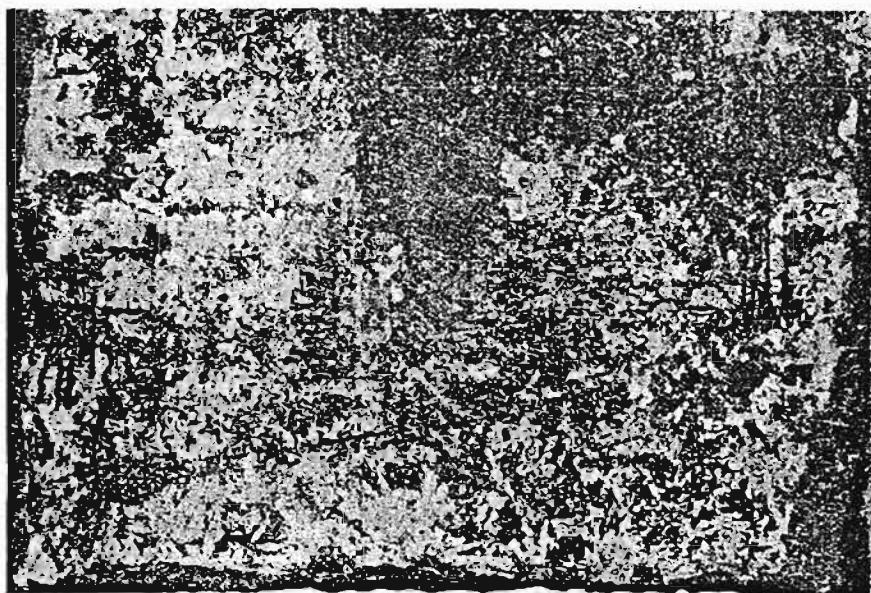


Fig. 3: Deposits on the inner surface of tank 610

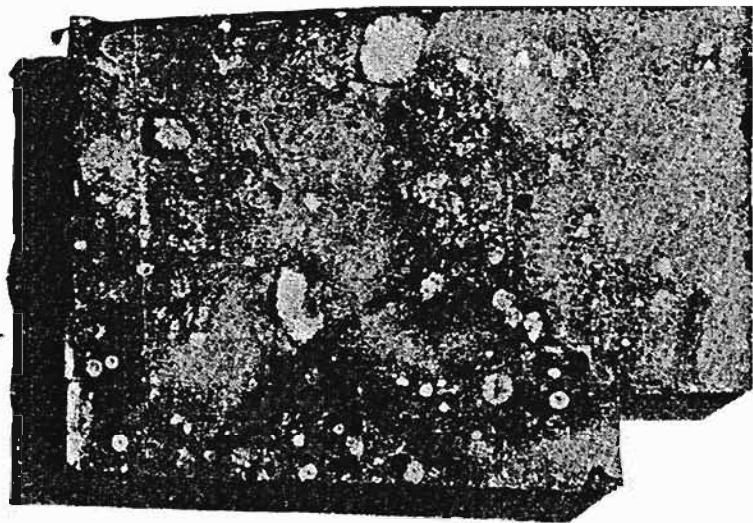
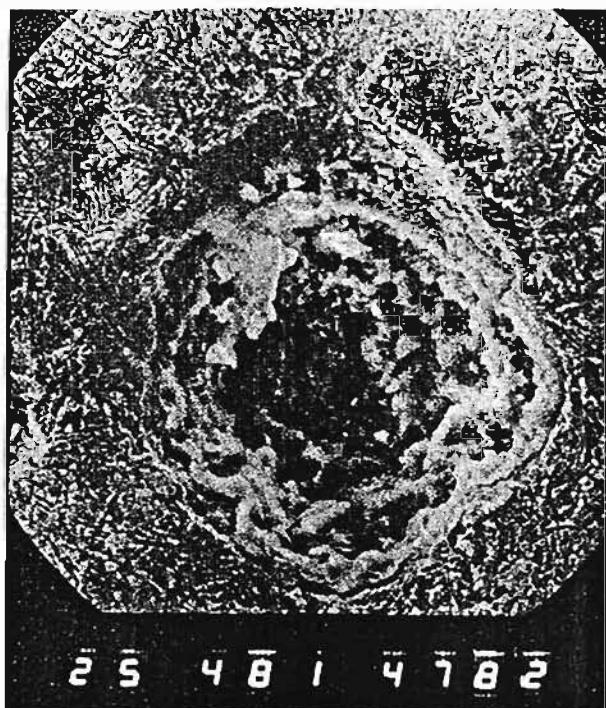


Fig.4: Brown stain on the inner surface of tank 611



25 101 4781

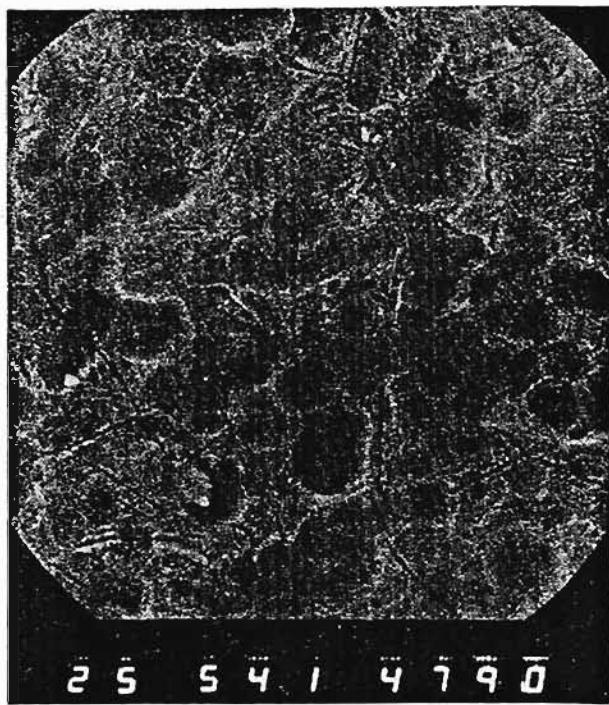
(a) 100X



25 481 4782

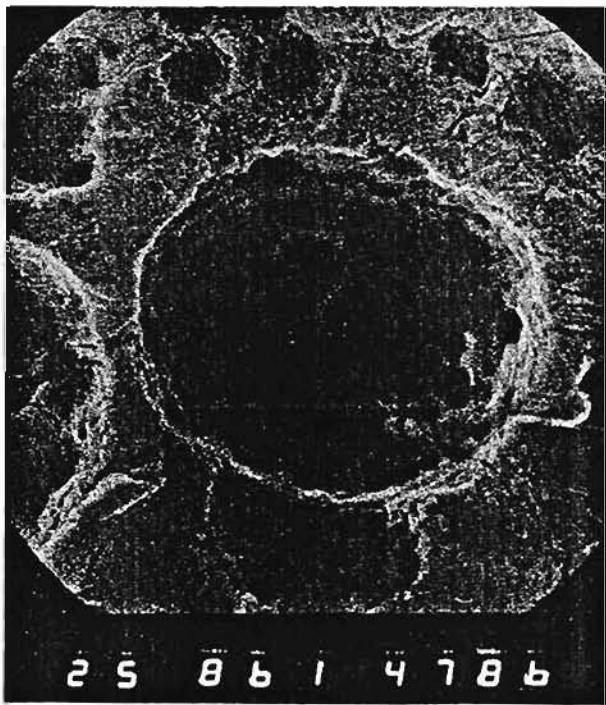
(b) 480X

Fig.5: SEM photographs of inner surface of plate WA of tank 610 showing pits



25 541 4790

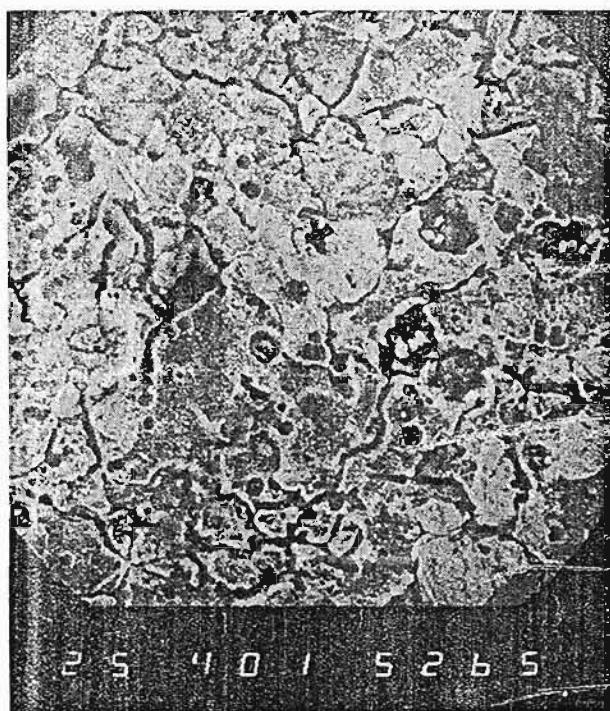
(a) 540X



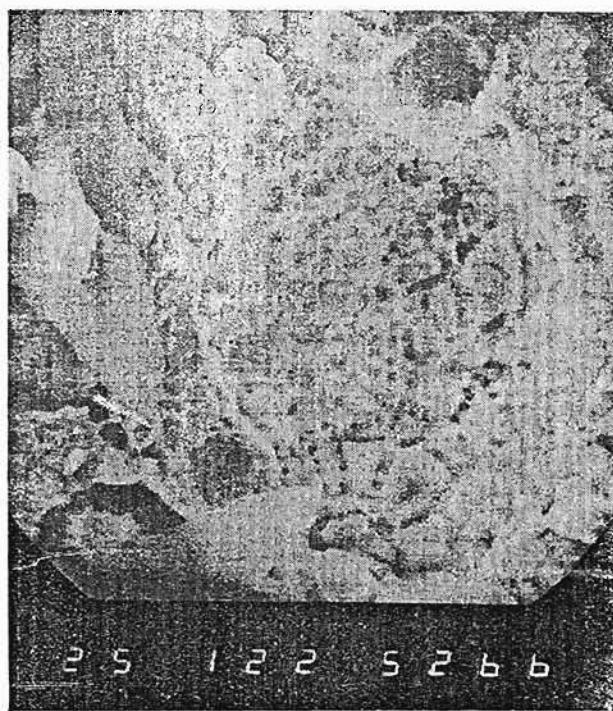
25 861 4786

(b) 860X

Fig.6: SEM photographs of inner surface of plate WB of tank 610 showing pits

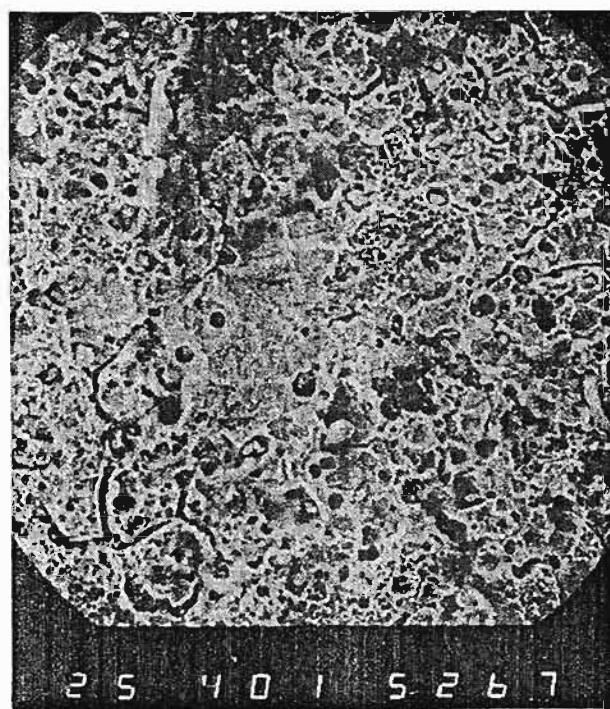


a) 400X

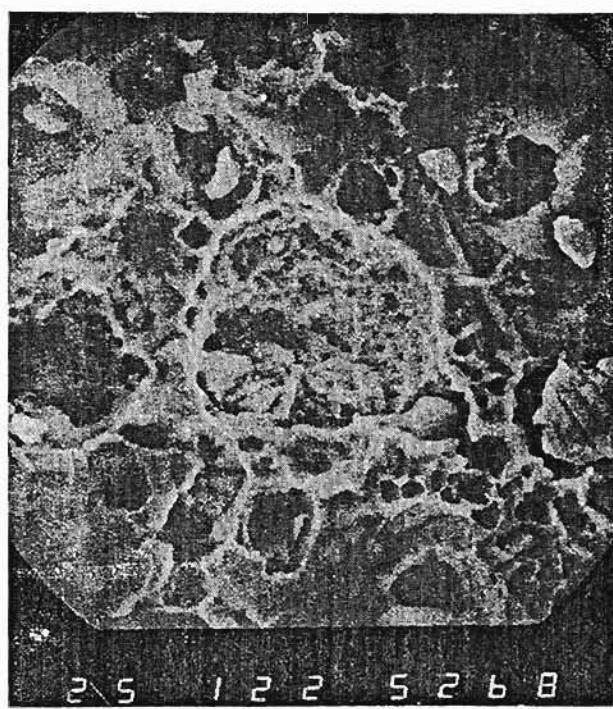


b) 1200X

Fig.7: SEM photographs of inner surface of plate WA of tank 611 showing pits

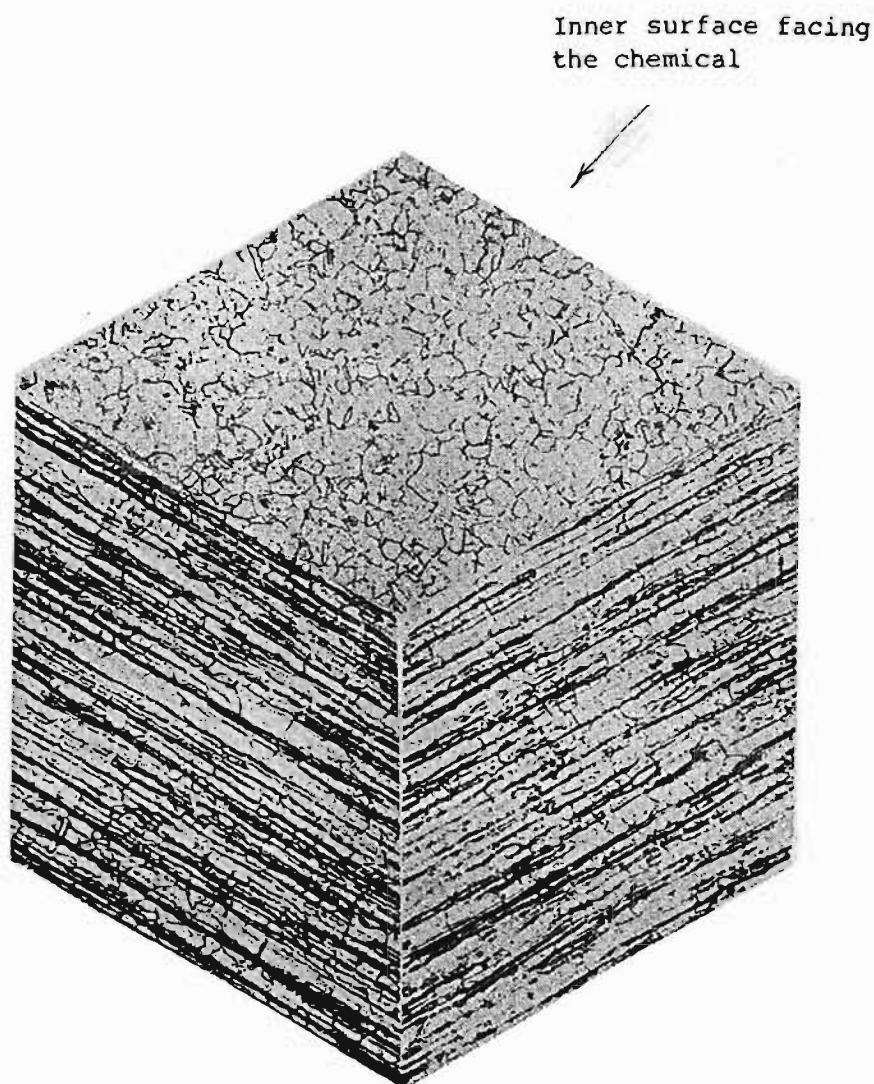


(a) 400X



(b) 1200X

Fig.8: SEM photograph of inner surface of plate WB of tank 611 showing pits



*Fig. 9(a): Microstructure of the three sides of specimen from plate WA Tank 610.
Magnification: 150X*

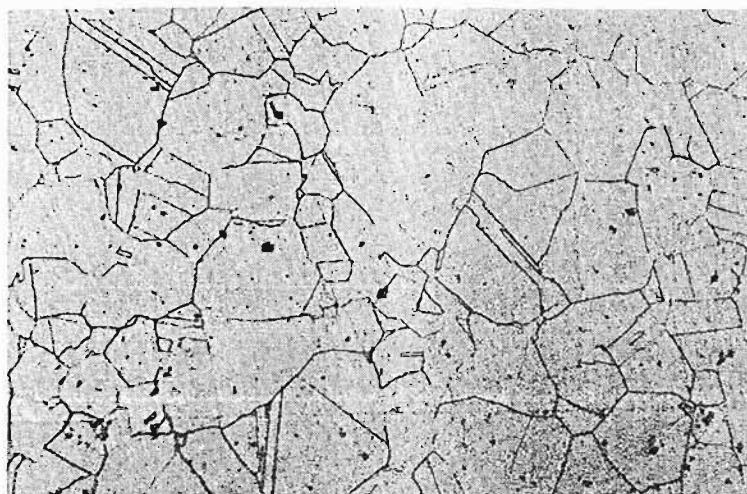


Fig.9(b): Microstructure of the inner surface of
specimen WB, Tank 610.
Magnification: 100X

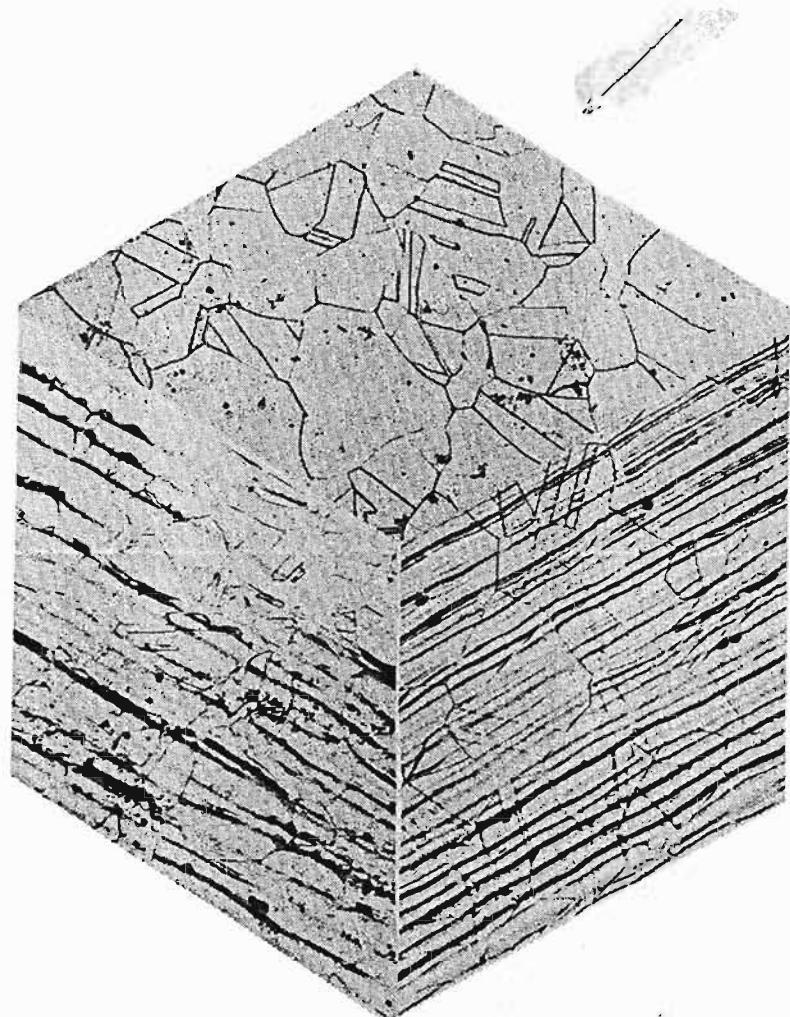


Fig.9(c): Microstructure of the inner surface of
specimen WC, Tank 610.
Magnification: 100X

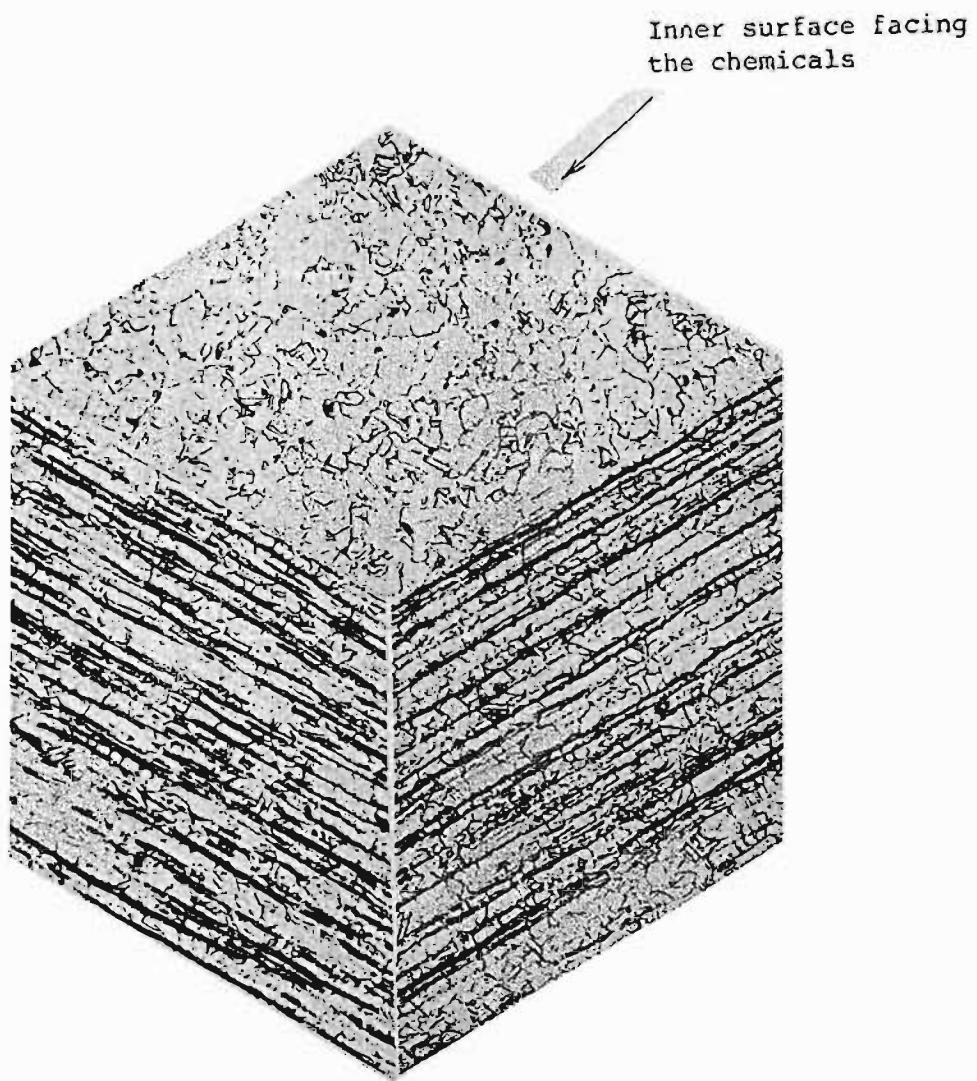


Fig.9(d): Microstructure of the inner surface of
specimen WD, Tank 610.
Magnification: 100X

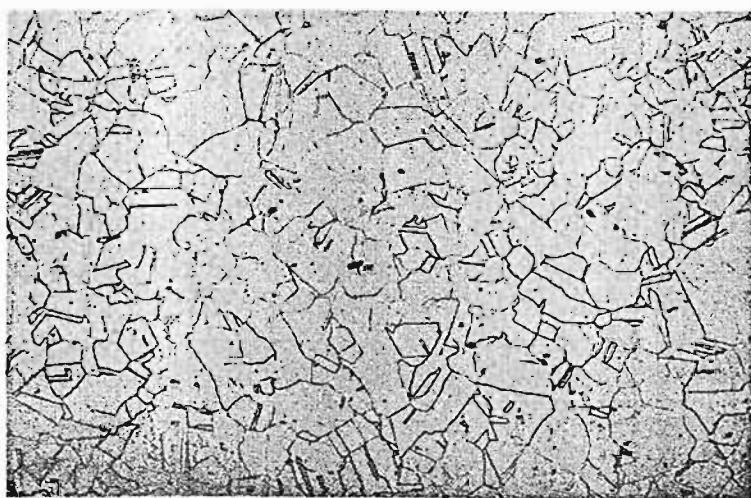
Inner surface fac
the -chemical



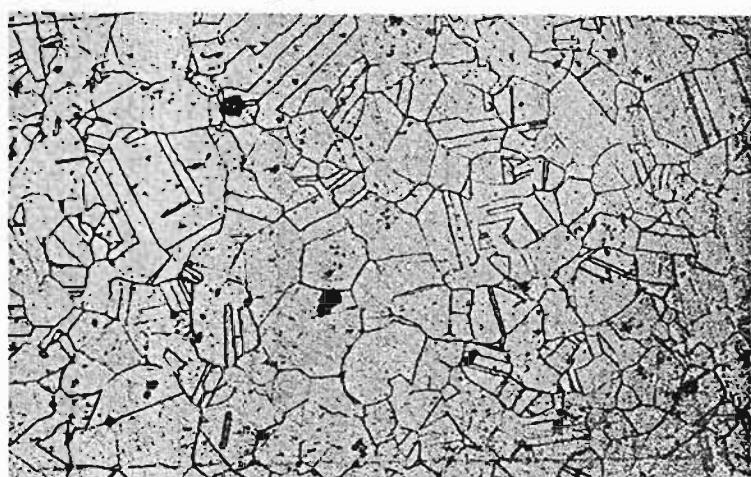
*Fig.9(e): Microstructure of the three sides of
specimen from plate WE, Tank 610.
Magnification: 150X*



*Fig.10(a): Microstructure of the three sides of
specimen from plate WA, Tank 611.
Magnification: 150X*



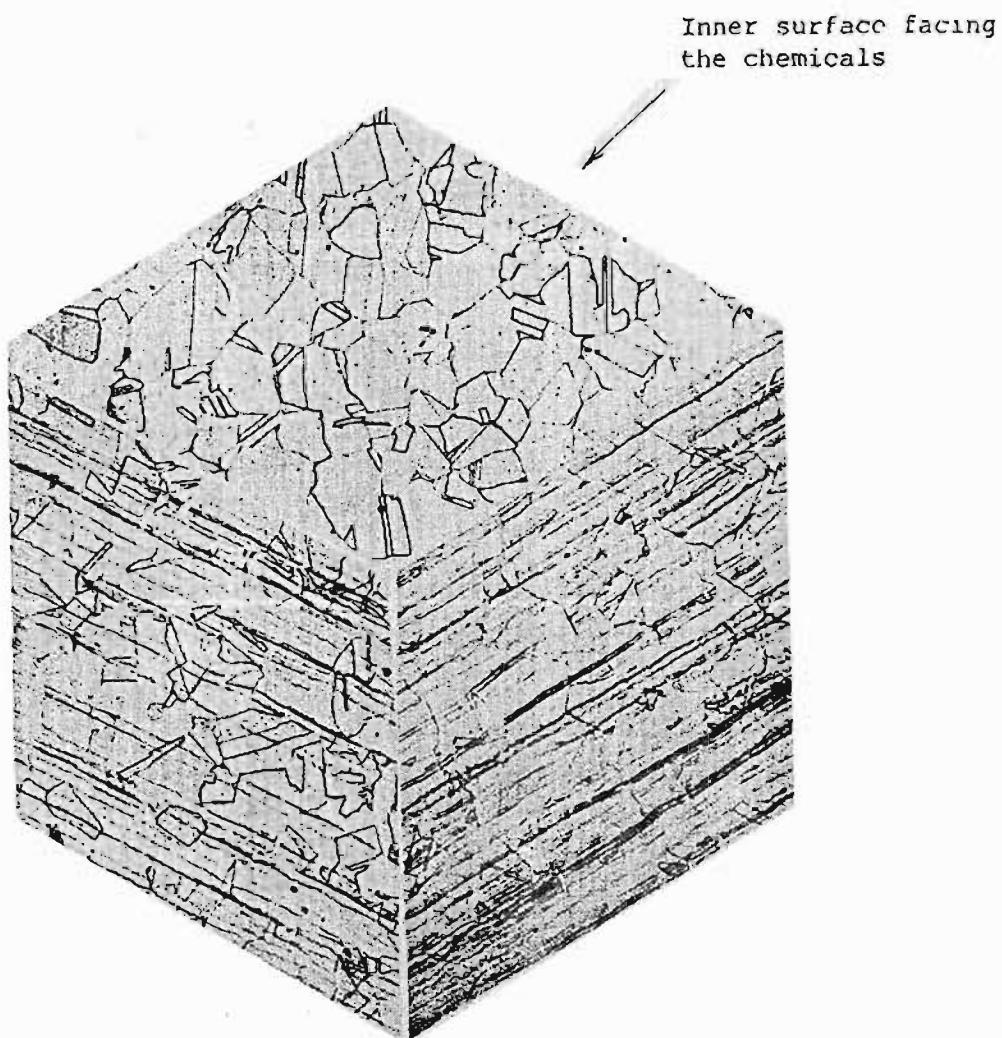
*Fig.10(b): Microstructure of the inner surface
of specimen WB, Tank 610.
Magnification: 100X*



*Fig.10(c): Microstructure of the inner surface
of specimen WC, Tank 611.
Magnification: 100X*



*Fig.10(d): Microstructure of the inner surface
of specimen WD, Tank 611.
Magnification: 100X*



*Fig.10(e): Microstructure of the three sides of
specimen from plate WE, Tank 611.
Magnification: 150X.*

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BIO-DEGRADATIONAL AND ANTI-CHOLINESTERASE ACTIVITIES
OF METHYL ISOCYANATE IN
AQUATIC ENVIRONMENTS OF BHOPAL

1985

The following pages contain a brief summary of studies on biodegradation and anti-cholinesterase activities of MIC in the aquatic environment, conducted by the National Institute of Oceanography (NIO), Goa, with samples collected in December 1984, February and April, 1985.

BIO-DEGRADATIONAL AND ANTI-CHOLINESTERASE ACTIVITIES OF METHYL ISOCYANATE IN AQUATIC ENVIRONMENTS OF BHOPAL

INTRODUCTION

A team of three scientists of NIO (Dr. R. Sen Gupta, Dr. A. Sarkar and Mr. T.W. Kureishy) initiated a study, three weeks after the leakage of methyl isocyanate (MIC) gas, in the environments of Bhopal. The study was confined to the examination of the end-products of degradation of MIC in aquatic environments by analysing water and fish samples from the Upper and the Lower Lakes. Besides, a few blood samples were collected from a representative age group of affected persons of the gas leakage and the plasma was analysed for acetylcholinesterase (AChE) activity.

The initial data indicated that there might be some long term influence in some fishes and, of course, in human beings. No data on the same components, collected earlier from the same environment, were available to compare our results with and to examine the eventual effects. We, therefore, planned a monitoring programme for a period of six month with bi-monthly observations. Data were collected during the last weeks of December 1984, February and April, 1985.

OBJECTIVES

MIC undergoes a series of exothermic polymerisation reactions with trace amounts of water in molar proportions to produce various bi-products, for example, N-methyl carbamic acid, N-N'-dimethyl uric acid, N-N'N trimethyl isocyanouric acid etc. But the end product of all these, in excess amount of water, is mono-methylamine. We, therefore, decided to measure pH and the concentrations of monomethylamine, ammonia-nitrogen and urea-nitrogen in water and the bio-accumulation of methylamine in the aquatic organisms. Moreover, MIC is known to inhibit the AChE activities in human blood and the same can be expected to occur in

the aquatic organisms as well. We attempted to estimate in both. The normal range of AChE activities in freshwater food fishes is not clearly known. We, therefore, collected a few samples of the same species of fishes from a MIC-uncontaminated environment, and analysed them for mono-methylamine and AChE activities to establish their normal ranges. We used these values as reference standards.

There are two lakes at Bhopal. One of them, the Upper Lake, is the source of water supply to the city and is quite far away from the Union Carbide factory, the source of MIC pollution. The other one, the Lower Lake, is very close to the factory, smaller in area and is completely eutrophicated.

SAMPLING AND ANALYSIS

The period of collections of the first set of samples was from 23 to 30 December 1984. Water samples were collected, using a Niskin PVC water sampler, from various depths of the Lower Lake. Due to technical problems, collection was restricted only to the surface water of the central part of the Upper Lake. All the samples were examined for their pH values on the spot using a field pH meter. The second and the third set of samples were collected from 25 to 26 February and 1 to 2 May 1985 respectively.

Ammonia-nitrogen and urea-nitrogen concentrations in water were estimated by applying the indophenol blue method and the diacetyl monoxime method respectively using a field spectrophotometer, at the Regional Research Laboratory, Bhopal (RRL):

10 litres of water samples from the surface and 5 metre depth of the Lower Lake and from the surface of the Upper Lake were each shaken continuously for 6 hours with activated charcoal and allowed to settle. The clear supernatant was decanted off and the rest was collected in PVC

bottles for analysis at the NIO laboratory in Dona Paula, Goa.

Several varieties of large common lake fishes were collected from the Upper Lake. Their identification, length, sex and stage of maturity were noted down as far as possible. They were dissected and representative portions of different body tissues were collected and deep frozen for analysis at NIO, Goa. The Lower Lake was completely eutrophicated and was devoid of the same varieties of fish as the Upper Lake. Whatever small fishes could be collected from this lake were frozen immediately for further analysis. However, all the species of fish were not available on all the occasion.

Four blood samples, 2 ml each, were collected from MIC poisoned male patients, still lying at the Hamidia Hospital only during our first visit to Bhopal. These samples were centrifuged and only the plasma were collected, frozen and brought back to NIO.

At the NIO laboratories, the activated charcoal extracts of the water samples were brought to acidic pH by adding 4N HCl to convert the amine into its hydrochloride. This was done as the hydrochloride is stable for analysis. The adsorbed amines were desorbed by shaking for 6 hours with 0.1 N HCl.

Different tissues of fishes were digested with 4N HCl overnight to extract the amine. The digested extracts were then neutralized by 10N NaOH in a reaction flask. The methylamine gas, thus released, was taken into 0.001N HCl using nitrogen gas as the carrier. All the aqueous solutions were treated similarly.

Attempts were made to analyse the hydrochloride solutions by both gas chromatography and spectrophotometry. An alkaline column (USCON 5% + 2% KOH) with column temperature at 50°C, N/P detector temperature 200°C and N₂ as carrier gas at the rate of 25 ml/min., was used in a Perkin Elmer Sigma Gas Chromatograph. But the peaks could hardly be detected. We, therefore, analysed the samples spectrophotometrically, concentrating the acid solutions to 5 ml, applying the lactose method. The red-coloured complex was measured at 540 nm. The detection limit of the method, calculated by replicates of several standard solutions, was 0.2 ug/ml of the test solution.

For the determination of AChE, enzymes from the different tissues of fishes were extracted by grinding in presence of saline water and phosphate buffer (pH 8) and centrifuged at 300 rpm under refrigerated conditions. These extracts and the plasma from human blood were

analysed spectrophotometrically for their AChE activities, using acetylcholine bromide as the substrate. The absorbance was measured at 620 nm. Detection limit, determined by replicate analyses of standards, was 0.01 ug/ml of the test solution.

RESULTS

The results of the measurements of the biodegradational products and anti-cholinesterase activities are presented in Tables 1 through V.

(i) *pH, ammonia and urea in water*

Table I indicates the values of pH, ammonia-nitrogen and urea-nitrogen concentrations of water at different depths of the two lakes on the three sampling occasions. It was noticed during some of the sampling that the effluents from the city of Bhopal were being discharged into the Upper Lake. These effluents can be expected to contain high amounts of nitrogen and phosphorus, the effects of which could be seen in the coastal areas of the Lake in the growth of copious amounts of weeds and algae. As stated earlier, the Lower Lake was fully eutrophicated which was evident from the large quantities of algae in water samples from all the depths. The presence of these algae will certainly add to the concentrations of nitrogen and phosphorus compounds in water, perhaps influenced by the instant toxic effect of MIC, before its breakdown in water.

Values for pH, ammonia-nitrogen and urea-nitrogen in the Lower Lake, in general, decreased from the first to the second occasion while on the third occasion they increased. We presume that due to the instant toxic effect of MIC the organisms died and sank to the bottom, which was evident from the high concentrations of ammonia-nitrogen and urea-nitrogen in the bottom waters. A considerable contribution must have also come from the degradation of MIC which resulted in very low concentration of methylamine in water (Table II). Values during the third occasion would indicate eutrophicated condition. High values at the surface waters of the upper Lake was due to the effluent discharges, as methylamine was absent on all the three occasions (Table II). For comparison, we also estimated pH, ammonia and urea in tap water of RRL during the first occasion. These values appear to be fairly reasonable by ISI standard.

We made an attempt to compute the mole-percentage of free ammonia, by applying litera-

ture data. In the Lower Lake, these were 13, 11 and 9% of ammonia-nitrogen during the first occasion, while during the subsequent occasions it increased from 60 to 63% at the surface, 5 to 42% at 5 m, and 5 to 26% at 10 m. The toxic limit of free ammonia for aquatic organisms, particularly fishes, is 1.2 mg/l. All the values in the Lower Lake were higher than this limit. No wonder, there is hardly any aquatic life there. In the Upper Lake the mole-percentage of free ammonia at the surface increased from 4 to 78% from the first to the third occasion. Care has to be taken to reduce free ammonia there to enable the aquatic life to sustain.

(ii) Methylamine in Water

Table II presents the mono-methylamine concentrations in water of both the lakes. The concentration in the Lower Lake water decreased from the first occasion (0.03 ug/l at the surface and 0.05 ug/l at 5 m) to the second (0.005 ug/l at the surface and 0.009 ug/l at 5 m). An increase of concentration with depth could be noted. Mono-methylamine was, however, not detectable during the third occasion. It was also not detectable at the surface waters of the Upper Lake on all the occasions. This indicates that the Lower Lake, being nearer to the Factory than the Upper Lake, was comparatively more affected by MIC.

(iii) Methylamine in Fishes

Methylamine concentrations from fish samples of both the lakes and from the uncontaminated environment (UCE) are presented in Table III. Some bio-accumulation of methylamine can be seen in the muscles of *Labio gonus*, *Puntius serrana* and *Mestacemphalus sp.*; in the swim bladder of *Labio calbasu*; and in gills of *Labio calbasu* and *Puntius serrana* from the Upper Lake on the first occasion. The gall bladder of *Labio calbasu* was observed to be highly distended. This may be due to some bacterial or viral infection. Methylamine concentrations in those species of fishes, which could be collected during subsequent occasions, were non-detectable. This would indicate that in course of time the metabolism of the fishes converted the methylamine to some other nitrogenous compounds.

Methylamine concentration in *Puntius ticto* from the Lower Lake was fairly high (9.2 ug/kg wet weight) during the first occasion. This reduced to 2.23 ug/kg during the second occasion to non-detectable during the third. Absence of

methylamine in other species of fishes from the Lower Lake on all the occasions would suggest that *Puntius ticto* was very susceptible to MIC poisoning and took longer time to convert methylamine to other nitrogenous compounds.

Fishes, collected at UCE, did not have methylamine in them. This lead us to conclude that methylamine is not naturally present in fishes. Whatever quantities were observed in fishes from the lakes of Bhopal were certainly the end-product of degradation of MIC. However, in the absence of definite information, it is not sure if these quantities were harmful to the fishes themselves or to human beings after their consumption.

(iv) Anti-cholinesterase activities in fishes

Pesticide poisoning is known to inhibit the AChE activities in human blood. We wanted to examine if the same happens in aquatic organisms, particularly fishes, as well. We, therefore, estimated the AChE activity in different tissues of fish samples from the lakes of Bhopal and from the UCE. The data are presented in Table IV.

On the first occasion, AChE activities of different tissues of fishes from the Lower Lake were markedly lower than those from the Upper Lake. In course of time the values in muscle, gill and liver of *Labio calbasu* of the Upper Lake increased. In fishes of the Lower Lake the values are definitely very low indicating, however, a relative increase with time. The AChE activity in *Glassogobius giurus* showed a significant decrease from the first to the second occasion. We also estimated AChE activities in different tissues of a few species of fishes from the UCE and assumed them to be normal values in those fishes. Comparing the two sets of data, from Bhopal and from the UCE, we could observe the following:

- (a) muscles, gills and liver of *Labio calbasu* from Bhopal, though affected, appear to be recovering with time, excepting the intestines;
- (b) muscles and gills of *Labio gonus* from Bhopal were unaffected, while liver and intestines appear to be affected somewhat; and
- (c) compared to *Puntius stigma* from the UCE, *Puntius ticto* from Bhopal appear to be badly affected.

Similar trends can be expected for the other species of fishes from Bhopal, at least at a first

approximation. We could not get those species of fishes at the UCE at the time of sampling.

(v) *Anti-cholinesterase activities in human blood*

These observations were made in an attempt to study the degree of lowering of AChE activities in human blood caused by MIC poisoning, since such results were expected. The normal process of splitting of acetylcholine by acetylcholine esterase within the nervous system of the body gets stopped due to the blockage of the active sites of the enzyme.

The AChE activities of blood plasma of the MIC-poisoned patients are highly significant. All the values in Table V are well below the expected range of 90 to 150 μ moles/mol of blood plasma in normal human beings with good health. Excepting for the 40-year old patient, the other three values indicate an inverse age-AChE relationship. This can also be due to different degrees of exposure to MIC. This is clearly an indication of some sort of neurological disorder in the nervous system.

CONCLUDING REMARKS

Our observations in the aquatic environments of Bhopal lead us to draw the following conclusions:

- (a) The waters of the Upper Lake appear to have recovered from the effects of MIC, but contain an excessive amount of free ammonia as a result of effluent

discharges. This should be regulated immediately in the interests of drinking water supply and fisheries.

- (b) The Lower Lake is completely eutrophicated and, after the effects of MIC, can be considered as dead for all practical purposes.
- (c) Fishes in the Upper Lake seemed to have recovered from methylamine but the AChE activities in some of their tissues appear to be low. Perhaps it will be useful to regulate the fishing activity, at least for a few months.
- (d) All fishing activities in the Lower Lake, if there are any, should be prohibited.

Depression of AChE activities in human beings leads to the disease *Myesthesia gravis*, marked symptom of which is constant general

marked symptom of which is constant general weakness. Persons affected by exposure to MIC are definitely suffering from this disease, which is said to be incurable. Low AChE activities in some of the fishes from the lakes of Bhopal would indicate that these too have been affected due to the effects of MIC on their environment.

It is not known if *Myesthesia gravis* can be communicable from fishes to human beings consuming them. It is also not known if this disease can be genetically transmitted from one generation to the next. Perhaps, this can form an interesting programme of research to study the long term effects of exposure of MIC.

TABLE I

pH, Ammonia and urea in lake and tap water of Bhopal

Locations	Depth	pH			$\text{NH}_4^+ - \text{N}$ mg/l			Urea-N mg/l		
		A	B	C	A	B	C	A	B	C
Lower Lake	0	7.91		9.52	5.1		9.6	4.7		7.04
Tap Water			7.70		2.75			4.25		
Lower Lake	0	8.39	9.28	9.19	5.49	2.83	6.98	5.50	1.43	2.81
	5	8.31	7.82	8.78	5.05	2.51	12.2	5.17	2.14	8.05
	10	8.18	7.82	7.98	21.07	10.8	24.5	5.25	3.57	11.7

A - after 20 days of MIC accident

B - after 80 days of MIC accident

C - after 140 days of the MIC accident

TABLE II

Methylamine concentrations in lake waters of Bhopal

Locations	Depth	Monomethylamine ($\mu\text{g/l}$)		
		A	B	C
Upper Lake	0	Nil	Nil	Nil
Lower Lake	0	0.03	0.005	Nil
	5	0.05	0.009	Nil
	10	-	-	Nil

A - after 20 days

B - after 80 days

C - after 140 days

TABLE III
Concentrations of Monomethyl amine in different tissues of fishes from
Bhopal and uncontaminated environment (ug/kg) wet weight)

Site of Collection	Name of the fish species name	Muscle			Swim Bladder			Gills		
		A	B	C	A	B	C	A	B	C
Upper Lake	<i>Labio calbasu</i>	N.D.	N.D.	N.D.	5.42	N.D.	N.D.	9.74	N.D.	N.D.
Upper Lake	<i>Labio gonius</i>	4.7	-	-	N.D.	-	-	N.D.	N.D.	-
Upper Lake	<i>Puntius serrana</i>	4.1	N.D.	-	N.D.	-	-	4.2	N.D.	-
Upper Lake	<i>Ompok bimaculatus</i>	N.D.	-	-	-	-	-	N.D.	-	-
Upper Lake	<i>Mesacemphalus sp</i>	4.5	-	-	-	-	-	-	-	-
Lower Lake	<i>Glossogobius giurus*</i>	N.D.	N.D.	-	-	-	-	-	-	-
Lower Lake	<i>Puntius ticto*</i>	9.2	2.23	N.D.	-	-	-	-	-	-
Lower Lake	<i>Chanda nana*</i>	N.D.	N.D.	N.D.	-	-	-	-	-	-
Uncontaminated Environment	<i>Labio calbasu</i> ^a	N.D.	-	-	-	-	-	N.D.	-	-
-do-	<i>Labio rohita</i> ^a	N.D.	-	-	-	-	-	N.D.	-	-
-do-	<i>Labio gonius</i> ^{a*}	N.D.	-	-	-	-	-	N.D.	-	-
-do-	<i>Puntius stigma</i>	N.D.	-	-	-	-	-	-	-	-

A- after 20 days

*- analysed as whole fish

B- after 80 days

a - only one collection

C- after 140 days

TABLE IV
Acetylcholinesterase activities of different tissues of fishes from
Bhopal and from uncontaminated environment in $\mu\text{moI}/\text{mg}$ wet weight

Site of Collection	Name of the fish species name	A			B			C			A			B			C		
		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Upper Lake	<i>Labio calbasu</i>	60.0	62.5	64.1	37.61	35.8	36.6	28.84	30.2	31.5	22.32	-	-	24.5					
	<i>Labio gonius</i>	67.31	-	-	40.19	-	-	29.53	-	-	26.6	-	-						
	<i>Puntius serrana</i>	66.48	-	-	43.4	-	-	33.33	-	-	22.82	-	-						
	<i>Ompok bimaculatus</i>	69.81	-	-	42.23	-	-	-	-	-	-	-	-						
	<i>Mesacemphalus sp.</i>	54.27	-	-	34.9	-	-	-	-	-	-	-	-						
Lower Lake	<i>Glossogobius giurus</i>	54.34	48.8	-	33.33	-	-	23.35	-	-	-	-	-						
	<i>Puntius ticto</i> *	47.35	45.6	48.5	34.48	-	-	-	-	-	-	24.24	-	-					
	<i>Chanda nana</i> *	-	50.5	54.5	-	-	-	-	-	-	-	-	-						
Uncontaminated Environment	<i>Labio calbasu</i> ^a	61.4	-	-	34.8	-	-	31.8	-	-	25.5	-	-						
	<i>Labio rohita</i> ^a	63.6	-	-	36.8	-	-	31.6	-	-	26.7	-	-						
	<i>Labio gonius</i> ^{a*}	60.5	-	-	33.6	-	-	32.5	-	-	30.8	-	-						
	<i>Puntius stigma</i>	65.4	-	-	-	-	-	-	-	-	-	-	-						

A - after 20 days

* - whole fish

B - after 80 days

a - only one collection

C - after 140 days

TABLE V
Acetylcholinesterase activities of MIC-Poisoned human blood after 20 days

Age of the patients (all male)	Acetylcholinesterase activities μmol/ml of blood plasma
45	54.54
35	57.14
25	68.18
40	75.0

NATIONAL ENVIRONMENTAL ENGINEERING RESEARCH INSTITUTE
NAGPUR

METHYL ISOCYANATE
CHEMICAL ACCIDENT
IN UCIL, BHOPAL

The report of work done by the National Environmental Engineering Research Institute (NEERI), Nagpur at Bhopal after the toxic gas leakage is presented in the following pages. The NEERI team visited Bhopal on 4 December 1984, the day after the incident and began analyzing air, water and soil samples. These were analyzed at Bhopal and at Nagpur. NEERI also coordinated the collection, collation and transmission of weather data with the Indian Meteorological Department. A sample of these reports is also given. A general note on environmental aspects of chemical accidents forms part of the Report. A number of annexures give details of analytical data, excerpts from a similar report of the Environmental Protection Agency, USA, on industrial pollutants, toxic effects of isocyanates in environments, etc.

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METHYL ISOCYANATE CHEMICAL ACCIDENT IN M/S UNION CARBIDE INDIA LTD, BHOPAL - A NEERI REPORT

1.0 INTRODUCTION

The chemical accident involving methyl isocyanate in the pesticide (carbaryl) manufacturing plant of M/s. Union Carbide India Limited (UCIL) at Bhopal has stunned the humanity. The accident reportedly occurred during the early hours on 3rd December, 1984. The next day (i.e. 4th Dec. 1984) the morning newspapers flashed the news as the lead item and DGSIR, around 5.15 pm instructed over telephone for a NEERI team to be present at Bhopal with testing kits for studying the environmental impact of this chemical accident.

2.0 NEERI'S PARTICIPATION

The first team of NEERI Scientists reached Bhopal on the 5th morning with sampling equipments and started working immediately as per the guidance and instructions from time to time given by Dr. S. Varadarajan, DGSIR on what came to be later known as 'OPERATION FAITH'.

NEERI was assigned the work on monitoring of environmental quality by sampling and analysing air, water and soil. Further NEERI also coordinated in the collection, collation and transmission of weather data with India Meteorological Department.

Laboratory facilities of Regional Research Laboratory, Bhopal were availed by NEERI for setting up of instruments for analysis of environmental samples. While this was going on at Bhopal, simultaneously work on evolving suitable analytical methods for MIC and related literature search commenced at NEERI, Nagpur on an emergency basis.

This document reports the efforts of NEERI in 'OPERATION FAITH'.

The Document contains a brief account of the manufacturing process for the pesticide, its production in India, Physico-chemical properties and toxicity data of MIC. Detailed information on the climatological study and weather forecast collected in coordination with IMD is included. The particulars of the analytical methods and their standardisation are given. The results of the analysis of air, water and soil samples are presented. Information on Environmental Aspects of Chemical Accidents, Emergency Response Systems and Approach is quoted.

3.0 MANUFACTURING PROCESSES

Methyl isocyanate (MIC) is an intermediate in the production of carbaryl which is a carbamate class of pesticide. MIC is synthesized from phosgene and monoethyl amine. In presence of an excess amine this reaction leads to substituted carbamides. In order to avoid this, the process is carried out with equimolar ratios of phosgene to amine or even with an excess of phosgene in a solution of toluene, chlorobenzene or o-dichlorobenzene.

The details of the manufacturing process are given in Annexure 1.

3.1 Status of Carbaryl Production in India

From the "Report of the working group on pesticides industry for the plan 1978-79 to 1983-84 (Govt. of India, Ministry of Petroleum, Chemicals and Fertilizers, Dept. of Chemicals and Fertilizers, 1979)", the following information shows the status of carbaryl production in the country:

Manufacturer	I/L No., date	Present validity	Capacity (tonnes per annum)
Paushak Ltd., Baroda	19/11/1966/70 14 Aug. 1970	Dec. 1978	2000
UCIL, Bhopal	CIL:409(75) 30 Oct. 1975	30 Oct. 1978	5000

Also from the Indian Chemical Statistics, Monitoring & Evaluation (Chem) Section, Ministry of Chemicals & Fertilizers, Govt. of India, New Delhi; Document prepared in 1982-83, the following additional information is obtained:

Year	1977-78	1978-79	1979-80	1980-81	1981-82	1982-83
(Installed capacity / Actual production)						
Total carbaryl produced (tonnes)	5000/361	5000/767	5000/1501	7000/1178	7000/3072	7000/2337

4.0 PHYSICO-CHEMICAL & TOXICOLOGICAL PROPERTIES OF MIC

The available information on the physico-chemical properties of MIC are as follows:

4.1 Physical Properties

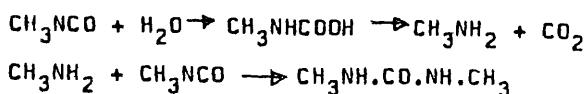
Mol. wt.	57
Density	0.9599 at 20/20°C
B.P.	39.1°C
Flash Point	below 7°C

MIC is sparingly soluble in water, it is colourless and extremely flammable.

4.2 Chemical Properties

(a) On prolonged standing MIC is reported to get converted to dimeric and trimeric isocyanic esters.

(b) MIC is hydrolysed rapidly by water giving alkyl amine and disubstituted urea.



The reactions are instantaneous. In view of the great reactivity of MIC, it is likely that the above chemical transformation will be most marked in the environment i.e. air, water and soil. Exposure to moisture leads to formation of CO₂ and the development of pressure in closed containers resulting in rupture of metal and glass containers.

4.3 Toxic Effects

Vapours of MIC irritates the respiratory system and/or severely causes lachrymation. The liquid irritates the eyes, skin and respiratory system. On inhalation it causes pulmonary oedema.

4.3.1 Toxic level in work environment (Inhalation)

Occupational Safety Health Administration Standards (OSHA USA) 1973	USSR-1972 and GDR - 1974
---	--------------------------

Maximum allowable exposure (8 hr weighted average): 0.02 ppm 0.05 mg/m³ or 0.05 mg/m³

4.3.2 Quantifying toxic dose - Inhalation (MIC)

Human	Lowest published toxic concentration in air - 2 ppm - toxic effect : irritant effect
Rat	Oral lethal dose 50% kill - 71 mg/kg

Rat

Inhalation - lowest published lethal concentration in air
- 31 ppm/4 hr

4.3.3 Work environment, Hygienic Standards in different countries for other intermediates of carbaryl

Chemical	USA 1974 (ppm)	OSHA 1974 (mg/m ³)	GDR 1974 (mg/m ³)	DDR 1973 (mg/m ³)	Sweden 1975 (mg/m ³)	CSSR 1969 (mg/m ³)	USSR - (mg/m ³)
Methylamine	10	12	12	-	-	-	1
Dimethylemine	10	18	18	-	-	-	1
Phosgene	0.1	0.4	0.4	0.5	0.2	0.4	0.5
Carbaryl	-	5	5	-	-	-	1.0

4.3.4 Priority pollutant

Environmental Protection Agency (EPA) of the USA in their code of Federal regulations (US-EPA July 1983) classifies methyl isocyanate (Hazardous Waste No.PO64) as an acute toxic compound (Annexure 2). Methyl isocyanate, mono and dimethyl amine and dimethyl urea do not appear as priority pollutants in the US EPA Tabulations for Priority Pollutant, as of April 1980. The compounds on the list (Annexure 3) are for their presence in the wastewaters from industries. Codes of safety prepared by Chemical Hazards Sectional Committee of ISI (CDC : 18) do not include information on MIC or methylamines. However IS: 8185-1976 refers to phosgene. Even in the proposed programme of CDC 18, ISI, MIC and alkylamines are not included.

4.3.5 Toxic effects of isocyanate in work environment

The available information on the toxic effects of isocyanates to humans in work environment are given in Annexure 4. these are Abstracts published in Industrial Hygiene Digest.

5.0 ANALYTICAL METHODS AND STUDIES FOR MIC, PRIMARY AND SECONDARY AMINES

Literature survey showed the possibility of two

analytical methods for the study of total isocyanates and amines in air samples. Following methods were studied:

Spectrophotometric Determination of Aliphatic Isocyanates in the Occupational Atmosphere - Part I - Determination of Total Isocyanate Concentration

R.F. Walker and M.A. Pinches; Analyst; October 1979, Vol. 101, p. 928-936.

(The above method recommends the use of 1,1,2-trichloroethane as the extracting solvent for complex. As this reagent was not available anywhere in India, experiments were done using carbon tetrachloride as the alternate solvent)

Tentative method of Analysis for Primary and Secondary Amines in the Atmosphere (Ninhydrin Method)

Ref: 43724-01-73T - Standard Methods for Air Analysis.

The details of the analytical methods, apparatus, reagents and procedure adopted are summarised in annexure 5. Ninhydrin Method was adopted for environmental monitoring.

6.0 MONITORING OF WATER QUALITY

6.1 Selection of Sampling Points

Bhopal city draws its water supply from Upper Lake where from it is taken to different Water Works before sending for potable use. This is a 12 km long lake lying in the heart of the city and terminates at a place called 'Bhadbhada'. At this point it meets a river. There is another lake known as Lower Lake which is not used for water supply. This lake is comparatively nearer to the Union Carbide factory. Further in the vicinity of the factory there are big dug wells (open wells) called 'Bawari'. Water is pumped from these wells and supplied to consumers after disinfection by bleaching powder. Water samples were collected from the wells in the vicinity of the factory as well as from the lakes and water works. A map of Bhopal city showing various sampling points and observatories is enclosed.

6.2 Collection of Water Samples

Water samples were collected on two different occasions. First schedule was between 5th and 8th December, 1984; the second was on 18th December, 1984; respectively as has been shown in Tables 6.2.1 and 6.2.2.

6.3 Analysis of Water Samples

Water samples were analysed for their physico-chemical characteristics as well as for the presence of methylamine, the most probable compound supposed to have been formed in water from methyl isocyanate. Physico-chemical parameters were determined using the procedures given in Standard Methods, 15th Edition 1981. Methylamine was determined by the method described below.

*Table 6.2.1
Details of Water Samples Collected in the First Schedule*

Sr. No.	Sample Code No.	Description of sample	Date of sample collection
1.	1(R)	Raw water from 5 MGD treatment plant of Arera Hill at TT Nagar near Birla temple	5-12-84
2.	1(F)	Finished water from 5 MGD treatment plant of Arera Hill at TT Nagar near Birla temple	5-12-84
3.	2	Water from lower lake from the bridge (Pul Bogda)	5-12-84
4.	3(F)	Filter water from Pul Pokhta treatment plant	5-12-84
5.	4(R)	Raw water from railway Water Works	6-12-84
6.	5(R)	Raw water from Upper Lake pump house near Idgah hill	7-12-84
7	A	Pond water, Kailash Garden M.P. State Fisheries Corporation	8-12-84
8.	B	Water from a pipe feeding upper lake water to dry bund at M.P. State Fisheries Corporation	8-12-84
9	C	Water from farm pond at M.P. State Fisheries Corporation	8-12-84
10.	D	Pond water half kilometre north of Union Carbide	8-12-84

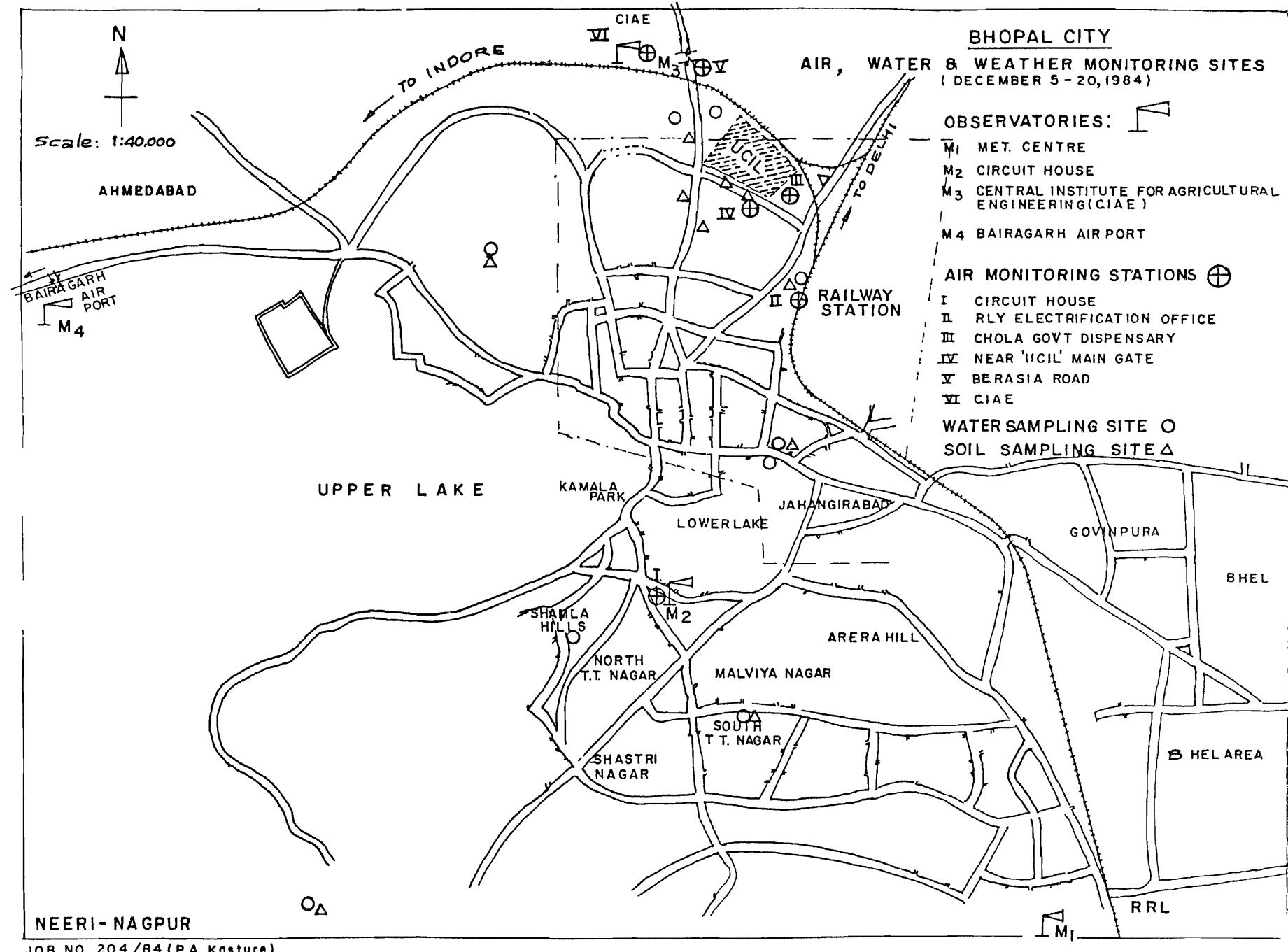


Table 6.22
Details of Water Samples Collected in the Second Schedule

Sr. No.	Sample Code No.	Description of sample	Date of sample collection
1.	1	Raw water from TT Nagar water treatment plant	18-12-84
2.	2	Raw water 2 MGD water treatment plant Shamla Hill	18-12-84
3.	3	Raw water from pump house Upper Lake	18-12-84
4.	4	Water from Lower Lake near police line headquarters	18-12-84
5.	5	Raw water from Pulpokhta treatment plant (2 MGD)	18-12-84
6.	6	Dug well, Vishramghat, Chola road	18-12-84
7.	7	Dug well (Gangor Ki Bawri) behind Bafna colony	18-12-84
8.	8	Dug well No. 10, Pullighar, old RTO office	18-12-84
9.	9	Dug well (Purani Bawri, behind plot No.22), Risaldarpura, 300 metres in the south-west of the Union Carbide factory	18-12-84

6.4 Preparation of Water Samples for the Determination of Methylamines

A 250 ml of water sample was transferred to a 500 ml separatory funnel. 5 ml of 4 N.NaOH was added to it and content was shaken for one minute. It was allowed to remain as such for 5 minutes. A 25 ml aliquot of carbon tetrachloride was added and the content was shaken for 2 minutes. The layers were allowed to separate. The organic layer was saved. Carbon tetrachloride extraction was repeated on the aqueous portion in the same way. The two carbon tetrachloride extracts were taken in a separatory funnel to which a 5 ml portion of 4 N hydrochloric acid was added. The contents were shaken vigorously for 2 minutes. The layers were allowed to separate. Organic layer was discarded and acidic aqueous portion was preserved for the determination of methylamine.

6.5 Determination of Methylamine

The 5 ml acid extract was mixed well with 5 ml of isopropanol. A 3 ml portion of this mixture was taken and subjected to the Ninhydrin reac-

tion as described under analytical procedure. A blank containing hydrochloric acid - isopropanol and standards containing various amounts of methyl amines in acid - isopropanol solution were similarly run. Absorbance of blue colour developed was recorded at 575 nm. Results were computed after subtracting the absorbance of the blank from the samples.

6.6 Results

The water samples collected on the two occasions have been analysed for the presence of methyl isocyanate as methylamine. Results of the analysis showed that methylamine was not present at detectable concentrations in any of the samples. Water samples were also analysed for their physico-chemical characteristics. The results of this analysis have been given in Annexure 6.

7.0 MONITORING OF AIR

Monitoring schedule : Air monitoring for methyl isocyanate was carried out on two occasions. The first was between 5th and 7th De-

ember, 1984, i.e. after the episode. The second was between 15th and 19th December, 1984 which includes a day prior to the start of the neutralization of MIC through the completion of the operation.

7.1 Sampling Locations

In the first instance air sampling was conducted at TT Nagar water treatment plant, Upper Lake pumping station and in Kanchi Chola. In the second schedule three permanent sampling stations were established at:

1. Railway Electrification, Railway Station, Bhopal.
2. Matru Shishu Kalyan Kendra, Government Dispensary, Risaldar Colony, Chola Naka, Bhopal.
3. Central Institute of Agricultural Engineering, Nabibagh, Bhopal.

Apart from these, air samples were also taken from :

1. Circuit house
2. Birasia Road
3. Infront of Union Carbide factory gate.

7.2 Sample Collection Equipments

Air samples at railway station and government dispensary were collected by using the trapping provided in NEERI developed High Volume Sampler. At Central Institute of Agricultural Engineering it was taken through a suction pump operated at electric main. At other places air samples were collected by battery operated air sampler.

7.3 Air Sample Collection

Air samples were collected by bubbling air in gas impinger containing one per cent hydrochloric acid in isopropanol as absorption solution. The air was passed at a rate of 1 litre/minute for one hour. Flow rate of air was constantly monitored and any change in flow rate was immediately adjusted.

7.4 Estimation of Methyl Isocyanate as Methylamine

A 3 ml portion of absorbing solution from the impinger was taken and processed for the

determination of methylamine by the Ninhydrin method described under 'Analytical Studies'.

7.5 Results

The results of air analysis have clearly indicated the presence of methylamine (as itself or as degradation product of MIC) at concentrations far below the TLV (threshold limit value) for methylamine during December 16-17, 1984. Monitoring studies were also continued up to December 19, 1984. Results of this study have indicated that the levels of methylamine were decreasing steadily with time (Annexure 7).

8.0 MONITORING OF SOILS

It is likely that methyl isocyanate (MIC) or its degradation products will ultimately find their way into soil. In view of this, soil samples were collected.

8.1 Collection of Samples

Surface soil samples were collected from the vicinity of the Union Carbide factory, affected areas and Water Works campus. A detailed description of soil samples has been given in Table 8.1.1 and as shown on the map.

8.2 Preparation of Soil Samples for the Determination of Methyl Isocyanate/Methylamine

A 10 g portion of soil samples was powdered and suspended in 125 ml distilled water in an Erlenmeyer flask. 2.5 ml of 4 N.NaOH was added to it for the release of methylamine. The soil suspension was shaken for an hour for complete extraction of methylamine. The suspension was then centrifuged and supernatant was decanted. Extraction was repeated once again. The two aqueous extracts were combined and the total volume was made up to 250 ml with distilled water.

This aqueous extract was treated similarly with carbon tetrachloride and HCl as water samples for the determination of methylamine.

A duplicate portion of the soil was dried at 105°C for the determination of moisture. The results are expressed on dry and moisture free basis.

8.3 Results

Ninhydrin method was employed for methyl-

Table 8.1.1
Details of Soil Samples Collected

Sr. No.	Code No.	Description of samples	Date of collection
1.	1(S)	Surface soil from the compound of 5 MGD TT Nagar water treatment plant at Arera Hill near Birla temple	5-12-84
2.	3(S)	Surface soil from Pulpokhta water treatment plant	5-12-84
3.	4(S)	Surface soil from the compound of railway water works	6-12-84
4.	5(S)	Surface soil from the bank of Upper Lake at Idgah Hill pump house	7-12-84
5.	6	Surface soil from Kainchi Chola (half kilometre in the south-east direction of the Union Carbide factory)	7-12-84
6.	2	Surface soil from Chola Road	7-12-84
7	A	Surface soil from Kailash garden, M.P. State Fisheries Corporation near cement cistern	8-12-84
8.	C	Surface soil sample from circular pond	8-12-84
9.	D	Surface soil sample from JP Nagar in front of gate No.2 of Union Carbide	8-12-84
10.	E	Surface soil sample from JP Nagar, 0.25 km from the gate No.1 of Union Carbide	8-12-84
11.	F	Surface soil sample from Berasia Road near Firdaus Nagar sign board, 0.25 km away from the Union Carbide factory	8-12-84
12.	G	Surface soil sample from Berasia Road towards Bhopal	8-12-84

amine in soil. The soil samples collected have been analysed for the presence of methyl isocyanate as methylamine. Results of the analysis showed that methylamine was not present at detectable concentrations in any of the samples.

9.0 CLIMATOLOGICAL STUDY & WEATHER REPORT

NEERI coordinated with India Meteorological Department (IMD) in the collection of meteorological data. This information was required to arrange the neutralization/utilization of MIC (during favourable weather conditions to pre-

vent any further exposure of MIC to the community in the area).

It was felt that the data from the regular observatory at Bairagarh airport may not be useful in the context of micro-meteorological aspect of the demanding situation. Bhopal city is hilly and basinlike. Three more observatories in addition to the one already existing observatory of IMD were set up to ascertain the weather features of the local areas. Besides, temperature inversion data was collected with a frequency of four radiosonde ascents in 24 hours, every day.

NEERI in coordination with IMD installed observatories at circuit house and Central Institute for Agriculture Engineering (CIAE). These observatories were initially manned and operated by NEERI and later taken over by IMD. Automatic weather recording instruments of NEERI and CIAE were used. NEERI extended

coordination through RRL, Bhopal and other State agencies to meet requirements of IMD, including transport, accommodation and flow of data/information to authorities.

Local observatories operated at following locations :

Sr. No.	Place	Code No.	Remarks
1.	Meteorological Centre, Arera Colony	M1	IMD equipment installed
2.	Circuit House	M2	NEERI owned equipment installed
3.	Central Institute for Agriculture Engg (CIAE)	M3	Existing observatory at CIAE was availed
4.	Bairagarh Airport	M4	Regular IMD observatory

Wireless sets were provided at the four observatories for transmitting hourly and 24 hourly data on 'current weather' to control room at the Secretariat building. This arrangement was one of the 'zero risk' precautionary measures, prior to commencement of operation of neutralization of MIC.

9.1 Weather Forecast

Daily forecasts valid for next 24 hours were issued twice, at 1100 hr and 2100 hr. These were in (i) technical and (ii) plain version. Technical report dealt with individual weather parameters: synoptic features, surface winds, temperature and inversions. Plain language dealt with the direction and speed of winds in relation to factory (UCIL) location. This was for identification of vulnerable areas in the event of an unlikely untoward incident. Forecast information was used to brief officials whenever necessary. Specimen copy of weather report and forecast data are appended (Annexure 8).

9.2 Weather at Bhopal from 10-12-84 to 19-12-84

Bhopal is located in a geographically rough terrain surrounded by hillocks. Anticyclones persisted for the most part of time over Bhopal during the period of survey which caused stable atmosphere over the city. There was no deviation from the normal wind pattern during the fortnight except on 12th and 13th December,

1984. On 12th, there was a low pressure trough in the lower troposphere over Bhopal, which caused a change in the normal wind pattern, i.e. rise in wind speed up to 15 to 30 kmph and wind direction westerly to south-westerly on 12th and 13th of Dec. 1984 (Annexure 8). Otherwise wind speed varied from 10 to 15 kmph and wind direction north-west to easterly through northerly.

Maximum temperature varied from 24°C to 30.5°C

Minimum temperature varied from 8.4°C to 13.7°C.

Each day, ground based inversion started in the late evenings, i.e. around 2200 hr and peak of inversion reached maximum height of about 400 m in the early morning and varied by 1000 hr. During day time, elevated inversions were observed at 2 km height and above.

10.0 ENVIRONMENTAL ASPECTS OF CHEMICAL ACCIDENTS

10.1 Chemical manufacture, wherever it is carried out, is a multi-product and multi-process industry using a wide range of basic raw materials and intermediates, which makes several heterogeneous products of diverse nature. Thousands of tonnes of hazardous chemical compounds are daily produced, transported, stored and used all over the world. Currently, about 45,000 substances are found in world

markets in different combinations, of which 150 chemicals are produced in amounts in excess of 50,000 tonnes/year, but their impact on the environment is yet to be assessed fully.

10.2 Emergency Response Systems - Approach

A sizeable number of chemical compounds that are being handled today are highly toxic to humans and their environment, and the accidental release of small amounts of such substances into environment may have extremely serious consequences. Hence a preplanned procedure for handling major and minor emergencies, arising out of chemical accidents, which utilise the combined resources of local, national and international services including all available technical and scientific information is being developed and updated as well as practised in all the industrialised countries. Having recognised the need for such contingency planning the World Health Organization, EURO, Copenhagen under 'Health Aspects of Chemical Safety' has brought out an Interim Document entitled "Emergency Response to Chemical Accidents - 1981". A brief outline of the approach suggested in the interim document 'Planning Emergency Response Systems for Chemical Accidents' is presented and discussed for suitable modification if necessary and adoption to Indian context (Annexure 9).

10.3 To meet any emergency due to chemical accidents, it may be necessary that sustained efforts are made and continued at CSIR level to develop suitable emergency systems. This may necessitate consideration of the following:

- i) Investigation of vulnerable points, processes and/or activities;
- ii) Estimation of possible chemical emissions;
- iii) Knowledge of effects of toxic chemicals;
- iv) Identification of chemical industries using raw materials, intermediates and producing end products which are known to be potentially hazardous. To begin with large and medium scale industries should be included in the survey;
- v) Development of analytical capabilities for identification and assaying of various toxic and hazardous chemicals used in chemical industries;

- vi) Data bank to provide timely information on the properties, reactions, toxicity, methods of handling of spills, etc., on hazardous chemicals;
- vii) Knowledge of possible protective and remedial measures;
- viii) Designation of responsibilities;
- ix) Establishment of the liaison with external authorities;
- x) Resources for handling the emergency
- xi) Communication.

The above aspects are necessary to develop structure and elements of emergency response systems: The four levels of Emergency Planning Contingency plan for chemical accident identified and suggested in the WHO document referred are given in Annexure 10.

10.4 In order that NEERI can play a more effective role in meeting environmental aspects of chemical accidents, the Institute has to develop and strengthen capabilities in the following areas :

- i) Estimation of possible chemical emissions from selected industries handling and/or producing toxic or hazardous chemicals;
- ii) Monitoring of air, water and soil for specific pollutants with hazardous potential;
- iii) Assistance in information dissemination of effects on toxic and/or hazardous chemicals;
- iv) Provide action teams to assist in monitoring items (i) and (ii) indicated above;
- v) Competence build-up for spillage handling; and
- vi) Safe disposal of toxic and/or hazardous wastes.

NEERI can also actively participate in drawing up emergency response systems, for handling chemical accidents, in collaboration with other agencies which will be working in this area.

Most of the information given in this note is freely taken from the WHO Publication 'Emergency Response to Chemical Accidents' - An Interim Document under Health Aspects

of Chemical Safety, brought out by the Regional Office for Europe, Copenhagen, 1981.

11.0 CONCLUSION

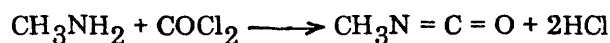
In summary, a NEERI team had visited Bhopal, established laboratory facilities and collected air, water and soil samples. The samples were

analysed at Bhopal as well as at Nagpur. Staff of the RRL, Bhopal were also associated in the investigations and trained for continuing air monitoring studies. The environment at Bhopal was found to be safe for the citizens. The results of the investigations are incorporated in this report.

Manufacturing Processes

Methyl isocyanate is produced by reacting phosgene with methylamine. The reaction takes place in two stages. The first stage consists of the reaction of phosgene with monomethylamine leading to the formation of carbamoyl chloride ($2\text{CH}_3\text{NH}_2 + \text{COCl}_2 \rightarrow \text{CH}_3\text{NHCOCl} + \text{CH}_3\text{NH}_2\cdot\text{HCl}$). The amine is added to the phosgene dissolved in one of the solvents stated earlier (p.2) so that phosgene is in excess.

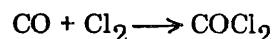
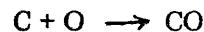
In the second stage the suspension obtained is heated up to $150\text{-}200^\circ\text{C}$. At elevated temperature amine hydrochloride dissociates, the phosgene reacts with the liberated amine and the carbamoyl chloride splits off HCl, giving an isocyanate. The overall reactions is as follows:



There are two methods for the continuous liquid phase synthesis of MIC. In one method, the process is carried out in two steps in two separate reactors - one operates at a low temperature and the other at a higher temperature. In the other method, the reaction takes place in one step in a column type reactor at a high temperature (about 200°C). The yield of MIC exceeds 90%.

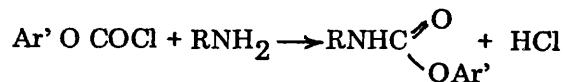
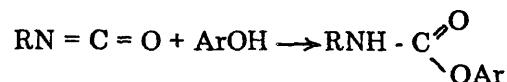
Phosgene required for MIC synthesis is prepared from carbon monoxide, obtained by passing air over red hot coke, in a controlled manner

and then reacting with chlorine gas.



Carbaryl can be synthesised by two principal methods.

- (i) Interaction of isocyanate with alpha naphthol
- (ii) Amidation of the esters of chlorocarbonic acid.



Both reactions are exothermic and practically irreversible. While the first method is used at UCIL, Bhopal, at present, the second method was followed up to 1978 at their plant at Institute, West Virginia. The esterification of isocyanate is carried out at $60\text{-}80^\circ\text{C}$ and the isocyanate is gradually added upon stirring to an excess of alpha naphthol. Solvents (e.g. carbon tetrachloride) may be used for the reaction with naphthol. Both methods give a high yield of product (more than 95%) and have similar cost indices.

ANNEXURE 2

Chapter I—Environmental Protection Agency

§ 261.33

Industry and EPA hazardous waste No	Hazardous waste	Hazard code
K042	Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4-S-T	(M)
K043	2,6-Dichlorophenol waste from the production of 2,4-D	(B)
K099	Untreated wastewater from the production of 2,4-D	(B)
Explosives	Wastewater treatment sludges from the manufacturing and processing of explosives	(R)
K044	Spent carbon from the treatment of wastewater containing explosives	(R)
K045	Wastewater treatment sludges from the manufacturing, formulation and loading of lead-based initiating compounds	(M)
K046	Pink/red water from TNT operations	(R)
K047	Decanted air flotation (DAF) float from the petroleum refining industry	(B)
Petroleum refining:	Slop oil emulsion solids from the petroleum refining industry	(B)
K048	Heat exchanger bundle cleaning sludge from the petroleum refining industry	(B)
K049	API separator sludge from the petroleum refining industry	(B)
K050	Tank bottoms (leaded) from the petroleum refining industry	(B)
K051	Emission control dust/sludge from the primary production of steel in electric furnaces	(M)
K052	Spent pickle liquor from steel finishing operations	(C, T)
Iron and steel:	Emission control dust/sludge from secondary lead smelting	(M)
K061	Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting	(M)
Secondary lead:	Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds	(M)
K062	Distillation tar residues from the distillation of ariline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds	(M)
K063	Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds	(M)
K064	Solvent washes and sludges, caustic washes and sludges or water washes and sludges from cleaning tube and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead	(M)
Veterinary pharmaceuticals:	Ammonia still lime sludge from coking operations	(M)
K101	Decanter tank tar sludge from coking operations	(M)
K102	Ammonium still lime sludge from coking operations	(M)
Ink formulation: K065	Decanter tank tar sludge from coking operations	(M)
Coking:	Ammonium still lime sludge from coking operations	(M)
K066	Decanter tank tar sludge from coking operations	(M)
K067	Ammonium still lime sludge from coking operations	(M)

[46 FR 4618, Jan. 16, 1981, as amended at 46 FR 27476-27477, May 20, 1981]

§ 261.33 Discarded commercial chemical products, off-specification species, container residues, and spill residues thereof.

The following materials or items are hazardous wastes if and when they are discarded or intended to be discarded:

(a) Any commercial chemical product, or manufacturing chemical intermediate having the generic name listed in paragraph (e) or (f) of this section.

(b) Any off-specification commercial chemical product or manufacturing chemical intermediate which, if it met specifications, would have the generic name listed in paragraph (e) or (f) of this section.

(c) Any residue remaining in a container or an inner liner removed from a container that has held any commercial chemical product or manufac-

uring chemical intermediate having the generic name listed in paragraph (e) of this section, unless the container is empty as defined in § 261.7(b)(3) of this chapter.

[Comment: Unless the residue is being beneficially used or reused, or legitimately recycled or reclaimed; or being accumulated, stored, transported or treated prior to such use, re-use, recycling or reclamation, EPA considers the residue to be intended for discard, and thus a hazardous waste. An example of a legitimate re-use of the residue would be where the residue remains in the container and the container is used to hold the same commercial chemical product or manufacturing chemical product or manufacturing chemical intermediate it previously held. An example of the discard of the residue would be where the drum is sent to a drum reconditioner who reconditions the drum but discards the residue.]

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(d) Any residue or contaminated soil, water or other debris resulting from the cleanup of a spill into or on any land or water of any commercial chemical product or manufacturing chemical intermediate having the generic name listed in paragraph (e) or (f) of this section, or any residue or contaminated soil, water or other debris resulting from the cleanup of a spill, into or on any land or water, of any off-specification chemical product and manufacturing chemical intermediate which, if it met specifications, would have the generic name listed in paragraph (e) or (f) of this section.

[Comment: The phrase "commercial chemical product or manufacturing chemical intermediate having the generic name listed in . . ." refers to a chemical substance which is manufactured or formulated for commercial or manufacturing use which consists of the commercially pure grade of the chemical, any technical grades of the chemical that are produced or marketed, and all formulations in which the chemical is the sole active ingredient. It does not refer to a material, such as a manufacturing process waste, that contains any of the substances listed in paragraphs (e) or (f). Where a manufacturing process waste is deemed to be a hazardous waste because it contains a substance listed in paragraphs (e) or (f), such waste will be listed in either §§ 261.31 or 261.32 or will be identified as a hazardous waste by the characteristics set forth in Subpart C of this part.]

(e) The commercial chemical products, manufacturing chemical intermediates or off-specification commercial chemical products or manufacturing chemical intermediates referred to in paragraphs (a) through (d) of this section, are identified as acute hazardous wastes (H) and are subject to be the small quantity exclusion defined in § 261.5(e).

[Comment: For the convenience of the regulated community the primary hazardous properties of these materials have been indicated by the letters T (Toxicity), and R (Reactivity). Absence of a letter indicates that the compound only is listed for acute toxicity.]

These wastes and their corresponding EPA Hazardous Waste Numbers are.

Hazardous waste No	Substance
P023 . . .	Acetaldehyde, chloro-
P002 . . .	Acetamide N-(2-methoxyethyl)-
P057 . . .	Acetamide 2-fluoro-
P058 . . .	Acetic acid fluoro-, sodium salt
P066 . . .	Acetamide acid, N-[(methylcarbamoyl)oxy]thio-, methyl ester and salts
P001 . . .	3-(alpha-acetonylbenzyl)-4-hydroxycoumarin
P002 . . .	1-Acetyl-2-thiouracil
P003 . . .	Acrolein
P070 . . .	Aldicarb
P004 . . .	Aldrin
P005 . . .	Allyl alcohol
P006 . . .	Aluminum phosphide
P007 . . .	5-(Aminomethyl)-3-azauzolidin-4-amine
P008 . . .	Ammonium picrate (R)
P119 . . .	Ammonium vanadate
P010 . . .	Arsenic acid
P012 . . .	Arsenic (III) oxide
P011 . . .	Arsenic (V) oxide
P012 . . .	Arsenic pentoxide
P038 . . .	Asame, diethyl-
P054 . . .	Azidine
P013 . . .	Barium cyanide
P024 . . .	Benzeneamine, 4-chloro-
P077 . . .	Benzeneamine, 4-nitro-
P026 . . .	Benzene, (chloromethyl)-
P042 . . .	1,2-Benzenediol, 4-[1-hydroxy-2-(methylamino)ethyl]-
P014 . . .	Benzethanol
P028 . . .	Benzyl chloride
P015 . . .	Beryllium dust
P016 . . .	Bis(chloromethyl) ether
P017 . . .	Bromacetone
P018 . . .	Bromoform
P021 . . .	Calcium cyanide
P123 . . .	Camphene, octachloro-
P103 . . .	Carbamimidodiseleninic acid
P022 . . .	Carbon bisulfide
P022 . . .	Carbon disulfide
P095 . . .	Carbonyl chloride
P033 . . .	Chlorine cyanide
P023 . . .	Chloroacetaldehyde
P024 . . .	p-Chloroaniline
P026 . . .	1-(o-Chlorophenyl)thiourea
P027 . . .	3-Chloropropionitrile
P029 . . .	Copper cyanides
P030 . . .	Cyanides (soluble cyanide salts), not elsewhere specified
P031 . . .	Cyanogen
P033 . . .	Cyanogen chloride
P036 . . .	Dichlorophenylarsane
P037 . . .	Diethylformamide
P038 . . .	Diethylarsane
P039 . . .	O,O-Diethyl S-[2-(ethylthio)ethyl] phosphorodithioate
P041 . . .	Diethyl-p-nitrophenyl phosphate
P040 . . .	O,O-Diethyl O-pyrazinyl phosphorothioate
P043 . . .	Diisopropyl fluorophosphate
P044 . . .	Dimethoate
P145 . . .	3,3-Dimethyl-1-(methylthio) 2-butanon-1-(methylamino)carbonyl] oxime
P071 . . .	O,O-Dimethyl O-p-nitrophenyl phosphorothioate
P062 . . .	Dimethylnitrosamine
P046 . . .	alpha, alpha-Dimethylphenethylamine
P047 . . .	4,6-Dinitro-o-cresol and salts
P034 . . .	4,6-Dinitro-o-cyclohexylphenol
P048 . . .	2,4-Dinitrophenol
P020 . . .	Dinoseb

Hazardous waste No	Substance	Hazardous waste No	Substance
P085	Diphosphonamide, octamethyl-	P088	7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid
P039	Disulfoton	P089	Parathion
P049	2,4-Dithiobutene	P034	Phenol, 2-cyclohexyl-4,6-dinitro-
P109	Orthocyanoephosphoric acid, tetraethyl ester	P048	Phenol, 2,4-dinitro-
P050	Endosulfan	P047	Phenol, 2,4-dinitro-6-methyl-
P088	Endosulfan	P020	Phenol, 2,4-dinitro-6-(1-methylpropyl)-
P051	Eronin	P009	Phenol, 2,4,6-trinitro-, ammonium salt (R)
P042	Epenephrine	P036	Phenyl dichloroarsine
P046	Ethanamine, 1,1-dimethyl-2-phenyl-	P082	Phenylmercuric acetate
P084	Ethanamine, N-methyl-N-nitroso-	P093	N-Phenylnitrourea
P101	Ethyl cyanide	P084	Phorate
P054	Ethylenimine	P095	Phosgene
P097	Famphur	P036	Phosphine
P056	Fluorine	P041	Phosphoric acid, diethyl p-nitrophenyl ester
P057	Fluoracetamide	P044	Phosphorothioic acid, O,O-dimethyl S-[2-(methylamino)-2-oxethyl]ester
P058	Fluoresceic acid, sodium salt	P043	Phosphorofluoric acid, bis(1-methylethyl)-ester
P065	Fulminic acid, mercury(II) salt (R,T)	P094	Phosphorothioic acid, O,O-diethyl S-
P059	Heptachlor	P069	(ethylthiomethyl)ester
P051	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo,endo-1,4,5,8-dimethanophthalene	P040	Phosphorothioic acid, O,O-diethyl O-p-nitrophenyl ester
P037	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo,exo-1,4,5,8-dimethanophthalene	P097	Phosphorothioic acid, O,O-dimethyl O-[1-(dimethylamino)-sulfonyl]phenyl]ester
P060	1,2,3,4,10,10-Hexachloro-1,4,4a,5,6,8a-hexahydro-1,4,5,8-endo, endo-dimethanophthalene	P110	Plumbane, tetraethyl-
P004	1,2,3,4,10,10-Hexachloro-1,4,4a,5,6,8a-hexahydro-1,4,5,8-endo, exo-dimethanophthalene	P098	Potassium cyanide
P060	Hexachlorohexahydro-exo,exo-dimethanophthalene	P099	Potassium silver cyanide
P062	Hezaathylytetrabosphate	P070	Propanal, 2-methyl-2-(methyldio), ((methylamino)carbonyl)oxime
P116	Hydrazinecarboethoamide	P101	Propanenitrile
P068	Hydrazine methyl-	P027	Propanenitrile, 3-chloro-
P063	Hydrocyanic acid	P069	Propanenitrile, 2-hydroxy-2-methyl-
P063	Hydrogen cyanide	P081	1,2,3 Propanetriol nitrate (R)
P096	Hydrogen phosphide	P017	2-Propenone, 1-bromo-
P064	Isocyanic acid, methyl ester	P102	Propargyl alcohol
P007	3(2H)-Isouazolone, 5-(aminomethyl)-	P003	2-Propenal
P092	Mercury, (acetato-O)phenyl-	P005	2-Propen-1-ol
P065	Mercury fulminate (R,T)	P067	1,2-Propylenimine
P016	Methane cyano(chloro-	P102	2-Propyn-1-ol
P112	Methane, tetra(nitro-) (R)	P008	4-Pyridynamine
P118	Methanethiol, Inchloro-	P075	Pyrdine, (S)-3-(1-methyl-2-pyrrolidinyl)-, and salts
P059	4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	P111	Pyrophosphonic acid, tetraethyl ester
P066	Methomyl	P103	Selenourea
P067	2-Methylazidine	P104	Silver cyanide
P068	Methyl hydrazine	P105	Sodium azide
P064	Methyl isocyanate	P106	Sodium cyanide
P069	2-Methylfuranone	P107	Strontron sulfide
P071	Methyl parathion	P108	Strychnidin-10-one and salts
P072	alpha-Naphthylthiourea	P018	Strychnidin-10-one, 2,3-dimethoxy-
P073	Nickel carbonyl	P106	Strychnine and salts
P074	Nickel cyanide	P115	Sulfuric acid thallium(I) salt
P074	Nickel(II) cyanide	P109	Tetraethylthiopyrophosphate
P073	Nickel tetracarbonyl	P110	Tetraethyl lead
P075	Nicotine and salts	P111	Tetraethylpyrophosphate
P076	Ninc oxide	P112	Tetrantromethane (R)
P077	p-Nitroaniline	P062	Tetraphosphonic acid hexaethyl ester
P078	Nitrogen dioxide	P113	Thallium(III) oxide
P076	Nitrogen(II) oxide	P114	Thallium(II) selenite
P078	Nitrogen(IV) oxide	P115	Thallium(II) sulfate
P081	Nitroglycerine (R)	P045	Tholanox
P082	N-Nitrosodimethylamine	P049	Thiodidocarbonic diamide
P084	N-Nitrosomethylvinylamine	P014	Thiophenol
P050	5-Norbomene 2,3-dimethanol, 1,4,5,6,7,7 hexachloro cyclic sulfide	P116	Thiosemicarbazide
P085	Octamethylpyrophosphoramido	P026	Thourea (2-chlorophenyl)
P087	Osmium oxide	P072	Thourea, 1-naphthalenyl
P087	Osmium tetroxide	P093	Thourea phenyl
		P123	Tozaphene

§ 261.33

Hazardous Waste No	Substance
P118	Trichloromethanethiol
P119	Vanadic acid, ammonium salt
P120	Vanadium peroxide
P120	Vanadium(V) oxide
P001	Wartann
P121	Zinc cyanide
P122	Zinc phosphide (R,T)

(f) The commercial chemical products, manufacturing chemical intermediates, or off-specification commercial chemical products referred to in paragraphs (a) through (d) of this section, are identified as toxic wastes (T) unless otherwise designated and are subject to the small quantity exclusion defined in § 261.5 (a) and (f).

(Comment: For the convenience of the regulated community, the primary hazardous properties of these materials have been indicated by the letters T (Toxicity), R (Reactivity), I (Ignitability) and C (Corrosivity). Absence of a letter indicates that the compound is only listed for toxicity.)

These wastes and their corresponding EPA Hazardous Waste Numbers are:

Hazardous Waste No	Substance
U001	Acetaldehyde (I)
U034	Acetaldehyde trichloro-
U187	Acetamide N-(4-ethoxyphenyl)-
U005	Acetamide N-9H-fluoren-2-yl-
U112	Acetic acid, ethyl ester (I)
U144	Acetic acid, lead salt
U214	Acetic acid, thallium(I) salt
U002	Acetone (I,T)
U003	Acetonitrile (I,T)
U004	Acetophenone
U005	2-Acetylaminofluorene
U006	Acetyl chloride (C,R,T)
U007	Acrylamide
U008	Acrylic acid (I)
U009	Acrylonitrile
U150	Alanine, 3-[p-(2-chloroethyl)amino]phenyl-L-
U011	Amibrol
U012	Aniline (I,T)
U014	Auramine
U015	Azaearmine
U010	Azirino(2',3',4')pyrrolo(1,2-a)indole-4,7-dione 6-amino-8-((ammonocarbonyl) oxy)methyl)- 1,1a,2,8,8a,8b-hexahydro-8a-methoxy-5-methyl-
U157	Benz[i]aceanthrylene, 1,2-dihydro-3-methyl-
U016	Benz[c]acridine
U016	3,4-Benzodiazine
U017	Benzal chloride
U018	Benz[a]anthracene
U018	1,2-Benzanthracene
U094	1,2-Benzanthracene 7,12-dimethyl-
U012	Benzanamine (I,T)

Title 40—Protection of Environment

Hazardous Waste No	Substance
U014	Benzanamine, 4,4-carbonimidoyls(N,N-di-methyl-
U049	Benzanamine 4-chloro-2-methyl-
U093	Benzanamine, N,N-dimethyl-4-phenylazo-
U158	Benzanamine, 4,4-methylenbis(2-chloro-
U222	Benzanamine 2-methyl hydrochloride
U181	Benzanamine 2-methyl 5-nitro
U019	Benzene (I,T)
U038	Benzeneacetic acid 4-chloro-alpha-(4-chlorophenyl)-alpha-hydroxy ethyl ester
U030	Benzene 1-bromo-4-phenoxy
U037	Benzene chloro-
U190	1,2-Benzenedicarboxylic acid anhydride
U028	1,2-Benzenedicarboxylic acid 1-[b(2-ethylhexyl)] ester
U069	1,2-Benzenedicarboxylic acid dibutyl ester
U088	1,2-Benzenedicarboxylic acid diethyl ester
U102	1,2-Benzenedicarboxylic acid dimethyl ester
U107	1,2-Benzenedicarboxylic acid d-n-octyl ester
U070	Benzene 1,2-dichloro-
U071	Benzene, 1,3-dichloro-
U072	Benzene, 1,4-dichloro-
U017	Benzene (dichloromethyl-I)-
U223	Benzene 1,3-disiocyanatomethyl- (R,T)
U239	Benzene dimethyl-(I,T)
U201	1,3-Benzenediol
U127	Benzene hexachloro-
U056	Benzene, hexahydro- (I)
U188	Benzene, hydron
U220	Benzene methyl
U105	Benzene 1-methyl 1,2,4-dinitro-
U106	Benzene, 1-methyl 2,6-dinitro-
U203	Benzene, 1,2-methylenedioxy-4-ethyl-
U141	Benzene, 1,2-methylenedioxy-4-propenyl-
U090	Benzene 1,2-methylenedioxy-4-propyl
U055	Benzene [1-methylethyl]- (I)
U169	Benzene, nitro- (I,T)
U183	Benzene pentachloro-
U185	Benzene pentachloro-nitro-
U020	Benzenesulfonic acid chloride (C,R)
U020	Benzenesulfonyl chloride (C,R)
U207	Benzene, 1,2,4,5-tetrachloro-
U023	Benzene, (trichloromethyl)-(C,R,T)
U234	Benzene, 1,3,5-trinitro- (R,T)
U021	Benzidine
U202	1,2-Benzothiazolin-3-one, 1,1-dioxide
U120	Benzol(j,k)fluorene
U022	Benzol(s)pyrene
U022	3,4-Benzopyrene
U197	p-Benzquinone
U023	Benzotrichloride (C,R,T)
U050	1,2-Benzphenanthrene
U085	2,2'-Bisoxane (I,T)
U021	(1,1-Biphenyl)-4,4-diamine
U073	(1,1-Biphenyl)-4,4-diamine 3,3-dichloro-
U091	(1,1-Biphenyl)-4,4-diamine 3,3-dimethoxy-
U095	(1,1-Biphenyl)-4,4-diamine 3,3-dimethyl-
U024	Bis(2-chloroethoxy) methane
U027	Bis(2-chloroisopropyl) ether
U244	Bis(dimethylthiocarbamoyl) disulfide
U028	Bis(2-ethylhexyl) phthalate
U246	Bromine cyanide
U225	Bromotorm
U030	4-Bromophenyl phenyl ether
U126	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-
U172	1-Butanamine, N-butyl-N-nitroso-
U035	Butanoic acid 4-[Bis(2-chloroethyl)amino]benzene-
U031	1-Butanol (I)
U158	2-Butanone (I,T)
U180	2-Butanone peroxide (R,T)
U053	2-Butenal

ANNEXURE 3

TABULATION OF PRIORITY POLLUTANTS BY PERCENTAGE
As Of April 15, 1980

Sl. No.	Priority Pollutant	Number of Times Found ¹ (Greater Than 10 ppb)	No. of Samples ²	Percentage	Number of Industrial Categories ³
1	2	3	4	5	6
1.	acenaphthene	154	3961	3.9	18
2.	acrolein	30	3823	.78	6
3.	acrylonitrile	85	3824	2.2	14
4.	benzene	881	3823	23.0	29
5.	benzidine	9	3960	.23	7
6.	carbon tetrachloride	213	3824	5.6	19
7.	chlorobenzene	143	3824	3.7	12
8.	1,2,4-trichlorobenzene	52	3958	1.2	9
9.	hexachlorobenzene	33	3958	.83	9
10.	1,2-dichloroethane	208	3824	5.4	21
11.	1,1,1-trichloroethane	459	3824	12.0	27
12.	hexachloroethane	26	3959	.66	6
13.	1,1-dichloroethane	84	3824	2.2	15
14.	1,1,2-trichloroethane	62	3824	1.6	13
15.	1,1,2,2-tetrachloroethane	112	3824	2.9	15
16.	chloroethane	12	3824	.31	5
17.	bis(chloromethyl)ether	5	3846	.13	4
18.	bis(2-chloromethyl)ether	39	3960	.98	7
19.	2-chloroethyl vinyl ether	38	3846	.99	1
20.	2-chloronaphthalene	30	3960	.76	11
21.	2,4,6-trichlorophenol	161	3943	4.1	18
22.	parachlorometa cresol	59	3943	1.5	12
23.	chloroform	1304	3828	34.1	32
24.	2-chlorophenol	80	3943	2.0	14
25.	1,2-dichlorobenzene ⁴	207	3960	5.2	16
26.	1,3-dichlorobenzene ⁴				
27.	1,4-dichlorobenzene ⁴				
28.	3,3'-dichlorobenzidine	3	3960	.08	2
29.	1,1-dichloroethylene	223	3824	5.8	20
30.	1,2-trans-dichloroethylene	223	8324	6.1	22
31.	2,4-dichlorophenol	123	3943	3.2	17

32. 1,2-dichloropropane	55	3824	1.4	6
33. 1,3-dichloropropylene (1,3-dichloropropene)	29	3824	.76	5
34. 2,4-dimethylphenol	183	3943	4.6	19
35. 1,4-dinitrotoluene	33	3960	.83	8
36. 2,6-dinitrotoluene	45	3960	1.1	15
*37. 1,2-diphenylhydrazine	34	3958	.89	14
38. ethylbenzene	558	3824	14.6	29
39. fluoranthene	223	3961	5.6	14
40. 4-chlorophenyl phenyl ether	3	3960	.08	3
41. 4-bromophenyl phenyl ether	1	3960	.03	1 (rubber)
42. bis(2-chloroisopropyl) ether	44	3960	1.1	8
43. bis(2-chloroethoxy) methane	19	3959	.48	8
44. methylene chloride di(chloromethane)	1409	3824	36.8	32
45. methyl chloride (chloromethane)	62	3824	1.6	12
46. methyl bromide (bromomethane)	2	3824	.05	1 (organics)
47. bromoform (tribromomethane)	57	3824	1.5	14
48. dichlorobromomethane	158	3824	4.1	23
49. trichlorofluoromethane	199	3824	5.2	15
50. dichlorodifluoromethane	5	3824	.13	5
51. chlorodibromomethane	79	3824	2.1	17
52. hexachlorobutadiene	7	3960	.08	1 (organics)
53. hexachlorocyclopentadiene	3	3960	.08	1 (organics)
54. isophorone	59	3960	1.5	20
55. naphthalene	390	3960	9.8	26
56. nitrobenzene	76	3960	1.9	14
57. 2-nitrophenol	102	3943	2.5	16
58. 4-nitrophenol	99	3943	2.5	16
59. 2,4-dinitrophenol	64	3943	1.6	14
60. 4,6-dinitro-o-cresol	32	3943	.81	10
*61. N-nitrosodimethylamine	9	3960	.23	2
*62. N-nitrosodiphenylamine	63	3961	1.6	16
63. N-nitrosodi-n-propylamine	5	3960	.13	4
64. pentachlorophenol	250	3943	6.3	24
65. phenol	960	3943	24.3	30

66. bis(2-ethylhexyl) phthalate	1468	3961	37.0	32
67. butyl benzyl phthalate	275	3960	6.9	23
68. di-n-butyl phthalate	611	3963	15.4	28
69. di-n-octylphthalate	194	3960	4.9	20
70. diethyl phthalate	291	3962	7.3	25
71. dimethyl phthalate	166	3960	4.1	18
72. 1,2-benzanthracene (benzo(a)anthracene)	96	3961	2.4	12
73. benzo(a)pyrene (3,4-benzofluoranthene)	107 48	3959 3959	2.7 1.2	14 8
74. 3,4-benzofluoranthene	107	3959	2.7	14
75. 11,12-benzofluoranthene	59	3960	1.5	11
76. chrysene	171	3960	4.3	12
77. acenaphthylene	143	3959	3.6	15 ⁵
78. anthracene	341	3960	8.6	23
79. 1,12-benzoperylene (benzo(ghi)-perylene)	26	3960	.66	7
80. fluorene	189	3957	4.8	17
81. phenanthrene ⁵	352	3961	8.9	22
82. 1,2,5,6-di-benzanthracene (dibenzo(a,h)anthracene)	25	3961	.63	7
83. indeno(1,2,3-cd) pyrene (1,2-o-phenylene pyrene)	32	3960	.81	7
84. pyrene	240	3961	6.1	17
85. tetrachloroethylene	384	3824	10.0	22
86. toluene	1014	3824	26.5	33
87. trichloroethylene	382	3824	9.9	25
88. vinylchloride (chloroethylene)	9	3824	.24	5
'89. aldrin	17	4022	.42	7
90. dieldrin	8	4022	.19	5
91. chlordane (technical mixture)	6	4022	.15	4
92. 4,4'-DDT	8	4022	.19	5
93. 4,4'-DDE(p,p'-DDX)	3	4022	.05	2
94. 4,4'-DDD (p,p'-TDE)	7	4022	.17	4
95. alpha endosulfan	14	4022	.35	7
96. beta endosulfan	9	4022	.22	3
97. endosulfan sulfate	5	4022	.12	2
98. endrin	6	4022	.15	3
99. endrin aldehyde	4	4022	.09	2
100. heptachlor	9	4021	.22	5
101. heptachlor epoxide	9	4022	.22	3

102. alpha-BHC	28	4022	.69	8
103. beta-BHC	20	4022	.49	8
104. gamma-BHC (lindane)	15	4022	.37	5
105. delta-BHC	12	4022	.29	6
106. PCB-1242 (Arochlor 1242)	26	4022	.65	5
107. PCB-1254 (Arochlor 1254)	21	4022	.52	4
108. PCB-1221 (Arochlor 1221)	14	4022	.35	1
				(organics)
109. PCB-1232 (Arochlor 1232)	23	4022	.57	2
110. PCB-1248 (Arochlor 1248)	18	4022	.45	3
111. PCB-1260 (Arochlor 1260)	13	4022	.32	1
112. PCB-1016 (Arochlor 1016)	15	4022	.37	2
113. Toxaphene	6	4022	.15	3
114. Antimony	544	2998	18.1	20
115. Arsenic	598	2998	19.9	19
116. Asbestos ⁶	-	-	-	-
117. Beryllium	423	2994	14.1	18
118. Cadmium	918	2994	30.7	25
119. Chromium	1609	2994	53.7	28
120. Copper	1663	2994	55.5	28
121. Cyanide	1019	3051	33.4	19
122. Lead	1312	2994	43.8	27
123. Mercury	491	2971	16.5	20
124. Nickel	1038	2994	34.7	27
125. Selenium	566	2997	18.9	21
126. Silver	688	2998	22.9	25
127. Thallium	570	2976	19.2	19
128. Zinc	1635	2993	54.6	28
129. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	-	-	-	-

* Indicates compound identification as a probable artifact.

¹ Represents the total number of times a particular pollutant was found in all the tabulated industries.

² Represents the total number of samples analyzed over all industrial categories.

³ Represents the number of industrial categories in which the pollutant was found (total number tabulated = 36 organics and 28 metals). Where a compound was identified in only one category, that category has been indicated in parentheses.

⁴ Resolution of these isomers is often difficult.

⁵ Under the conditions of the screening protocol, anthracene and phenanthrene coelute.

⁶ Not reported because so few industries have been sampled.

Toxic Effects of Isocyanates in Work Environment

A comprehensive information regarding physiologic effects, toxicity, industrial hygiene and medical control of those isocyanates generally associated with polyurethanes is given by Woolrich (1982). The characteristics and most significant physiological effect of exposure to the isocyanates is a direct irritant or sensitization response not unlike asthma. It is most unlikely that long-term exposure to TDI, MDI and PMPI vapours would produce oncogenic effects.

Thirty seven workers with isocyanate asthma were studied by Innocenti *et al* (1981) longitudinally to determine the chronic pulmonary effects due to isocyanates after cease of exposure. After a mean time of 40 months the asthmatic symptoms had disappeared in 32 (86%) workers, while chronic bronchitis developed in 6 (24%). The progressive impairment of ventilatory function was evaluated by means of a longitudinal study of the decrease in FVC and FEV_{1.0} after cease of exposure: a mean annual decrease of 86.3 ml and 67.7 ml, respectively, was observed. These data suggest that TDI induces chronic and irreversible damages even if the exposure is discontinued, and support the view that the FVC is more impaired than the FEV_{1.0}.

The prevalence of atopy in 20 patients

with bronchial asthma due to isocyanates and in 19 patients with chronic obstructive lung disease (COLD) exposed to isocyanates was evaluated by Pagiarro *et al* (1979). Sixteen asthmatic patients showed different types of response to an isocyanate challenge; however, delayed response, isolated or preceded by transient immediate reaction, appeared more characteristic of asthmatic patients with atopy. Three of the patients with COLD showed an immediate response and two a dual type response to the challenge, usually of mild degree. These data suggest that there is an immunological basis to asthma induced by isocyanates and raise the question of the relationship between the various clinical patterns of hypersensitivity.

Isocyanates are likely to be carcinogenic to man. A case of lung cancer which developed in the course of an occupational chronic bronchopulmonary disease due to isocyanates has been reported by Mortillare and Schiavon (1982).

Certain types of firefighting foams are reported by Hardy and Purnell (1978) to be useful for the suppression of the vapour from isocyanate liquid surfaces. In the case of a large isocyanate release within a bund enclosure, the technique may allow the insertion of a pipe through the overlying foam and gel 'skin' into the organic layer in order to pump the latter into suitable containers for subsequent disposal.

ANNEXURE 5

A. ANALYTICAL METHODS AND STUDIES

Spectrophotometric Determination of Aliphatic Isocyanates in Air

APPARATUS

Spectrophotometer: Spectronic-21, equipped with 1 cm path length quartz cell.

Heating tubes: Glass tubes (30 ml cap.) with stopper and tapered at the bottom.

Water bath: Thermostat for constant heating arrangement at 75°C.

Separating funnels: 30 ml cap. for separating the organic layer.

REAGENTS

Standard sodium hydroxide solution: 4 M and 0.1 M

Absorbing solution: Dilute 36 ml of conc. HCl to 100 ml with distilled water. Mix 50 ml of the resulting solution with 50 ml of dimethyl sulfoxide (DMSO).

Sodium borate buffer solution: Dissolve 30.0 gm of boric acid in 700 ml of distilled water. Add slowly, while stirring, 4.0 M sodium hydroxide solution until the pH is 8.8, as indicated by a pH meter.

1-Fluoro-2,4-dinitrobenzene solution: Take 30 μ l of 1-fluoro-2,4-dinitrobenzene by micro-syringe into 5 ml of DMSO in a 10 ml volumetric flask. Dilute the solution to volume with DMSO. Prepare a fresh solution daily.

Stock isocyanate solution: Take 10 μ l of hexamethylene diisocyanate (HMDI) in 50 ml of DMSO in a 100 ml volumetric flask. Dilute the solution to volume with DMSO. Prepare fresh solution daily (1 ml = 52.50 μ g isocyanate).

Standard isocyanate solution: Take 2.5 ml of stock isocyanate solution and dilute to 25 ml with DMSO (1 ml = 5.25 μ g isocyanate).

Carbon-tetrachloride: Spectroscopy grade material was used.

ANALYTICAL PROCEDURE

1. Take 0, 0.95, 1.90, 2.85, 3.80 ml of standard isocyanate solution in heating tubes and dilute to 10 ml with absorbing solution (this corresponds to 0, 5, 10, 15 and 20 μ g of isocyanates).
2. Neutralise the solutions in the tubes with 5.0 ml of 4.0 M sodium hydroxide solution.
3. Add 1.5 ml of sodium borate by pipette and mix.
4. Add 0.1 ml of 0.3% 1-fluoro-2,4-dinitrobenzene solution and again mix.
5. Heat the tubes for 15 minutes at 75°C in a thermostatic water bath.
6. Remove the tubes and cool for 5 minutes. Next add 5.0 ml of 0.1 M sodium hydroxide solution and mix.
7. Add 3.0 ml of CCl_4 by pipette (using rubber bulb) in each tube. Mix the contents of the tube for one minute and transfer the liquid to 30 ml separating funnel, allow the two phases to separate.
8. Take the organic layer in a 5 ml volume flask.
9. Add 20 ml CCl_4 to the aqueous phase in the separating funnel and repeat the extraction.
10. Transfer the organic layer into 5 ml volumetric flask and make up the solution to volume with CCl_4 .
11. Absorbance of CCl_4 extract is measured at 352 nm, using the blank solution to zero of the spectrophotometer. Plot the calibration graph.
12. Determine the amount of isocyanate in the unknown sample by reference to the calibration graph.

Experimental Observations

HMDI Solution

Mol. wt. 168.2 Formula: $\text{OCN}(\text{CH}_2)_6\text{NCO}$
Density 1.05

$$\begin{aligned} 168.2 \text{ mg HMDI} &= 84 \text{ mg NCO (isocyanate)} \\ 1 \text{ mg HMDI} &= \frac{84}{168.2} = 0.5 \text{ mg NCO} \\ &\quad 168.2 \\ 1 \text{ ml HMDI} &= 1.05 \text{ gm} \\ \text{i.e. } 1000 \mu\text{l HMDI} &= 1050 \text{ mg} \\ 1 \mu\text{l} &= \frac{1050}{1000} \text{ mg} \\ 10 \mu\text{l} &= \frac{1050 \times 10}{1000} = \\ &\quad = 10.5 \text{ mg HMDI} \end{aligned}$$

$10 \mu\text{l} = 10.5 \text{ mg HMDI in 100 ml}$
or 105 mg HMDI in 1000 ml or 105 ppm
or 52.5 ppm isocyanate (stock)

Standard isocyanate : 5.25 ppm or 5.25 $\mu\text{g/ml}$

Sodium hydroxide solution

40 gm NaOH in 250 ml (to give 4M, NaOH). Dilute 2.5 ml of above solution to 100 ml (0.1 M, NaOH). Prepare Standard Pot. Hyd. Phthalate solution (0.1 M) (2.042 gm in 100 ml).

$$\begin{aligned} \therefore 5 \text{ ml of KH phthalate} &= 4.65 \text{ ml NaOH} \\ \text{NaOH normality} &= \frac{5 \times 0.1}{4.65} \\ &= 0.107 \end{aligned}$$

$$\therefore \text{Normality of stock NaOH} = 0.107 \times 40 = 4.30 \text{ M}$$

$$\begin{aligned} 4.30 \text{ X V} &= 250 \times 4.0 \\ \therefore V &= \frac{1000}{4.30} = 232.5 \end{aligned}$$

232.5 ml of stock NaOH dil. 250 ml, gives 4.0 M NaOH.

Absorbance Values Produced by the Proposed Method

Wavelength : 352 nm

Amount of isocyanate μg	Absorbance
5	0.151
10	0.268
15	0.421
20	0.582

B. Determination of Primary & Secondary Amines in the Atmosphere (Ninhydrin Method)

Apparatus

Spectrophotometer: Spectronic-21 equipped with 1 cm path length cells.

Heating tubes: Glass tubes (30 ml capacity) with stopper and tapered at the bottom.

Water bath: Thermostat for constant heating arrangement at 85°C .

Reagents

Ninhydrin reagent: Prepare a 0.2 % (w/w) solution of ninhydrin in isopropanol (0.16 gm dissolved in 100 ml isopropanol). This reagent is stable for 2 weeks if kept in a brown bottle.

Absorbing solution: Dilute one volume of conc. HCl to 100 volumes with isopropanol.

Reagent Grade Pyridine

n-Butylamine stock solution: (500 $\mu\text{g/ml}$). Weigh 0.250 gm of n-butylamine in a weighing bottle and dilute to 500 ml with absorbing solution.

n-Butylamine calibrating solution: Prepare a series of standards containing 2 to 100 $\mu\text{g/ml}$ n-butylamine by diluting 0.4 to 20 ml of n-butylamine stock solution to 100 ml with absorbing solution. Take 1 ml of each solution and follow the analytical procedure.

Analytical Procedure

1. Take 3 ml of the sample from the absorbing solution (or 1 ml of n-butylamine calib-

rating solution and dilute to 3 ml) in the heating tubes.

2. To each of the tubes add 5 ml pyridine.
3. Then add 2 ml ninhydrin solution and mix.
4. Place the tubes in water bath at 85°C for 7 minutes.
5. Remove the tubes in water bath and immerse them in cold water for 10 min.
6. Transfer the solution to measuring cells and read the absorbance against that of the blank in the spectrophotometer set at 575 nm.
7. Plot the absorbance of the calibrating solu-

tion as the ordinate versus the concentration as the abscissa on a linear graph paper.

Absorbance Values Produced by Ninhydrin Method

Wavelength : 575 nm

ppm-n-butylamine	Absorbance
2	0.066
5	0.147
10	0.239
15	0.358
20	0.580
25	0.615

Absorbance

ANNEXURE - 6

PHYSICO-CHEMICAL CHARACTERISTICS OF WATER - FIRST SCHEDULE

Sr. No.	Parameter	Sample Serial Number*									
		1	2	3	4	5	6	7	8	9	10
1.	Appearance	Clear	Clear	Hazy	Clear	Clear	Clear	Clear	Clear	Hazy	Clear
2.	Colour	4	3	8	2	3	5	2	2	9	4
3.	Turbidity, NTU	190	190	265	210	185	190	240	220	310	675
1.	Appearance	Clear	Clear	Hazy	Clear	Clear	Clear	Clear	Clear	Hazy	Clear
2.	Colour	None	None	None	None	None	None	None	None	None	None
3.	Turbidity, NTU	4	3	8	2	3	5	2	2	9	4
4.	Conductivity, uS/cm	190	190	265	210	185	190	240	220	310	675
5.	Dissolved solids, mg/l	114	114	159	126	111	114	144	132	186	405
6.	pH, 25°C	7.6	8.0	7.5	7.7	8.0	8.0	8.0	7.9	8.0	8.1
7.	pHs, 25°C	-	-	-	-	-	-	-	-	-	-
8.	Langelier index, 25°C	-	-	-	-	-	-	-	-	-	-
9.	P-alkalinity, as CaCO ₃	0	0	0	0	0	0	0	0	0	0
10.	M-alkalinity "	78	82	103	60	83	83	107	100	116	212
11.	Total hardness "	88	76	96	84	80	82	100	94	116	296
12.	Alkaline hardness	78	76	96	60	80	82	100	94	116	212
13.	Non-alkaline hardness	2	0	0	24	0	0	0	0	0	84
14.	Free CO ₂	-	-	-	-	-	-	-	-	-	-
15.	Calcium as Ca	22.4	22.4	29	27	23	24	30	28	34	82
16.	Magnesium as Mg	5.8	4.9	6	4	5	5	6	6	7	22
17.	Sodium as Na	9.0	9	15	8	8	7	9	9	14	24
18.	Potassium as K	3.0	3	6	3	2	2	1	1	3	1
19.	Ammonia as N	0.13	0.13	0.12	0.111	0.17	0.12	0.20	0.1	0.17	0.1
20.	Iron as Fe	0	0	0	0	0	0	0	0	0	0
21.	Manganese as Mn	0	0	0	0	0	0	0	0	0	0
22.	Chlorides as Cl	9.0	8	17	16	8	8	9	8	9	70
23.	Sulphates as SO ₄	9.0	7	8	26	6	6	6	4	10	20
24.	Fluorides as F	0.5	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
25.	Nitrates as N	0.8	0.5	1.2	0.3	0.7	0.5	0.7	0.5	0.7	6.3
26.	Phosphates as PO ₄	0	0	0	0	0	0	0	0	0	0
27.	Silica as SiO ₂	8.0	0	7	8	12	9	4	4	6	15
28.	Permanganate value+	1.2	0.9	2.7	0.7	1.2	1.3	1.4	1.2	1.5	0.7
29.	Cyanide CN	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

* Sample details are in page 8.

All parameters except those at Sr. Nos. 1,2,3,4,6,7,8 are in mg/l

+ As oxygen, 4 hours at room temperature on whole sample.

PHYSICO-CHEMICAL CHARACTERISTICS OF WATER - SECOND SCHEDULE

Sr. No.	Parameter	Sample Serial Number*								
		1	2	3	4	5	6	7	8	9
1.	Appearance	Clear	Hazy	Clear	Hazy	Clear	Clear	Clear	Clear	Clear
2.	Colour	None	None	None	None	None	None	None	None	None
3.	Turbidity, NTU	3	5	4	12	4	2	1	1	2
4.	Conductivity, uS/cm	170	175	170	240	175	370	1100	700	1900
5.	Dissolved solids, mg/l	102	105	102	144	105	222	660	420	1140
6.	pH, 25 °C	7.3	7.1	7.4	7.5	7.7	7.5	6.0	7.4	8.0
7.	pHs, 25 °C	8.2	8.2	8.1	8.0	8.1	7.8	7.0	7.3	6.7
8.	Langelier index, 25 °C	-0.9	-1.1	-0.7	-0.5	-0.4	-0.3	-0.2	+0.1	+1.3
9.	P-alkalinity, as CaCO ₃	0	0	0	0	0	0	0	0	0
10.	M-alkalinity as CaCO ₃	76	72	80	100	82	104	290	224	456
11.	Total hardness as CaCO ₃	74	80	76	98	78	150	475	234	760
12.	Alkaline hardness	74	72	76	98	78	104	298	224	456
13.	Non-alkaline hardness	0	8	0	0	0	46	177	10	312
14.	Free CO ₂	17	26	14	14	7	15	213	40	21
15.	Calcium as Ca	22	24	24	29	23	40	106	70	189
16.	Magnesium as Mg	5	5	4	6	5	12	51	14	72
17.	Sodium as Na	5	6	7	12	6	18	60	50	130
18.	Potassium as K	2	3	3	5	2	2	2	22	4
19.	Iron as Fe	0	0	0	0	0	0	0	0	0
20.	Manganese as Mn	0	0	0	0	0	0	0	0	0
21.	Chlorides as Cl	5	6	6	13	5	50	160	62	300
22.	Sulphates as SO ₄	0	10	0	1	0	10	50	30	160
23.	Fluorides as F	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5
24.	Nitrates as N	0.4	0.4	0.4	0.9	0.5	0.8	8.0	5	1.9
25.	Phosphates as PO ₄	0	0	0	0.3	0	0	0	0	0.4
26.	Silica as SiO ₂	8	6	8	7	8	9	18	13	25
27.	Permanganate value+	-	-	-	1.5	-	0.4	-	0.3	2.4

* Sample details are in page 9

All parameters except these at Sr. No.s 1,2,3,4,6,7,8 are in mg/l.

+ As oxygen, 4 hours at room temperature on whole sample.

ANNEXURE 7

**MIC CONCENTRATION (ESTIMATED AS METHYLAMINE)
IN AMBIENT ENVIRONMENT OF BHOPAL**

Locality	Date	Sample No.	Timings of sampling	Conc. of MIC g/m ³
Circuit House	16-12-84	7	10.30 am - 01.00 pm	44.40
		26A	06.00 pm - 06.40 pm	28.80
		26	06.40 pm - 07.40 pm	76.80
	17-12-84	15	10.20 am - 11.05 am	125.58
		16	11.00 am - 11.42 am	285.80
Railway Electrification Office	16-12-84	5	07.30 am - 11.00 am	38.16
		9	11.00 am - 12.50 pm	39.30
	17-12-84	20	08.45 am - 09.45 am	71.00
		17	11.05 am - 11.25 am	N.D.
Govt. Dispensary, Chola Naka	16-12-84	6	07.45 am - 11.30 am	36.70
		10	11.30 am - 12.30 pm	307.98
		14	12.30 pm - 01.30 pm	70.00
		22	06.30 pm - 07.20 pm	120.00
	17-12-84	21	09.15 am - 10.20 am	325.00
	16-12-84	8	11.46 am - 12.21 pm	270.00
		18	06.45 pm - 07.16 pm	48.00
Central Instt. of Agricultural Engineering	16-12-84	11	12.00 pm - 01.00 pm	N.D.
		12	01.15 pm - 02.15 pm	N.D.
		13	02.40 pm - 03.40 pm	198.00
	17-12-84	23	11.00 am - 11.45 am	N.D.
Berasia Road	17-12-84	19	11.53 am - 12.00 pm	576.00
Railway Electrification Office	18-12-84	101	11.55 am - 12.40 pm	29.00
		109	10.50 am - 11.50 am	26.00
		110	11.50 am - 12.50 am	40.00
Govt. Dispensary	18-12-84	102	12.45 pm - 01.45 pm	55.00
	19-12-84	111	11.20 am - 12.20 pm	15.00
		112	12.20 pm - 01.20 pm	32.00
Chola Vidyut Kendra (in front of UCIL)	19-12-84	117	12.00 pm - 01.10 pm	45.00
		118	01.10 pm - 01.40 pm	91.00

N.D. = Not detected

ANNEXURE - 8

SPECIMEN COPY OF A WEATHER REPORT AND FORECAST

Summary of Weather over Bhopal and Neighbourhood on 16-12-84 at 1100 IST & Forecast for next 24 hrs.

Synoptic Features

Surface anticyclone lies over M.P. Dry air prevails over Bhopal and neighbourhood.

Weather

Sky clear

Surface winds

Mainly calm during night and early morning hours and variable to south-easterly 5 km/hr during afternoon.

Temperatures

Maximum	26.6°C on 15-12-84
Minimum	10.3°C on 16-12-84

Inversions

- (1) At 2330 hrs IST of 15-12-84 ground inversions of 229 M Thickness with ground temperature 15.6.°C and top 21.2°C wind at ground calm and south-east 15 km/hr at top.
- (2) At 0530 hrs IST on 16th ground inversion 379 M thick, ground temp. 11.8 and 19°C at top. Wind at surface calm and SSE 6 km/hr at top.
- (3) Above this inversion there is an isothermal layer of temperature 14.4°C and thickness 316 M. Wind at bottom of inversion layer SW/12 km/hr and at top west 20 km/hr.

Forecast for next 24 hours

Weather

Sky clear with haze in the night and morning.

Surface winds

East/south-east 5-10 km/hr in the forenoon becoming south-west 5-10 km/hr in the afternoon and calm during night and morning.

Temperatures.

Maximum on 16th is likely to be around 27°C. Minimum on 17th is likely to be around 10°C.

Inversions

Morning's ground inversion is likely to end by 1130 hrs IST today and fresh inversion likely commence by 10.00 pm and increase to 400 metre thickness by 17th morning.

Outlook for next 3 days

Surface winds likely to change to SW/W with speed of 10-15 km/hr from 17th afternoon for about a day. No significant change in the other parameters.

Plain Language Version

Clear skies, haze during night/morning hours. Maximum temperatures on 16th will be around 27°C and minimum on 17th around 10°C.

Surface winds will blow towards west to north-west with a speed 5-10 km/hr in the forenoon and towards north/north-east with speed 5-10 km/hr in the afternoon and calm during night and morning.

Sd./-
(D.V. RAO)
Meteorologist (Gr. I)

on tour
16-12-84 issued at 1030 hrs

SUMMARY OF WEATHER DATA AT BHOPAL

(December 10-20, 1984)

Date	Wind			Temperature		Remarks
	Speed	kmph	Direction	Max. °C	Min. °C	
10-12-84	I	5-13	N,W	30.0	11.2	Normal
	II	Calm	-			
11-12-84	I	19	W,NW,N	29.9	13.0	Normal but starting with westerly.
	II	Calm	-			
12-12-84	I	10-19	SW,W,NW	30.3	13.0	Deviated from normal
	II	Calm	-			
13-12-84	I	10-30	SW,W,NW	29.2	13.7	-do-
	II	10	SW,W			
14-12-84	I	10	N,NE	24.0	08.4	Normal
	II	Calm	-			
15-12-84	I	10	E	26.6	9.6	Normal
	II	Calm	-			
16-12-84	I	5-8	Variable	28.4	10.3	Normal
	II	Calm	-			
17-12-84	I	10	SE,NW	28.5	11.0	Normal
	II	Calm	-			
18-12-84	I	5-10	NW,NE	27.0	10.6	Normal
	II	Calm	-			
19-12-84	I	5	NE,E	26.9	10.6	Normal
	II	Calm	-			

I : day time
II : night time

ENVIRONMENTAL ASPECTS OF CHEMICAL ACCIDENTS

A. Emergency Response System

Any emergency response system is designed to reduce the impact of an accident by rapid containment. In the case of toxic chemical accidents, it is essential to know the nature of the chemicals, how to deal with them, the toxic, physical chemical properties and the level of risk involved in contact, both for the emergency crews and the adjacent population. Thus, the accident involving the release of potentially toxic or hazardous chemicals is different from the normal emergency (traffic accident, fire, train derailment, etc).

By definition, an accident is an unplanned event and thus no two accidents are exactly the same. Further accidents are going to happen regardless of our efforts to prevent them. Hence it is of paramount importance that Governments prepare adequate contingency planning as it will help in prompt mobilization of expert services, manpower and equipment to minimize the effects of accidents. The strategies suggested for reducing the threats from chemical accidents include: (i) to minimise risk of accident occurrence (prevention), (ii) to rapidly contain (emergency response), and (iii) to effectively rehabilitate damaged areas (restoration).

The document suggested guidelines to assist countries to develop compatible strategies for preparing contingency planning systems which are both adequate and rapidly and effectively implementable to respond to specific emergencies.

B. Types of Emergencies

The more important chemical emergencies that may arise are as follows:

- disaster/explosion in a plant handling or producing potentially toxic substances
- accidents in storage facilities handling large quantities of various chemicals

- accidents during transportation of chemicals
- misuse of chemicals, resulting in contamination of foodstuffs, the environment, overdosing of agrochemicals, etc.
- improper waste management, such as uncontrolled dumping of toxic chemicals, failure in waste management systems or accidents in wastewater treatment plants.

Depending on the quality and quantity of chemicals involved in an accident and the local condition the emergency may be classified from various perspectives.

(a) Environmental health aspects:

- *low* contamination of all or part of the environment with only minor annoying effects, but not requiring protective and/or extensive remedial measures
- *serious* contamination of all or part of the environment creating difficulties for man's activities and requiring some protective and/or remedial measures
- *dangerous* contamination of all or part of the environment, limiting some of man's activities in the area
- *extremely dangerous* contamination of all or part of the environment preventing the continuation of many activities.

(b) Duration of adverse effects:

- short-term effects (several hours to a few days)
- long-term effects (several weeks or months)
- almost permanent effects (to last for years)

(c) Extent of remedial action required:

- minor short-term remedies provided at the operator level - this is normally inbuilt in all industries
- considerable remedial activities often of long-term character and exceeding the capabilities of the local level
- considerable long-term rehabilitation of the environment in the affected area.

C. Level of Accident

Accident level is classified depending on the scope or level of accident. Four levels of accidents are considered and these are described below:

Level I (Operator level): An accident where the adverse effects are limited to confines of one facility (e.g. a plant, railway station, storage depot, farm, gas or oil pipeline booster stations and/or terminals) and can be contained and controlled by the operator on the site. Although in some instances it may require the resources of the whole facility to control, the effects of which are not expected to spill over into the community.

Level II (- Local/community level): This involves an accident where the effects are spread to the community but can be contained by the resources of the community, plus resources of the industry involved. The majority of transportation accidents, *viz.*, those occurring 'on route' will fall in this category.

Level III (Regional/national level): This may be large and/or more serious accident or it may be simply that it occurred at the border between two jurisdictions (regional or communities) within one nation or country. This may be described as an inter-jurisdictional emergency and may be handled with the resources available at the regional or national level, employing also the resources of the communities and industries involved (e.g. Bhopal MIC gas tragedy).

Level IV (International level): This is more than a complex accident exceeding the boundaries or resources of one nation. This may be a very large-scale national disaster or it may be unique event requiring for its handling special skills or facilities not available in that country and/or it may simply be a small accident which occurs close to the border of a

neighbouring country. The last type of emergency may be contained using national resources, but the management of the control may be undertaken by an international team (2 or more affected nations) established for the purpose.

D. Criteria for Contingency Planning

There is continuous need for assessment of the risks imposed on the community by potentially hazardous installations, development and/or operations involving toxic chemicals. A hazard is a property of a system which could cause injury or damage, whereas a risk is the probability of an accident occurring multiplied by the damaging effects of the accident.

No precise definitions/distinctions are possible for a toxic or hazardous chemical but can be generally defined as one which can directly cause death or serious irreversible or incapacitating disease, behavioural abnormalities, carcinogenic, teratogenic, mutagenic or other long-term effects in man. Naturally these effects are directly related to the concentration and form of such chemicals in environment as well as mode of entry or contact with the population.

For development of contingency plan the following criteria are important.

- type of operation (probability of accident)
- probable character of potential accident (e.g. explosion, fast release of chemicals into environment, slow release and/or dispersion of the chemicals)
- characteristics of chemical involved in possible accident (toxicity, volatility, persistence)
- local conditions (layout and processes of plant, neighbouring industries, settlements, resources available for emergency response)
- possible consequences of potential accident (area potentially affected, risk to people, spread of damage).

The complexity of individual systems involved, as well as the variety of influences and condition, require the preparation of contingency plans for each particular situation.

EMERGENCY PLANNING
CONTINGENCY PLAN FOR CHEMICAL ACCIDENT

LEGEND

○	Internal resources of operator
△	Resources of the local community
◇	Regional and/or national resources
▽	International resources
AR	Military services
A	Ambulances
DB	Data bank of information
E	Equipment
ES	Expert services (environmental)
F	Fire brigades
HS	Health services
L	Laboratories
M	Material
P	Police
PE	Personnel
NS	Environmental services, water and waste management
Red	Alert
Blue	Information
Green	Physical resources and action

Fig 4

EMERGENCY PLANNING CONTINGENCY PLAN FOR CHEMICAL ACCIDENT – LEVEL I

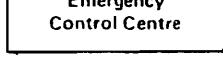
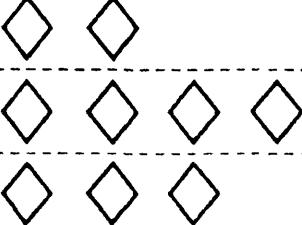
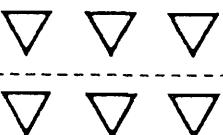
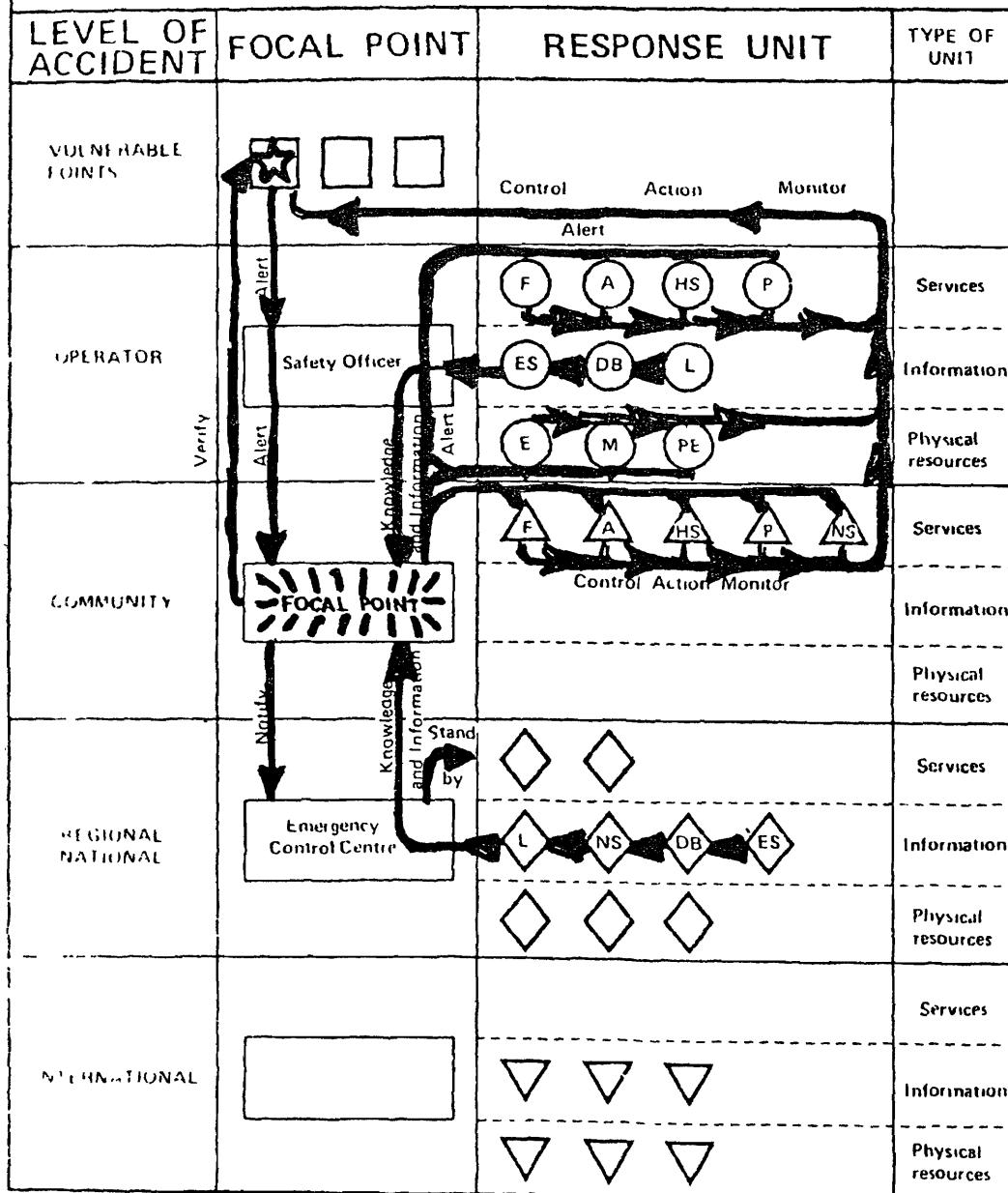
LEVEL OF ACCIDENT	FOCAL POINT	RESPONSE UNIT	TYPE OF UNIT
VULNERABLE POINTS			
OPERATOR	<p>Verify Alert</p> <p>Alert</p> <p>Notify</p> <p>FOCAL POINT</p> <p>ES DB L</p> <p>E M PE</p>	 <p>Control Action Monitor</p>	Services Information Physical resources
COMMUNITY	 <p>Stand by</p> <p>Emergency Control Centre</p>	 <p>Control Action Monitor</p>	Services Information Physical resources
REGIONAL NATIONAL		 <p>Diamonds (Services, Information, Physical resources)</p>	Services Information Physical resources
INTERNATIONAL		 <p>Inverted triangles (Services, Information, Physical resources)</p>	Services Information Physical resources

Fig 6

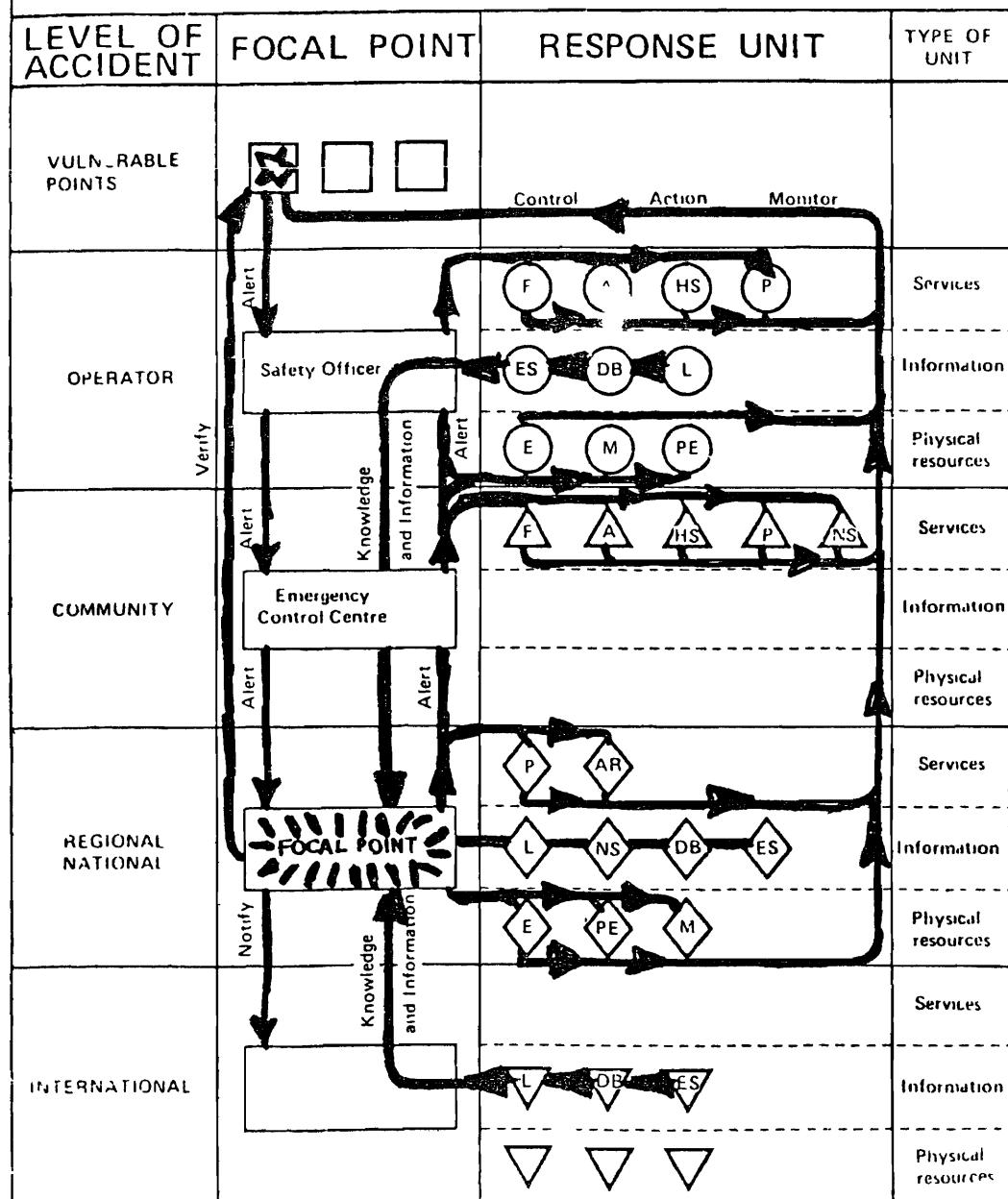
EMERGENCY PLANNING CONTINGENCY PLAN FOR CHEMICAL ACCIDENT – LEVEL II



The legend for this figure appears on page 24.

Fig. 7

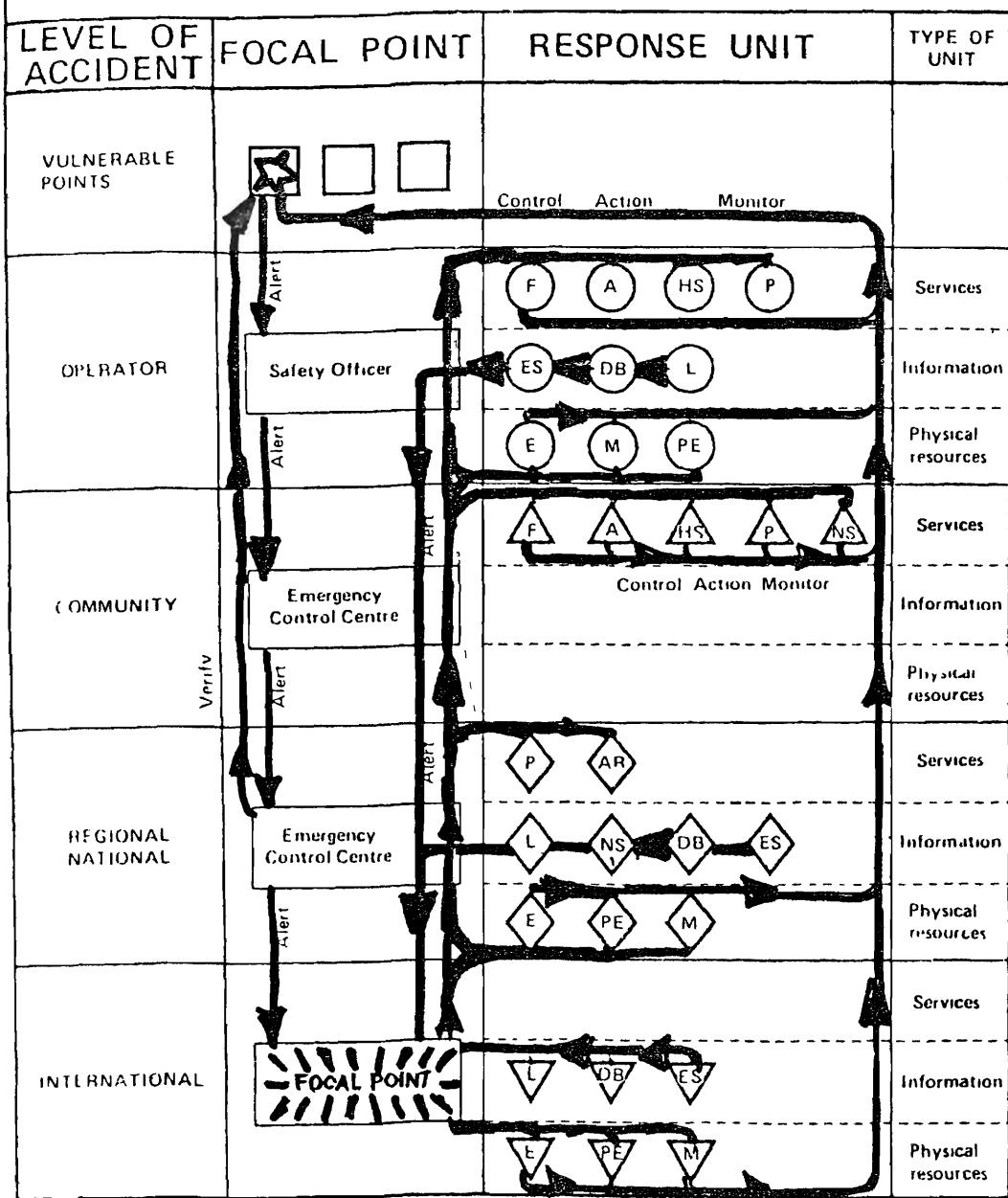
EMERGENCY PLANNING CONTINGENCY PLAN FOR CHEMICAL ACCIDENT – LEVEL III



The legend for this figure appears on page 24.

Fig 8

EMERGENCY PLANNING CONTINGENCY PLAN FOR CHEMICAL ACCIDENT - LEVEL IV



The legend for this figure appears on page 24.

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(6th to 21 December, 1984)**

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In addition seventy three personnels from Bhopal, Delhi, Nagpur and Indore of India Meteorological Department also contributed.

INDIAN TOXICOLOGY RESEARCH CENTRE
LUCKNOW

BHOPAL DISASTER
A FOLLOW UP STUDY PHASE I & II

1986

The report on phase I and II follow up studies conducted by the Indian Toxicology Research Centre (ITRC), Lucknow is contained in the following pages. ITRC established a small follow-up Study Centre at Bhopal, which began operating on 14 February 1985, to monitor various clinical parameters of the gas-victims. About 687 patients were examined during the phase I. Systematic investigations for studying ten different parameters involving history, clinical examination, chest X-rays, lung function tests, haematological, behavioural immunological biochemical studies and chromosomal conditions were undertaken. Phase II commenced from 18th March 1985 and lasted for three more weeks.

The data presented, particularly those showing various abnormal physiological functions in the population group studied by ITRC are indicative of various deleterious effects which appear to have been caused due to exposure to the toxic gas. All the people had complained about signs and symptoms which had a great degree of similarity indicating that they were exposed to similar type of toxic gas. Therefore, the signs and symptoms and after-effects recorded in the study appear to be related to their exposure to methyl isocyanate gas and any others produced and released after the run-away reaction in the storage tank of methyl isocyanate.

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BHOPAL DISASTER—A FOLLOW-UP STUDY

Participating Organisation :

Industrial Toxicology Research Centre
(Council of Scientific & Industrial Research)
Lucknow, India.

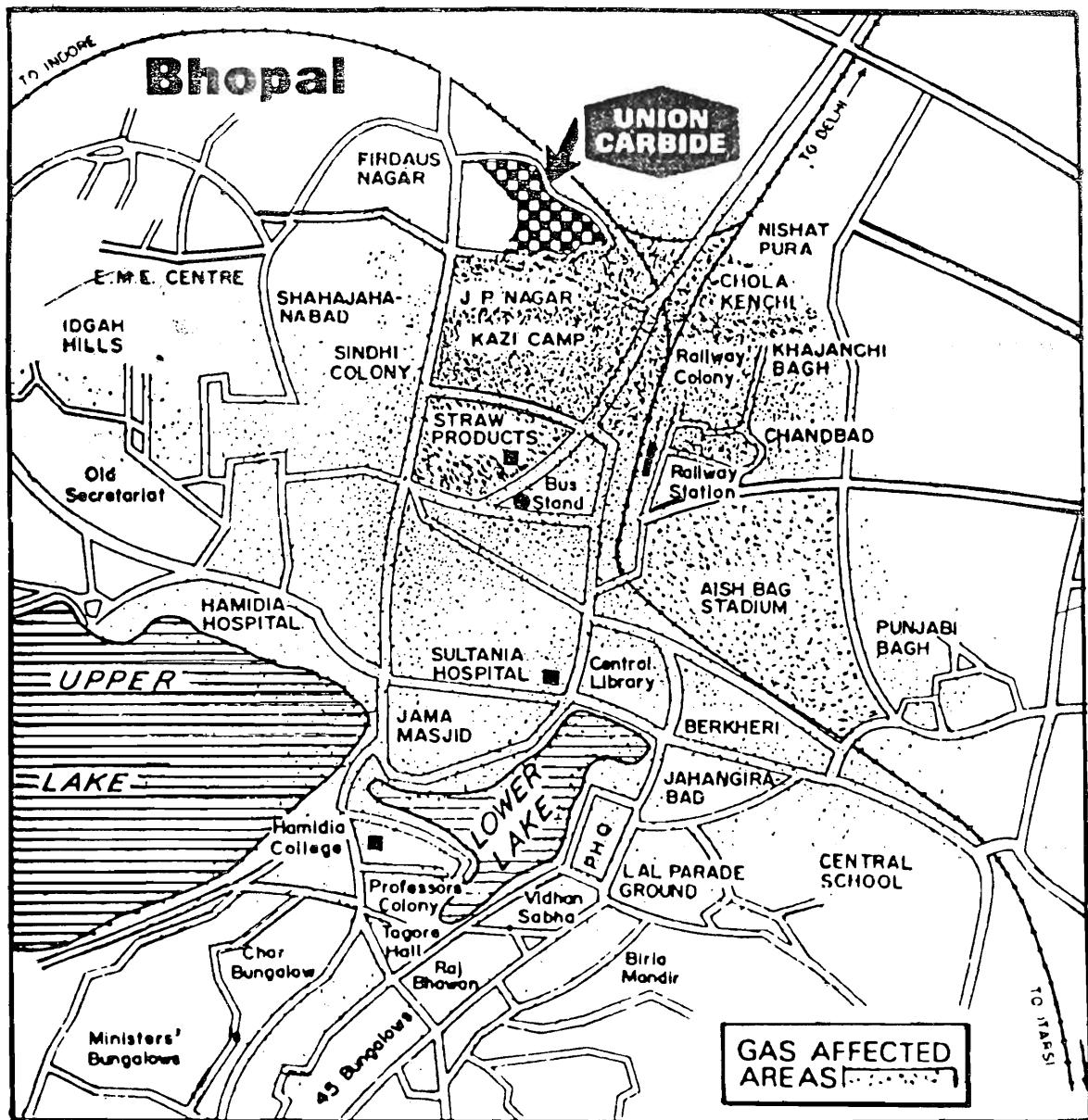
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Map of Bhopal showing gas affected areas

INTRODUCTION

BACKGROUND INFORMATION

The Bhopal Disaster

Bhopal, (Lat. 23.16° N; 77.24° E) the capital of Madhya Pradesh, having, a population of approximately nine lakhs and located 355 miles south of Delhi, had world's worst chemical disaster that took place around midnight of 2nd December, 1984. Deadly methyl isocyanate had escaped from a storage facility at a local Union Carbide plant situated at the north-east end about 2 km from the Bhopal Railway Station. The escaping gas quickly spread in a fog like cloud over a large and highly populated area of about 7-8 sq. km mostly to the south and east of the plant (please see the map on the adjacent page).

The leakage created panic among the residents of Bhopal. Almost one third to half of the population left the city to save their lives. Many died, while many others managed to survive with severe lung problems, eye irritations, confusion, mental problems etc.

The early acute effects, aside from the pathetic death toll were frightening, particularly in their indication of possible long-term prognoses. As the cloud of gas swept over parts of the city, striken residents experienced a burning sensation in the eyes, nose and throat. Many burst out of their homes coughing, and gasping for breath. Some began vomiting uncontrollably, others just collapsed. Ulcers formed on the corneas of some victims, blinding them.

The immediate reaction of the scientific and medical community of the country was to offer, in the best possible way, whatever help could be given to save the lives of the unfortunate victims and to prevent untoward health effects in future. ITRC team and medical doctors from all over the country rushed to Bhopal carrying with them the necessary medicines and other requisites and alongwith their colleagues in Bhopal did a yeomen job in providing medical assistance to the suffering humanity of Bhopal. The medical fraternity of India specially that of Bhopal has a sense of pride. The pride comes from the way in which the immediate medical response to the disaster was handled. By all accounts, Bhopal's considerable medical establishment reacted spontaneously and adeptly to the unprecedented emergency. But, once the acute problem was over it was time to concentrate on what long-term effects this gas will have on the health of the exposed population. The exposure posed some important questions :

1. What are the long-term effects in the surviving population of Bhopal ?
2. Since the gas caused pulmonary edema, is it likely that the victims may develop pulmonary fibrosis in due course of time ?

3. What is the effect of the exposure on the pulmonary function of the victims and whether the pulmonary function will remain stationary, improve or deteriorate with passage of time ?
4. Whether immunological functions have been impaired ?
5. Whether the victims have become prone to develop respiratory infections—viral, bacterial and others ?
6. It is likely that exposure to methyl isocyanate may have resulted in hypoxia which in turn might have affected the nervous tissue and caused neuronal damage. It would be beneficial to conduct a battery of behavioural and psychological tests which could detect the earliest changes of the central nervous system.
7. Since methyl isocyanate affects the eyes, many of the exposed population must have suffered with varying degrees of ocular damage ranging from only a slight irritation of the eyes to severe injury.
8. The exposed population has received varying amounts of methyl isocyanate which entered the body system through inhalation, got reacted with functional biomolecules, metabolised and ultimately excreted causing systemic toxicity.

The follow-up study was undertaken by ITRC to find some answers to the above questions.

Prof. P. K. Ray, Director, ITRC organised a team of scientists and technicians who reached Bhopal on 11th February, 1985 to conduct a follow-up study of methyl isocyanate exposed population. Dr R. K. Bisaria, the Mayor of Bhopal was contacted to get a suitable venue to establish the follow-up study Centre so that the affected people could be studied under one roof. Dr Bisaria extended full cooperation in providing two rooms in the Nagar Nigam Building. Dr M. I. Khan, Principal, Hahnemann Homœopathic Medical College and Hospital at Noor Mahal Road, Bhopal, provided eight rooms in his hospital. ITRC established follow-up-study Centre at this place on 14th February, 1985. The clinic was inaugurated by Dr R. K. Bisaria, the Mayor of Bhopal.

During the first phase we studied 687 gas affected people both male and female including children, of various age groups and from different affected areas like Chola Road, Kaji Camp, Islampure, Bazaria railway station, Chandbari etc. The daily inflow of patients ranged from 70 to 80 cases. Our whole team worked hard to cover up this large rush. The following parameters were studied in each case :

1. History taking
2. Clinical examination
3. Chest X-ray

4. Lung function tests
5. Haematology
6. Behavioural studies
7. Immunological studies
8. Biochemical studies
9. Metabolic studies
10. Chromosomal studies

Since the studies could not be completed in one phase, the second phase commenced from 18th March, 1985 and these studies were conducted for another three weeks. The detailed data are presented in subsequent sections of this volume.

GENERAL CHARACTERISTICS OF THE SUBJECTS

Description of the population studied

The general characteristics of the population studied during the follow-up studies of MIC exposed population at Bhopal were recorded on a questionnaire proforma by personal interview and details of name, father's name, address, age, sex, marital status, food habits, religion, educational qualifications, occupation, personal income, total family income and per capita income, details of living conditions, type of the house, type and size of the family, distance from Union Carbide Factory were recorded and later on this data was analysed to divide the population under study in different groups depending upon their age, sex, distance from the factory etc. etc. and to place them in different socio-economic groups and different levels of exposure groups. The information collected is given in the following tables :

TABLE—1
Age and sex-wise distribution of population studied

Age Group (years)	Sex		Total
	Male	Female	
≤15	85	91	176 (16%)
16—25	124	166	290 (26%)
26—35	124	147	271 (24%)
36—45	84	103	187 (17%)
46—55	42	54	96 (9%)
≥56	49	40	89 (8%)
Total	508 (45.81%)	601 (54.19%)	1109

A population of 1109 subjects, effected by MIC gas was studied at Bhopal. Out of these 508 subjects (45.81%) were males while 601 subjects (54.19%) were females (Table 1)

The whole population was divided into age groups ≤15, 16-25, 26-35, 36-45, 46-55 and more than 56 years and according to such a division the percentage of population in above age groups was 16, 26, 24, 17, 9 and 8 respectively.

TABLE—2
Religion and age-wise distribution of population studied

Age Group (years)	Hindu	Religion		Total
		Muslim	Others	
≤15	17	155	4	176 (16%)
16—25	56	230	4	290 (26%)
26—35	57	210	4	271 (24%)
36—45	42	145	—	187 (17%)
46—55	21	74	1	96 (9%)
≥ 56	9	80	—	89 (8%)
Total	202 (18.21%)	894 (80.61%)	13 (1.17%)	1109

Out of 1109 persons studied, 202 subjects (18.21%) were Hindus, 894 subjects (80.61%) were Muslims and 13 subjects (1.17%) belonged to other religions. This high proportion of Muslims in the population under study is because of the fact that most of the residents in the areas worst affected by the gas exposure were Muslims (Table 2).

TABLE—3
Age-wise marital status of population studied

Age Group (years)	Bachelor	Marital Status		Total
		Married	Others	
≤15	176	—	—	176 (16%)
16-25	156	134	—	290 (26%)
26-35	20	251	—	271 (24%)
36-45	4	183	—	187 (17%)
46-55	3	93	—	96 (9%)
≥ 56	3	86	—	89 (8%)
Total	362 (32.64%)	747 (67.36%)	—	1109

In Bhopal gas tragedy, study of 1109 patients was taken up. Out of these 32.64% were bachelors and 67.36% married. In age groups less than 15, 16-25, 26-35, 36-45, 46-55, and above 56, the percentage of bachelors were 100, 54, 7, 2, 3 and 3 respectively. Rest were married (Table 3)

TABLE—4
Food habits and age-wise distribution of population

Age Group (years)	Vegetarian	<i>Food Habits</i>		Total
		Non-vegetarian		
≤15	20	156	176	(16%)
16-25	33	257	290	(26%)
26-35	35	236	271	(24%)
36-45	25	162	187	(17%)
46-55	13	83	96	(9%)
≥ 56	8	81	89	(8%)
Total	134 (12.08%)	975 (87.92%)	1109	

Out of 1109 subjects studied, 134 subjects (12.08%) were on vegetarian diet while 975 subjects (87.92%) were non-vegetarians. The higher percentage of non-vegetarian population was because the population under study comprised of a majority of Muslims who are usually non-vegetarians (Table 4).

TABLE—5
Type of family and age-wise distribution of the population studied

Age Group (years)	Nuclear	<i>Type of family</i>		Total
		Joint		
≤15	51	125		176
16-25	71	219		290
26-35	68	203		271
36-45	35	152		187
46-55	16	80		96
≥ 56	18	71		89
Total	259	850		1109

In the studied population of 1109 subjects, 259 subjects (23.35%) were residing in nuclear type of family while 850 subjects (76.65%) belonged to the joint type of the family. Twenty nine per cent in age group of less than 15 years, 24% in 16-25 years, 25% in 26-35 years, 19% in 36-45 years, 17% in 46-55 years and 20% in more than 56 years age group respectively belonged to nuclear family. The remaining persons belonged to joint family (Table 5)

TABLE—6
Age-wise distribution of population living at various distances
from Union Carbide factory

Age Group (years)	Distance (Km)				Total
	<2	2—4	4—6	>6	
≤15	112	53	10	1	176 (16%)
16-25	170	86	20	14	290 (26%)
26-35	152	95	18	6	271 (24%)
36-45	102	68	9	8	187 (17%)
46-55	70	22	3	1	96 (9%)
≥ 56	65	21	3	—	89 (8%)
Total	671 (60.5%)	345 (31.1%)	63 (5.68%)	30 (2.71%)	1109

Out of the total population studied (1109 subjects), 671 subjects (60.5%) were residing at a distance of less than 2 kilometers from Union Carbide Factory. This population (60.50%) was worst affected by the gas exposure. 345 subjects (31.11%), 63 subjects (5.68%) and 30 subjects (2.71%) were residing at a distance of 2-4 kilometers, 4-6 kilometers and more than six kilometers from the Union Carbide Factory.

TABLE—7
Age-wise distribution of population on the basis of family size

Age Group (years)	Family size			Total
	<5	6—10	>11	
≤15	55	97	24	176 (16%)
16-25	107	142	41	290 (26%)
26-35	84	149	38	271 (24%)
36-45	68	95	24	187 (17%)
46-55	34	54	8	96 (9%)
≥56	38	36	15	89 (8%)
Total	386 (34.81%)	573 (51.67%)	150 (13.53%)	1109

Out of 1109 population studied, 386 subjects (34.81%) were having less than five members in the family while 573 subjects (51.67%) and 150 subjects (13.53%) were having six to ten members and more than eleven members in the family respectively. Six to ten members or more than eleven members reflect the crowding in the family (Table 7)

TABLE—8
Age-wise distribution of educational qualifications of population studied

Age Group (years)	<i>Educational qualifications</i>							Total
	Illiterate	Primary	Middle	High School	Inter	Degree		
≤15	39	92	21	17	10	—	176 (16%)	
16-25	71	42	32	27	43	75	290 (26%)	
26-35	97	49	26	20	37	42	271 (24%)	
36-45	70	29	20	13	25	30	187 (17%)	
46-55	45	13	5	11	6	16	96 (9%)	
≥56	38	15	10	8	8	10	89 (8%)	
Total	360 (32.46%)	240 (21.64%)	114 (10.28%)	96 (8.66%)	129 (11.63%)	173 (15.60%)	1109	

Out of 1109 cases studied in Bhopal gas tragedy 32.46% were illiterate, 21.64% primary, 10.28% middle, 8.66% High School, 11.63% Intermediate and 15.6% degree holders. So many among those surveyed were either illiterate or had just primary education (Table 8).

TABLE—9
Age-wise distribution of population on the basis of open and closed houses

Age Group (years)	<i>Type of house</i>		Total
	Open Houses	Closed Houses	
≤15	75	101	176 (16%)
16-25	121	169	290 (26%)
26-35	84	187	271 (24%)
36-45	81	106	187 (17%)
46-55	35	61	96 (9%)
≥56	42	47	89 (8%)
Total	438 (39.5%)	671 (60.5%)	1109

In the studied population of 1109 subjects, 438 (39.5%) used to sleep in open while 671 (60.5%) were residing in close (covered) houses (Table 9)

Age-wise distribution of population on the basis of per capita income

Age Group (years)	Per Capita Income (Rupees per month)				Total
	≤300	301—500	501—800	≥801	
≤15	162	9	2	3	176 (16%)
16-25	260	17	10	3	290 (26%)
26-35	247	18	4	2	271 (24%)
36-45	161	21	4	1	187 (17%)
46-55	84	5	3	4	96 (9%)
≥56	79	8	1	1	89 (8%)
Total	993 (89.54%)	78 (7.03%)	24 (2.16%)	14 (1.26%)	1109

Out of 1109 cases studied, 993 subjects (89.54%) had per capita income upto or less than Rs 300/- per month, 78 (7.03%) had per capita income between 301-500 rupees per month, 24 (2.16%) had per capita income between 501-800 rupees per month and 14 (1.26%) had per capita income of Rs 801/- or more (Table 10).

SYMPTOMATOLOGY

Complaints related to the respiratory and ocular systems constituted the majority, being 22.1 and 20.2 per cent respectively of the overall complaints, this was followed by complaints pertaining to the gastrointestinal (16.4%) and musculo-skeletal systems (12.3%). Psychogenic complaints were noted in 11.0 per cent of cases. Complaints related to the cardiovascular system, skin, urinary, genital and central nervous system were observed in 3.1, 1.2, 0.8, 0.2 and 0.1 per cent subjects respectively. Headache, ear and dental problems and thirst, included in the miscellaneous group, formed 10.4 per cent of the total.

Symptomatology involving the various body systems was analysed with reference to distance from the factory. The average number of complaints per subject showed a declining trend with increasing distance from the factory. The prevalence of symptoms pertaining to respiratory and gastrointestinal systems was significantly higher in population residing less than 4 km as compared to those residing beyond that distance from the factory. Sleep was normal in only 69.8 per cent subjects while 344 (31.2%) subjects complained of insomnia.

SYSTEM - WISE DIVISION OF COMPLAINTS

- A. Cardiovascular system
- B. Respiratory system
- C. Gastro-intestinal system
- D. Musculo-skeletal system
- E. Urinary system
- F. Genital system
- G. Ocular system
- H. Psychological complaints
- I. Dermal complaints
- J. Central nervous system
- K. Miscellaneous
 - Headache
 - Ear conditions
 - Dental problems
 - Thirst

TABLE—1
Age-wise complaints and systems involved

System involved	Age-Group (years)						Total	Percentage
	≤15	16–25	26–35	36–45	46–55	≥56		
215	A	36 (2.5)	68 (2.9)	54(2.3)	80(5.6)	21(2.5)	15(2.4)	274 (3.1)
	B	281(20.1)	549(23.8)	483(20.7)	317(22.0)	192(23.5)	142(22.9)	1964 (22.1)
	C	280(20.1)	316(13.7)	407(17.4)	233(16.2)	123(15.0)	101(16.3)	1460 (16.4)
	D	171(12.2)	353(15.3)	330(14.1)	209(14.5)	138(16.9)	64(15.1)	1295 (14.5)
	E	10(0.7)	14(0.6)	14(0.6)	19(1.3)	13(1.5)	1(0.6)	71 (0.8)
	F	0	5(0.2)	3(0.1)	6(0.4)	5(0.6)	1(0.2)	20 (0.2)
	G	322(23.0)	444(19.3)	460(19.7)	270(18.8)	160(19.6)	144(23.2)	1800 (20.2)
	H	132(9.4)	239(10.0)	312(13.3)	150(10.4)	90(11.0)	52(8.4)	975 (11.0)
	I	18(1.2)	36(1.5)	20(0.8)	14(0.9)	5(0.6)	10(1.6)	103 (1.2)
	J	—	6(0.3)	1(0.4)	—	2(0.2)	—	9 (0.1)
	K	149(10.6)	268(11.6)	249(10.6)	137(9.5)	66(8.0)	59(9.5)	928 (10.4)
Total complaints		1399	2298	2333	1435	815	619	8899
Total cases studied		182	284	282	174	93	82	1097
No. of complaints per person		7.6	8.1	8.3	8.2	8.8	7.6	

Figures in parenthesis are the percentages of total complaints

TABLE—2
Distance-wise complaints and systems involved
 Distance from factory (Km)

System involved	<2	2-4	>4*
A	207(3.5)	60(2.4)	7(1.3)
B	1311(22.2)	551(22.3)	102(19.4)
C	957(16.2)	446(18.1)	57(10.8)
D	872(14.8)	329(13.3)	94(12.9)
E	49(0.8)	20(0.8)	2(0.4)
F	11(0.2)	5(0.2)	4(0.8)
G	1175(19.9)	516(20.9)	109(20.8)
H	609(10.3)	286(11.6)	80(15.2)
I	65(1.1)	24(1.0)	14(2.7)
J	3(0.1)	6(0.2)	—
K	646(10.9)	226(9.1)	56(10.7)
Total	5905	2469	525
Total population studied	655	351	91
Average number of complaints per person	9.0	7.0	5.8

Figures in parenthesis are the percentages of total complaints

*Number of subjects over 6 km distance was very small hence it was pooled with 4-6 km category

CLINICAL FINDINGS

All the cases studied were subjected to a thorough clinical examination, the findings of which are as follows:

The percentage of population having good physique was 17.5. The general appearance of about 66 per cent subjects was fair, 44 subjects (4.0%) were of obese built while 139 subjects (12.5%) had a poor general appearance.

Examination of tongue showed a normal clean tongue in 735 subjects (66.3%), 309 subjects (27.9%) had coated tongue. Furring, ulceration, dryness and cyanosis were observed in 0.8, 0.5, 4.2 and 0.3 per cent cases respectively.

The throat was found normal in 729 subjects (65.7%) while it was infected, congested or granulated in 44 subjects (3.9%), 334 subjects (30.1%) and 2 subjects (0.2%) respectively.

The conjunctiva was normal in 574 subjects (51.8%), jaundiced in 15 subjects (1.4%), and congested in 338 subjects (16.4%).

The examination of the oral cavity revealed that the teeth and gums were normal in 790 subjects (71.2%) and 1039 subjects (93.6%) respectively. The incidence of caries was found in 195 subjects (17.6%) and teeth were missing in 124 subjects (11.3%). Bleeding, hypertrophy and infection of gums were noted in 42 subjects (3.8%), 26 subjects (2.3%) and 2 subjects (0.2%) respectively.

Lymphadenopathy was seen in 95 subjects (8.5%).

Tachycardia (pulse rate more than eighty beats per minute) was found in 754 (67.8%) subjects while remaining 32.2 per cent had a pulse rate less than 80 per minute.

Abnormal breath sounds on auscultation were heard in 131 subjects (11.8%). Out of this 5.8 per cent had ronchi, 3.4 per cent had crepts and 2.6 per cent had diminished breath sounds. In the remaining population (88.2%) normal bronchovascular breath sounds were heard in all areas of chest.

Clinical examination of heart and blood vessels did not reveal any significant abnormality in the majority of subjects examined.

Out of total persons examined, 895 (80.5%) had no abnormality in the abdomen on palpation. 211 subjects (19%) showed mildly tender and palpable liver. Spleen was found palpable in 5 subjects (0.4%).

LUNG FUNCTION STUDIES

Isocyanates are highly reactive substances and present a toxic hazard since exposure to isocyanate vapours have been reported to cause acute irritation of respiratory tract and bronchospastic reactions. The inhaled isocyanates may react with components in the lung, leading to changes or to the inhibition of biological functions. The isocyanates have also been shown to cause pulmonary impairment and typical attacks of bronchial asthma and hypersensitivity and pneumonitis in the exposed workers. In view of this it was aimed to evaluate the pulmonary function status of the methyl isocyanate gas affected population of Bhopal and to determine the prevalence of respiratory impairment observed in the exposed population.

MATERIAL AND METHODS

Lung spirometry was conducted in 783 cases out of 1135 gas victims examined in the present respiratory screening programme during February/March 1985 at Bhopal. Out of 783 cases, 371 males and 412 females took part in the pulmonary function testing. Children below the age of 10 years were not included in this study since they were unable to perform lung function tests properly. Among the 371 male population studied, there were 179 (48.2%) non-smokers and 192 (51.7%) revealed smoking habit while in the female population there was none with the smoking history.

The study population was broadly classified into two sub-groups depending upon the presence or absence of respiratory symptoms viz., dry or wet cough, exertional dyspnoea of varying grades, chest pain, chest irritation, chest tightness etc., induced by methyl isocyanate gas exposure.

1 Asymptomatic Population

This comprised of the sample of the study population which was unaffected by the methyl isocyanate gas exposure as evidenced by the absence of any pulmonary symptom as revealed during interrogation while completing the MRO, modified respiratory questionnaire. Hence this sample was treated as NAD group with respect to pulmonary function study.

2 Symptomatic Population

This set of population complained of various upper and lower respiratory tract symptoms ranging from cough to throat irritation caused by the inhalation of methyl isocyanate gas.

METHODOLOGY

The following spirometric lung functions were recorded using calibrated Vitalograph (Model-S, U. K.) and Morgan's Dry Spirometer (Model M-8, U. K.) in standing position with nose clip on. The dry spirometers were frequently checked for calibration of volume and speed statically and dynamically with a 50 ml syringe.

- (i) Vital Capacity (VC)
- (ii) Forced Vital Capacity (FVC)
- (iii) Forced Expiratory Volumes ($FEV_{0.75}$, FEV_1)
- (iv) Tiffeneau Index, FEV_1/FVC Ratio
- (v) Maximal Voluntary Ventilation (MVV)
- (vi) Forced Expiratory Flow Rate FEFR ($200-1200\text{ml}$)
- (vii) Mid Expiratory Time (MET)
- (viii) Mid Expiratory Flow Rate (MEFR $25-75\%$)
- (ix) Air Velocity Index (AVI)
- (x) Peak Expiratory Flow Rate (PEFR)
- (xi) PEFR/MMEF Ratio

The population studied was instructed and demonstrated the correct technique to perform these spirographic tests. Patients performed at least three satisfactory VC and FVC manoeuvres. We determined the test satisfactory if the case understood the instructions and performed the test with a smooth continuous exhalation; with apparent maximal effort. The unsatisfactory spirograms were discarded on the following grounds :

- (a) No maximal effort observed while performing the spirometry
- (b) Early termination of expiration
- (c) Leakage through mouth
- (d) Mouth piece obstruction by the tongue or teeth

Thus only those spirograms were included in the study which showed less than 5% variation in FVC and FEV₁ among the three acceptable curves as recommended by Ferris (1978).

Peak Expiratory Flow Rate (PEFR) was recorded with the help of Peak Flow Meter designed by B.M. Wright (Standard Model, U. K.) and the highest value attained was included in the study. The values of spirometric lung functions were expressed at Body Temperature and Ambient Pressure Saturated with Water Vapour (BTPS). Maximal Voluntary Ventilation was calculated from $FEV_{0.75}$ by multiplying it by 40. AVI was calculated from the predicted VC and MVV as follows :

$$AVI = \frac{\% \text{ of Normal MBC}}{\% \text{ of Normal VC}}$$

Normal value was considered to be 1.0. Higher values indicated restrictive pattern and lower values showed obstructive type of respiratory impairment. The FEV_1/FVC percentage between 70-80% was considered within the normal range and values less than 70% indicated central airway obstruction.

The predicted normal values for the various lung function tests were derived from the regression equations laid by Rastogi et al (1983) for the adult male population. For the female population, the normal predicted values were calculated using Jain's (1966, 1967 & 1969) and

Bhattacharya & Banerjee (1966) regression equations. The FEF_{200-1200ml} and MMEF_{25-75%} were calculated over the FVC curve by the methodology of Leuallen and Fowler (1955). PEFR/MMEF was calculated according to Bhalla et al (1979).

The ventilatory disturbance was classified as follows :

1. Restrictive : Based on VC, FVC (Less than 80% of predicted)
2. Obstructive : Based on lowered FEV₁/FVC ratio (<70%)
3. Mixed : Mixture of restrictive & obstructive defect

80% of the predicted value was chosen as a reasonable level for all lung indices studied. The normal values ranged between 80-100% of the predicted ones. If the lung function values were less than 80% of the predicted they were classified as abnormal and the severity of impairment was graded as follows :

1. Mild impairment : Between 60-80%
2. Moderate impairment : Between 40-60%
3. Severe impairment : More than 40%

STATISTICAL PROCEDURE

Chi square test was used for the determination of the significance of the prevalence of various categories of respiratory impairment in the male and female MIC gas exposed population classified into different age and distance groups.

The pulmonary function assessment was done by applying students paired/unpaired 't' test in the methyl isocyanate gas exposed male and female population in different age and distance groups.

RESULTS

Physical Characteristics Of Study Population

The physical characteristics of the male and female population studied for lung function are detailed in Table 1. The mean age of the male population was found to be 33.8 ± 0.60 years ($\pm SEM$) while female population was slightly younger (mean age 32.9 ± 0.55 years). Thus it was seen that sexwise there was no significant difference observed between the male and female population drawn at random for the present study ($p < 0.05$). Among the male population, however there existed the age difference between non-smokers and smokers. Smokers were significantly older than the non-smokers ($p < 0.001$). Similarly the height also differed between the two groups ($p < 0.05$) thereby revealing that non-smoking male population was taller than their smoking counterparts. No significant difference could be observed in their respective weights.

The mean anthropometric measurement of methyl isocyanate gas exposed population affected by pulmonary impairment is presented in Table 2. The male population which suffered from obstructive, restrictive and combined restrictive cum obstructive ventilatory defects did not differ significantly in their mean age. Similarly, the female population also did not reveal any age difference except in those who were affected by obstructive and mixed ventilatory impairment ($p < 0.01$). Female population with combined spirometric abnormality was older than those with obstructive or restrictive ventilatory insufficiencies. The mean distance from the UCIL factory did not differ significantly in the male or female population affected by pulmonary impairment.

Prevalence Of Respiratory Impairment In The Study Population

The prevalence of ventilatory impairment in the male and female population is shown in Table 3. The overall prevalence of ventilatory impairment was found to be 33.9% in the male population in contrast to 44.1% observed in female population, which was slightly higher

TABLE—1
Physical characteristics of MIC exposed population

Study Group	n	Age (Years)		Height (cm)		Weight (Kg)		Distance from UCIL factory	
		\bar{X}	$\pm SE(\bar{X})$	\bar{X}	$\pm SE(\bar{X})$	\bar{X}	$\pm SE(\bar{X})$	\bar{X}	$\pm SE(\bar{X})$
Male Population	371	33.8	\pm 0.60	162.5	\pm 0.35	54.5	\pm 0.5	2.5	\pm 0.06
Non-Smokers	179	30.8	\pm 0.82	163.5	\pm 0.50	55.2	\pm 0.7	2.6	\pm 0.09
Smokers	192	36.7	\pm 0.81	161.7	\pm 0.49	53.9	\pm 0.6	2.4	\pm 0.07
Female Population	412	32.9	\pm 0.55	149.3	\pm 0.29	48.3	\pm 0.5	2.7	\pm 0.05

TABLE—2

Physical characteristics of MIC exposed population affected by pulmonary impairment

Characteristics	MALE			FEMALE		
	Obstructive (n = 14)	Restrictive (n = 54)	Mixed (n = 57)	Obstructive (n = 15)	Restrictive (n = 50)	Mixed (n = 117)
Age *(Years)	404.4±3.3	34.6±1.7	39.2±1.7	31.0±2.6	36.4±1.6	39.9±1.0
Height *(Cm)	161.2±1.7	163.7±0.9	161.9±0.8	149.7±1.3	150.1±0.8	147.6±0.6
Weight *(Kg)	52.1±2.5	54.1±1.5	54.2±1.5	47.4±2.1	50.6±1.5	48.3±0.9
Distance From UCIL Factory* (Km)	1.9±0.5	2.4±0.14	2.3±0.15	2.8±0.3	2.7±0.1	2.6±0.1

* Values expressed as mean ± SEM

TABLE—3

Prevalence of respiratory impairment in MIC gas exposed population

Study Population	n	Normal Spirometry		Respiratory Impairment				Overall	
		n	%	n	%	n	%	n	%
Male Population	371	245	66.0	14	3.7	55	14.8	57	15.3
Non-Smokers	179	125	69.8	3	1.6	26	14.5	25	13.9
Smokers	192	120	62.5	11	5.7	29	15.1	32	16.6
Female Population	412	230	55.8	15	3.6	50	12.1	117	28.3
TOTAL	783	475	60.6	29	3.7	105	13.4	174	22.2
								308	39.3

p<0.001 . Thus the female population was significantly more affected than the male population by ventilatory dysfunctioning.

Among the male population, the smokers revealed a greater overall prevalence (37.5%) of ventilatory abnormalities in comparison to that seen in non-smokers (30.1%). However, the difference did not attain statistical significance. Out of the 783 cases, 29 (3.7%) revealed the overall prevalence of airway obstruction within the lungs.

The pattern of obstructive ventilatory syndrome was observed to be 3.7% in the male population as against 3.6% reported in the female population. Thus sex-wise no significant difference was recorded in the obstructive ventilatory impairment. Among the non-smokers and smokers, the

male population revealed significant difference ($p<0.05$) in the prevalence of ventilatory obstructive abnormality, latter being more affected (5.7%) in contrast to non-smokers (1.6%).

In case of restrictive lung disease, 105 (13.4%) exhibited its overall prevalence in the study population, being insignificantly different between the male (14.8%) and female (12.1%) cases. Similarly, smoking-wise no significant difference could be seen in the prevalence of restrictive airway abnormality. Thus it was noted that the restrictive pattern of ventilatory defect was found to be independent of smoking habit.

The combined obstructive-cum-restrictive ventilatory defect was observed in 174 (22.2%) cases out of 783 cases who performed spirometry. It is clear from Table 3 that its prevalence was significantly higher (28.3%) in the female population in comparison to (15.3%) observed in the male population ($p<0.005$). Here also we were unable to mark any significant influence of smoking on the prevalence of mixed ventilatory abnormality.

The spirometric findings revealed that 60.6% cases had normal values of spirometry while 39.4% showed impaired values of various pulmonary functions.

It can be derived from Table 3 that among the types of respiratory impairment observed in the study population, the combined restrictive-cum-obstructive ventilatory syndrome was the most prevalent as a result of methyl isocyanate gas action on the human lung followed by restrictive pattern of the disease.

The details of obstructive pulmonary abnormality in the study population are described in Table 4. The overall prevalence of mild airway obstruction was noted in 3.0% population out of 783 cases studied. Mild bronchial obstruction was reported in 3.5% male population in comparison to 2.6% observed in the female population. This shows that sex-wise there was no significant difference observed in the prevalence of mild obstructive syndrome. Smoking revealed a significant effect on the prevalence of bronchial obstruction as smokers exhibited significantly higher prevalence (5.7%) of mild obstruction in the lungs in comparison to 1.1% noted in the non-smoking male population ($p<0.5$). Not a single case of moderate ventilatory obstruction was observed in the male population studied. In contrast to this the female population showed 0.7% cases affected by this category of obstruction. The overall prevalence of moderate airway obstruction was reported only in 0.3% cases in the whole population studied.

The overall severe ventilatory obstruction was reported in 0.2% cases in the study population. Sex-wise, it was seen that male and female population were equally affected by severe bronchospasm (0.2%). Among the non-smoking male population only 1 case (0.5%) showed the evidence of severe airway constriction while there was no case in the smoking population.

Thus it can be seen from the Table 4 that the reported bronchial obstruction was predominantly mild in nature in the methyl isocyanate gas affected population of Bhopal.

**TABLE—4
Prevalence of obstructive pulmonary abnormality in MIC exposed population**

Study Population	n	Normal Spirometry		Obstructive Ventilatory Impairment				Overall			
		n	%	Mild	%	Moderate	%				
		n	%	n	%	n	%	n	%		
Male Population	371	245	66.0	13	3.5	—	—	1	0.2	14	3.7
Non-Smokers	179	125	69.8	2	1.1	—	—	1	0.5	3	1.6
Smokers	192	120	62.5	11	5.7	—	—	—	—	11	5.7
Female Population	412	230	55.8	11	2.6	3	0.7	1	0.2	15	3.6
TOTAL	783	475	60.6	24	3.0	3	0.3	2	0.2	29	3.7

The different types of restrictive ventilatory impairment observed in the study population are shown Table 5. 97 (12.3%) cases revealed the prevalence of mild restrictive pattern of the lung disease in the study population. Spirometric results further indicated that its prevalence was significantly higher in the male population (14.8%) in comparison to (10.1%) observed in the female population ($p<0.05$). This shows that the restrictive lung disease induced by the methyl isocyanate gas, affected male population more.

The overall prevalence of moderate ventilatory restriction was found to be 0.3% in the study population. Sex-wise, it was seen that among the male population there was none with this category of the disease while only 3 (0.7%) reported moderate restriction in the lungs in the female population. Similarly, the severe form of the restrictive impairment was only observed in 5 (1.2%) female cases. No case of severe restriction was reported in the male population. The overall prevalence of severe pulmonary restrictive impairment was observed in 0.6% cases out of 783 cases studied. Thus it can be concluded from Table 5 that the observed restrictive abnormality was chiefly mild in nature induced by methyl isocyanate gas exposure.

Table 6 describes the prevalence of various forms of combined restrictive cum obstructive ventilatory impairment in the MIC exposed population. The mild restrictive-cum-obstructive pulmonary abnormality was observed in 117 (14.9%) cases in the MIC affected population. Sex-wise, it was seen that the female population was significantly more affected (18.2%) than the male population (11.3%) ($p<0.01$).

Among the male population the effect of smoking was clearly demonstrated as smokers revealed significantly higher prevalence of mild mixed lung abnormality (13.5%) ($p<0.005$).

TABLE—5

Prevalence of restrictive ventilatory impairment in MIC exposed population

Study Population	Normal Spirometry			Restrictive Ventilatory Impairment						Overall		
	n	n	%	n	Mild %	Moderate %	n	%	n	%	n	%
Male Population	371	245	66.0	55	14.8	—	—	—	—	—	55	14.8
Non-Smokers	179	125	69.8	26	14.5	—	—	—	—	—	26	14.5
Smokers	192	120	62.5	29	15.1	—	—	—	—	—	29	15.1
Female Population	412	230	55.8	42	10.1	3	0.7	5	1.2	50	12.1	
TOTAL	783	475	60.6	97	12.3	3	0.3	5	0.6	105	13.4	

TABLE—6
**Prevalence of restrictive-cum-obstructive pulmonary impairment
in MIC exposed population**

Study Population	n	Normal Spirometry		Restrictive-cum-Obstructive Impairment				Overall		
		n	%	Mild	%	Moderate	%	Severe	%	
Male Population	371	245	66.0	42	11.3	6	1.6	9	2.4	57 15.3
Non-Smokers	179	125	69.8	16	8.9	4	2.2	5	2.7	25 13.9
Smokers	192	120	62.5	26	13.5	2	1.0	4	2.0	32 16.6
Female Population	412	230	55.8	75	18.2	32	7.7	10	2.4	117 28.3
TOTAL	783	475	60.6	117	14.9	38	4.8	19	2.4	174 22.2

Moderate restriction/obstruction in the lungs revealed an overall prevalence of 4.8% in the study sample. Here also the female population exhibited a significantly higher prevalence (7.7%) of mixed impairment in comparison to 1.6% noticed in the male population ($p < 0.001$). However, smoking did not influence its prevalence in males.

The severe combined restrictive/obstructive ventilatory syndrome affected 9 (2.4%) cases out of the 783 cases studied. Sex-wise, there did not appear any significant difference in its prevalence. Smoking also did not have any effect on the prevalence.

Like obstructive and restrictive pulmonary impairment the observed combined ventilatory defect was also predominantly mild in nature as revealed by the spirographic tracing recorded in the exposed population.

Age-wise Prevalence of Pulmonary Impairment in Male Population

The study population was divided into 5 age groups viz., 16-25 years, 26-35 years, 36-45 years, 46-55 years and 55-64 years to assess the prevalence of ventilatory impairment in various age groups and to establish a correlation between the age and the prevalence of respiratory abnormality.

The prevalence of various types of respiratory impairment in different age groups in the male population is shown in Table 7. The overall prevalence of ventilatory impairment was found to range from 25.0% in the 26-35 year age group to 82.3% in the 56-64 year age group which was highly significant ($p < 0.001$). The overall prevalence of ventilatory impairment failed to demonstrate any positive correlation with age. The 46-55 year age group revealed the minimum prevalence (2.2%) of obstructive syndrome and the maximum (17.6%) was revealed in the 56-64 year age group. We could not find any association between the prevalence of tracheo-bronchial obstruction with increasing age.

TABLE—7

Age-wise prevalence of respiratory impairment in MIC exposed male population

Age Group (years)	n	Normal Spirometry		Prevalence of Respiratory Abnormality						Overall	
		n	%	Obstructive	n	%	Restrictive	n	%	Mixed	n
16-25	110	81	73.6	3	2.7	17	15.4	9	8.2	29	26.3
26-35	120	90	75.0	3	2.5	13	10.8	14	11.6	30	25.0
36-45	79	47	59.4	4	5.1	11	14.0	17	21.5	32	40.5
46-55	45	24	53.3	1	2.2	10	22.2	10	22.2	21	46.6
56-64	17	3	17.6	3	17.6	4	23.5	7	41.1	14	82.3
TOTAL	371	245	66.0	14	3.7	55	14.8	57	15.3	126	33.9

The pattern of restrictive ventilatory abnormality was minimally (10.8%) observed in the 26-35 year age group while the maximal prevalence was recorded in the 56-64 year age groups. No significant correlation could be worked out between the age and the restrictive pattern of pulmonary abnormality in the male population.

The lowest prevalence (8.2%) of mixed pulmonary impairment was recorded in the youngest age group, 16-25 years and the highest (41.1%) was seen in the 56-64 year age group. The combined restrictive-cum-obstructive ventilatory impairment did not reveal any systematic correlation with age in the male population exposed to methyl isocyanate gas.

The prevalence of mild and severe obstructive impairment in different age groups in the male population is shown in Table 8. The mild bronchial obstruction was seen minimally (2.2%) in the 46-55 year age group while its maximal occurrence (17.6%) was observed in the 56-64 year age group which was significant at $p<0.05$ level. There was no case of moderate bronchial airway obstruction in the male population studied. Severe bronchial obstruction was reported only in the 36-45 year age group which revealed 1.2% prevalence. However, the mild obstruction did not reveal any significant correlation with advancing age.

The prevalence of restrictive pulmonary impairment in various age groups in the male population is presented in Table 9. The minimum prevalence (10.8%) of mild restriction in the lungs was observed in the age group of 26-35 years and the maximum prevalence (23.5%) was reported in the 56-64 year age group. This difference in the prevalence was found to be insignificant. The restrictive pattern of ventilatory abnormality did not bear any correlation with age.

The age-wise prevalence of combined restrictive-cum-obstructive ventilatory insufficiency in male population is shown in Table 10. Age group 16-25 year revealed the minimum overall prevalence (8.1%) while 56-64 year age group revealed the highest prevalence (41.1%) which was found to be highly significant ($p<0.001$). Among the various types of mixed ventilatory defects, the mild mixed defect showed minimum prevalence (7.2%) in the youngest age group while the maxi-

imum prevalence (23.5%) was recorded in the 56-64 year age group. In case of moderate mixed ventilatory abnormality, the lowest incidence (0.8%) was reported in the 26-35 year age group and the highest (5.0%) was noticed in the 36-45 year age group. There were no cases of moderate mixed ventilatory defect observed in 16-25 and 56-64 year age groups, while severe combined restrictive-cum-obstructive impairment cases were maximally (17.6%) recorded in the 56-64 year age group. The mixed ventilatory syndrome either mild or moderate or severe failed to reveal any significant association between its prevalence and the advancing age as there was no systematic trend observed in this study.

TABLE—8

Age-wise prevalence of obstructive ventilatory impairment in MIC exposed population (male)

Age Group (years)	n	Normal Spirometry		Obstructive Mild		Impairment Severe		Overall	
		n	%	n	%	n	%	n	%
16-25	110	81	73.6	3	2.7	—	—	3	2.7
26-35	120	90	75.0	3	2.5	—	—	3	2.5
36-45	79	47	59.4	3	3.7	1	1.2	4	5.0
46-55	45	24	53.3	1	2.2	—	—	1	2.2
56-64	17	3	17.6	3	17.6	—	—	3	17.6
TOTAL	371	245	66.0	13	3.5	1	0.2	14	3.7

TABLE—9

Age-wise prevalence of restrictive ventilatory impairment in MIC exposed male population

Age Group (years)	n	Normal Spirometry		Restrictive Mild		Impairment		Overall Prevalence	
		n	%	n	%	n	%	n	%
16-25	110	81	73.6	17	15.4	17	15.4	17	15.4
26-35	120	90	75.0	13	10.8	13	10.8	13	10.8
36-45	79	47	59.4	11	14.0	11	14.0	11	14.0
46-55	45	24	53.3	10	22.2	10	22.2	10	22.2
56-64	17	3	17.6	4	23.5	4	23.5	4	23.5
TOTAL	371	245	66.0	55	14.8	55	14.8		

TABLE—10
Age-wise prevalence of restrictive-cum-obstructive pulmonary impairment in MIC exposed male population

Age Group (years)	n	Normal Spirometry		Mixed Ventilatory Impairment						Overall Prevalence	
		n	%	Mild n %	Moderate n %	Severe n %	n	%	n	%	
16-25	110	81	73.6	8 7.2	— —	1 0.9	9	8.1			
26-35	120	90	75.0	11 9.1	1 0.8	2 1.6	14	11.6			
36-45	79	47	59.4	12 15.1	4 5.0	1 1.2	17	21.5			
46-55	45	24	53.3	7 15.5	2 4.4	1 2.2	10	22.2			
56-64	17	3	17.6	4 23.5	— —	3 17.6	7	41.1			
TOTAL	371	245	66.0	42 11.3	7 1.8	8 2.1	57	15.3			

Age-wise Prevalence of Respiratory Impairment in Female Population

The prevalence of obstructive, restrictive and the combined restrictive-cum-obstructive ventilatory impairment in different age groups in the female population is shown in Table 11. The youngest age group i.e., 16-25 years reported the minimum prevalence (26.8%) of overall respiratory impairment in contrast to the maximum prevalence (85.7%) observed in the 56-64 year age group ($p<0.005$).

TABLE—11
Age-wise prevalence of respiratory impairment in MIC exposed female population

Age Group (years)	n	Normal Spirometry		Prevalence of Respiratory Abnormality						Overall Prevalence	
		n	%	Obstructive n %	Restrictive n %	Mixed n %	n	%	n	%	
16-25	142	111	78.1	5 3.5	10 7.0	16 11.2	31	26.8			
26-35	126	73	57.9	6 4.7	17 13.4	30 23.8	53	45.3			
36-45	92	36	39.1	3 3.2	15 16.3	38 41.3	56	66.4			
46-55	38	8	21.0	1 2.6	5 13.1	24 63.1	30	79.0			
56-64	14	2	14.2	— —	3 21.4	9 64.2	12	85.7			
TOTAL	412	230	55.8	15 3.6	50 12.1	117 28.4	182	44.1			

The lowest prevalence (2.6%) of obstructive ventilatory syndrome was recorded in the 46-55 year age group while the highest prevalence (4.7%) was reported in the 26-35 year age group which was statistically insignificant. The obstructive pulmonary impairment did not reveal any systematic trend with advancing age.

The restrictive pattern of ventilatory defect ranged from 7.0% to 21.4% in the 16-25 year and 56-64 year age groups respectively, the difference being significant at $p<0.1$ level. Here also no significant correlation could be established between the prevalence of restrictive impairment and the advancing age.

In case of mixed ventilatory impairment, its lowest prevalence (11.2%) was observed in the 16-25 year age group while the maximal prevalence (64.2%) was recorded in the 56-64 year age group which was significantly higher in the latter group ($p<0.005$). Like obstructive and restrictive ventilatory defects, it also failed to observe any definite correlation with increasing age.

Age-wise prevalence of various forms of obstructive bronchial impairment in the female population exposed to MIC gas is presented in Table 12. Mild airway obstruction was maximally recorded (7.6%) in the 36-45 year age range while the age group 46-55 year revealed its minimum prevalence (2.6%) which was found to be insignificantly different from the highest incidence. We did not observe any case of mild bronchial obstruction in the age group of 56-64 years. No significant association could be established between its prevalence and the increasing age. Moderate obstructive syndrome ranged from 0.7% to 1.4% showing its highest prevalence in the youngest age group i. e. 16-25 years. No case of moderate obstruction could be detected in the 36-45 year, 46-55 year and the 56-64 year age groups. Severe ventilatory obstruction was recorded (1.0%) only in 36-45 year age group.

The prevalence of restrictive ventilatory defect in various age groups in female population is shown in Table 13. The maximal prevalence (14.1%) of mild restriction was observed in the 36-45 year age group while females in the age group of 16-25 year were minimally affected by this disorder. Moderate cases of restriction were observed only in 26-35 year (1.5%) and 46-55 year (2.6%) age groups. In case of severe restrictive lung disorder, the age groups 56-64 year suffered maximally (7.1%) whereas only 0.7% cases were affected in the 26-35 year age group. No case of severe restrictive pulmonary impairment was recorded in the 16-25 year age group. None of the types of restrictive disorders showed any systematic trend with advancing age.

The distribution of the prevalence of combined restrictive-cum-obstructive lung disorder in different age groups in female cases is presented in Table 14. Female cases in the age group of 46-55 year revealed the highest prevalence (31.5%) of mild combined ventilatory impairment in contrast to the minimum prevalence (9.8%) observed in the 16-25 year age group. However, mild mixed lung abnormality did not observe any definite pattern with the advancing age. The moderate degree of the combined impairment ranged from 1.4% in the 16-25 year to 35.7% in the 56-64 year age groups. Moderate type of the combined lung disorder revealed a significant correlation with the increasing age. The analysis of the results indicated a positive correlation between its incidence and the age. This shows that as the age increased the prevalence of combined pulmonary disorder also increased. Severe mixed spirometric defect ranged from 2.1% in the 36-45 year to 14.2% in the 56-64 year age groups. No case of severe restrictive-cum-obstructive impairment was reported in the 16-25 year age group. Unlike moderate mixed lung abnormality, it did not show any direct correlation with age.

TABLE—12

**Age-wise prevalence of obstructive airway impairment in
MIC exposed female population**

Age Group (years)	n	Normal Spirometry		Obstructive Mild Modérate Severe			Impairment		Overall Prevalence		
		n	%	n	%	n	%	n	%	n	
16-25	142	111	78.1	3	7.0	2	1.4	—	—	5	8.4
26-35	126	73	57.9	5	7.1	1	0.7	—	—	6	7.9
36-45	92	36	39.1	2	7.6	—	—	1	1.0	3	8.6
46-55	38	8	21.0	1	2.6	—	—	—	—	1	2.6
56-64	14	2	14.2	—	—	—	—	—	—	—	—
TOTAL	412	230	55.8	11	6.5	3	0.7	1	0.2	15	7.5

TABLE—13

**Age-wise prevalence of restrictive ventilatory impairment in
MIC exposed female population**

Age Group (years)	n	Normal Spirometry		Restrictive Mild Moderate			Pulmonary Impairment	Overall Prevalence			
		n	%	n	%	n	%	n	%		
16-25	142	111	78.1	10	7.0	—	—	—	—	10	7.0
26-35	126	73	57.9	14	11.1	2	1.5	1	0.7	17	13.4
36-45	92	36	39.1	13	14.1	—	—	2	2.1	15	16.3
46-55	38	8	21.0	3	7.8	1	2.6	1	2.6	5	13.1
56-64	14	2	14.2	2	14.2	—	—	1	7.1	3	21.4
TOTAL	412	230	55.8	42	10.1	3	0.7	5	1.2	50	12.1

Distance-wise Prevalence Of Respiratory Impairment In Male Population

The prevalence of respiratory impairment in the male population staying at various distances from the UCIL plant is shown in Table 15. The maximum prevalence (9.1%) of obstructive pulmonary impairment was observed in the population which stayed very close to the factory i. e. 0-1 km while its minimum incidence was reported in the male population which stayed between 1-2 km

TABLE—14

Age-wise prevalence of restrictive-cum-obstructive pulmonary impairment in MIC exposed female population

Age Group (years)	n	Normal Spirometry		Mixed Ventilatory Impairment						Overall Prevalence	
		n	%	Mild	%	Moderate	%	Severe	%		
		n	%	n	%	n	%	n	%		
16-25	142	111	78.1	14	9.8	2	1.4	—	—	16	11.2
26-35	126	73	57.9	21	16.6	6	4.7	3	2.3	30	23.8
36-45	92	36	39.1	26	28.2	11	11.9	2	2.1	39	42.3
46-55	38	8	21.0	12	31.5	8	21.0	3	7.8	23	60.5
56-64	14	2	14.2	2	14.2	5	35.7	2	14.2	9	64.2
TOTAL	412	230	55.8	75	18.2	22	5.3	10	2.4	117	28.3

TABLE—15

Distance-wise prevalence of respiratory impairment in MIC exposed male population

Distance from UCIL Factory (Km)	n	Normal Spirometry		Prevalence of Respiratory Abnormality						Overall Prevalence	
		Obstructive	Restrictive	Mixed	n	%	n	%	n		
		n	%	n	%	n	%	n	%		
0-1	77	45	58.4	7	9.1	9	11.6	16	20.8	32	41.5
1-2	65	42	64.6	1	1.5	15	23.0	7	10.7	23	35.4
2-3	157	103	65.6	4	2.5	26	16.5	24	15.2	54	34.3
3-4	53	41	77.3	2	3.7	3	5.6	7	13.2	12	22.6
4-5	19	14	73.6	—	—	2	10.5	3	15.7	5	26.3
TOTAL	371	245	66.0	14	3.7	55	14.8	57	15.3	126	33.9

away from the factory area. However, the prevalence of obstructive lung disorder did not reveal any definite correlation with the different distance groups. The restrictive pattern of lung disorder maximally (23.0%) affected male population residing 1-2 km from the factory area while minimum prevalence (5.6%) was observed in those who stayed 3-4 km from the UCIL Plant. The prevalence of restrictive lung disease also failed to show any correlation with the various distance groups in which the study male population was grouped. The mixed variety of ventilatory impairment showed

its highest prevalence (20.8%) in those who lived close by i. e. between 0-1 km distance from the Union Carbide factory at Bhopal. The lowest prevalence (10.7%) of the combined pulmonary defect was observed in those who lived at a distance of 1-2 km from the factory site. Like restrictive lung disorder it also failed to establish any correlation between its prevalence and the various distance groups.

The overall prevalence of respiratory impairment (obstructive, restrictive and the combined restrictive-cum-obstructive) was maximally (41.5%) observed in those males who stayed in the vicinity of the factory i.e. 0-1 km while its minimum prevalence (22.6%) was recorded in the study sample staying between 3-4 km from the factory. However, overall prevalence of respiratory impairment did not show any definite trend with respect to various distance groups in which male population was broadly classified.

The distribution of prevalence of mild, moderate and severe obstructive syndrome in different distance groups in the male population is shown in Table 16. The highest prevalence (9.1%) of mild pulmonary obstruction was seen in those who lived very close to the factory (0-1 km) and the lowest prevalence (1.9%) was reported in those who lived between 2-3 km from the factory. However, mild respiratory obstruction did not observe any significant correlation with the various distance groups. The moderate bronchial obstruction was conspicuously absent in the present male population studied whereas there was only 1 case (0.6%) reported for the severe obstructive syndrome staying between 2-3 km from the MIC producing factory.

The overall prevalence of obstructive ventilatory defect was maximally (9.1%) reported in the male population which stayed very close to the factory area (0-1 km) and the minimum (1.5%) was found in those who lived between 1-2 km from the factory area. The overall prevalence of bronchial obstruction also failed to correlate with the various distance groups.

TABLE—16
Distance-wise prevalence of obstructive pulmonary defect in
MIC exposed male population

Distance from UCIL Factory (Km)	n	Normal Spirometry		Obstructive		Impairment		Overall Prevalence	
		n	%	Mild	Moderate	n	%	n	%
0-1	77	45	58.4	7	9.1	—	—	—	9.1
1-2	65	42	64.6	1	1.5	—	—	—	1.5
2-3	157	103	65.6	3	1.9	—	—	1	0.6
3-4	53	41	77.3	2	3.7	—	—	—	3.7
4-5	19	14	73.6	—	—	—	—	—	—
TOTAL	371	245	66.0	13	3.5	—	—	1	0.2
								14	3.7

Table 17 presents the prevalence of mild restriction in the lungs in the male population in the various distance groups. The highest prevalence (24.6%) was recorded in the population which lived between 1-2 km from the factory area while the minimum prevalence (7.5%) was reported in those who stayed 3-4 km away from the factory. The mild restrictive pattern of the lung disease did not correlate well with various distance groups so as to give a definite trend between its prevalence and the different distance groups in which the male population was classified.

The distribution of prevalence of mixed ventilatory impairment in various distance groups in the male population is shown in (Table 18). The overall prevalence of combined ventilatory defect ranged from 11.3% in the 3-4 km distance groups. The minimum prevalence (5.3%) of mild mixed pulmonary abnormality was observed in the male population living farthest (4-5 km) from the factory area whereas its maximum prevalence (12.7%) was revealed by those who lived between 2-3 km distance from the UCIL plant. However, no correlation between its prevalence and the distance from the factory to living areas could be ascertained in the mild mixed variety of the lung disorder. In case of moderate degree of combined ventilatory defect, the minimum prevalence (1.9%) was observed in the male population which lived 2-3 km from the factory while population which stayed very close to factory revealed its maximal incidence (3.8%). Male population which stayed farthest from the factory (4-5 km) showed the highest prevalence (10.5%) of severe form of mixed respiratory abnormality while population living within 2-3 km from the factory were least (1.2%) affected by the severe combined ventilatory defect. The spirometric results, however, did not show any definite correlation between the prevalence of moderate or severe form of combined ventilatory impairment and the various distance groups.

TABLE—17

**Distance-wise prevalence of restrictive impairment in
MIC exposed male population**

Distance from UCIL Factory (Km)	n	Normal Spirometry		Restrictive Impairment Mild		Overall Prevalence	
		n	%	n	%	n	%
0-1	77	45	58.4	8	10.3	8	10.3
1-2	65	42	64.6	16	24.6	16	24.6
2-3	157	103	65.6	25	15.9	25	15.9
3-4	53	41	77.3	4	7.5	4	7.5
4-5	19	14	73.6	2	10.5	2	10.5
TOTAL	371	245	66.0	55	14.8	55	14.8

TABLE—18

Distance-wise prevalence of restrictive-cum-obstructive pulmonary impairment in MIC exposed male population

Distance from UCIL Factory (Km)	n	Normal		Mixed		Ventilatory		Impairment		Overall	
		Spirometry		Mild	%	Moderate	%	Severe	%	Prevalence	n
		n	%	n	%	n	%	n	%	n	%
0-1	77	43	55.8	8	10.3	3	3.8	3	3.8	14	18.1
1-2	65	42	64.6	8	12.3	1	2.4	—	—	9	13.8
2-3	157	99	63.0	20	12.7	3	1.9	2	1.2	25	15.9
3-4	53	40	75.4	5	9.4	—	—	1	1.8	6	11.3
4-5	19	13	68.4	1	5.3	—	—	2	10.5	3	15.8
TOTAL	371	245	66.0	42	11.3	7	1.8	8	2.1	57	15.3

Distance-wise Prevalence of Respiratory Impairment In Female Population

The prevalence of obstructive, restrictive and combined restrictive-cum-obstructive ventilatory impairment in female population exposed to MIC gas staying at various distances from the Union Carbide factory is shown in Table 19.

The highest overall prevalence of respiratory impairment was recorded in the study sample which lived in close proximity to the factory area i.e. 0-1 km and the lowest prevalence (35.0%) was observed in those who lived between 1-2 km from the factory. Those who lived farthest (4-5 km) from the factory showed 50.0% pulmonary abnormality.

Obstructive lung impairment was most prominently (6.2%) seen in the study population which lived at a distance of 3-4 km from the MIC producing factory in contrast to the lung restriction which showed its maximal prevalence (14.8%) in the females who lived 2-3 km from the factory premises, while the lowest prevalence of obstruction (1.6%) and restriction (3.2%) was recorded in the population who resided between 1-2 km from the factory. In contrast to this the combined pulmonary disorder affected females most (35.0%) living farthest from the UCIL plant and its minimum occurrence (25.3%) was recorded in the female cases who stayed 1-2 km from the MIC plant. Thus it can be seen from Table 19 that female population classified according to the distance from their place of living to the factory did not reveal any definite pattern of various respiratory disorders.

Distance-wise distribution of pulmonary obstruction in the female population is shown in Table 20. The results indicated the highest prevalence (5.0%) of mild airway obstruction in those who lived 0-1 km from the factory area while its lowest prevalence (1.1%) was reported in the female population staying 2-3 km away. Moderate bronchial obstruction was recorded in 3 (0.7 %) cases; 2 (1.06%) cases which lived at a distance of 2-3 km and 1 (1.2%) case stayed 3-4 km from the factory. Severe obstruction in the lungs was noticed only in one 1 (0.5%) case who lived 2-3 km from the UCIL plant.

TABLE—19

Distance-wise prevalence of lung impairment in MIC exposed female population

Distance from UCIL Factory (Km)	n	Normal Spirometry		Prevalence of Respiratory Abnormality			Overall Prevalence				
		n	%	Obstructive		Restrictive		n	%		
				n	%	n	%				
0-1	60	29	48.3	3	5.0	8	13.3	20	33.3	31	51.6
1-2	63	44	69.8	1	1.6	2	3.2	16	25.3	19	30.2
2-3	188	103	54.7	5	2.6	28	14.8	52	27.6	85	45.2
3-4	81	44	54.3	5	6.2	10	12.3	22	27.1	37	45.7
4-5	20	10	50.0	1	5.0	2	10.0	7	35.0	10	50.0
TOTAL	412	230	55.8	15	3.6	50	12.1	117	28.4	182	44.2

TABLE—20

Distance-wise prevalence of obstructive ventilatory impairment in MIC exposed female population

Distance from UCIL Factory (Km)	n	Normal Spirometry		Obstructive Impairment						Overall Prevalence	
		n	%	Mild		Moderate		Severe		n	%
				n	%	n	%	n	%		
0-1	60	29	48.3	3	5.0	—	—	—	—	3	5.0
1-2	63	44	69.8	1	1.6	—	—	—	—	1	1.6
2-3	188	103	54.7	2	1.06	2	1.06	1	0.5	5	2.6
3-4	81	44	54.3	4	4.9	1	1.2	—	—	5	6.2
4-5	20	10	50.0	1	5.0	—	—	—	—	1	5.0
TOTAL	412	230	55.8	11	2.7	3	0.7	1	0.2	15	3.6

The prevalence of lung restriction in female population classified into various distance groups is presented in Table 21. The mild form of restrictive disorder ranged from 3.1% in the 1-2 km group to 13.3% in those who lived close by within a radius of 0-1 km. Moderate cases of restriction (1.5%) were observed only in those females who lived between 2-3 km from the UCIL industry. While severe restrictive disorder was detected in 5 (1.2%) cases, 3 (1.5%) were affected in the 2-3 km distance group and 2 (2.4%) cases were found in those who lived 3-4 km from the factory premises. Mild restrictive ventilatory abnormality observed in the female population did not exhibit any correlation with the various distance groups.

The pattern of overall prevalence of lung restriction was maximally (14.8%) recorded in those who lived 2-3 km from the factory and its minimum prevalence (3.1%) was observed in the 1-2 km distance group.

The prevalence of mixed ventilatory impairment in the exposed female population according to various distance groups is described in Table 22. The farthest living group (4-5 km) from the UCIL plant suffered most (40.0%) from the overall mixed variety of respiratory impairment in comparison to those who suffered least (24.6%) in the 3-4 km distance group. Among the different categories of combined ventilatory disorder, the highest prevalence (30.0%) of mild combined defect was recorded in those who stayed 4-5 km from the pesticide factory while its lowest prevalence (13.5%) was noticed in the 3-4 km distance group. The moderate category of mixed ventilatory insufficiency ranged from 6.3% in the 1-2 km distance group to 10.0% in those who lived between 4-5 km from the Union Carbide factory. The severe mixed spirometric impairment showed its maximal prevalence (6.3%) in the 1-2 km distance group in contrast to its minimum occurrence (1.2%) which was recorded in those who lived 3-4 km from the factory area. Neither the overall nor the various categories of combined pulmonary impairment showed any definite trend in its prevalence with respect to various distance groups.

TABLE—21
Distance-wise prevalence of restrictive lung impairment in
MIC exposed female population

Distance from UCIL Factory (Km)	n	Normal Spirometry		Restrictive		Pulmonary		Impairment		Overall Prevalence	
		n	%	n	%	n	%	n	%	n	%
0-1	60	29	48.3	8	13.3	—	—	—	—	8	13.3
1-2	63	44	69.8	2	3.1	—	—	—	—	2	3.1
2-3	188	103	54.7	22	11.7	3	1.5	3	1.5	28	14.8
3-4	81	44	54.3	8	9.8	—	—	2	2.4	10	12.3
4-5	20	10	50.0	2	10.1	—	—	—	—	2	10.0
TOTAL	412	230	55.8	42	10.1	3	0.7	5	1.2	50	12.1

TABLE—22
Distance-wise prevalence of mixed respiratory impairment in
MIC exposed female population

Distance from UCIL Factory (Km)	n	Normal Spirometry		Mixed Ventilatory Impairment						Overall Prevalence	
		n	%	n	%	n	%	n	%	n	%
0-1	60	29	48.3	13	21.6	5	8.3	2	3.3	20	33.3
1-2	63	44	69.8	9	14.2	4	6.3	4	6.3	17	26.9
2-3	188	103	54.7	35	18.6	14	7.4	3	1.5	52	27.6
3-4	81	44	54.3	11	13.5	8	9.8	1	1.2	20	24.6
4-5	20	10	50.0	6	30.0	2	10.0	—	—	8	40.0
TOTAL	412	230	55.8	74	17.9	33	8.0	10	2.4	117	28.4

Pulmonary Function Status of MIC Exposed Population

Lung function values in asymptomatic and symptomatic male population exposed to MIC gas are shown in Table 23. It can be observed from the table that the mean spirometric values in the male population suffering from various respiratory symptoms (symptomatic group) were significantly decreased in comparison to those recorded in the asymptomatic male population. Thus the mean pulmonary function test viz. $FEV_{0.75}$, FEV_1 , FEV_1/FVC ratio and IMBC expressed as the percent of the normal predicted values, were considerably impaired in contrast to the corresponding values observed in the symptomless male population. The $FEV_{0.75}(P)$ revealed a mean value of 93.5% in the symptomatic population which was significantly reduced in comparison to 101.3% recorded in the asymptomatic male population ($p<0.05$). Similar reduction was also recorded with respect to FEV_1 parameter in the affected population ($p<0.05$) whereas VC and FVC, although decreased in the symptomatic population in comparison to asymptomatic group, did not reach the statistical significance. FEV_1/FVC ratio was found to be significantly lowered (78.9%) in the affected group in contrast to the mean value (84.4%) reported in the NAD male population ($p<0.001$). Similar trend was also reported in case of IMBC parameter wherein the symptomatic population revealed a mean value of 96.4% as against 103.9% exhibited by the asymptomatic population. However, PEFR and AVI showed identical mean values in both the groups unaffected by the respiratory symptoms induced by MIC exposure in the male population.

TABLE—23

Lung function values in MIC exposed male population

Lung Function Parameters		Asymptomatic (n=41)		Symptomatic (n=273)	
		\bar{X}	\pm	\bar{X}	\pm
VC % (P)		92.1	2.45	86.6	1.50
FVC % (P)		98.2	2.87	93.4	1.11
$FEV_{0.75} \%$ (P)		101.3	2.97	93.5	1.35
$FEV_{1.0} \%$ (P)		103.3	2.96	95.9	1.09
$FEV_1/FVC \%$		84.4*	1.22	78.9	1.10
IMBC % (P)		103.9	3.14	96.4	1.36
PEFR % (P)		113.4	3.36	113.4	1.37
AVI %		1.13*	0.03	1.11	0.01

% (P) = Figures presented here are the percentages of the predicted values

* = Observed values

The mean residual values and the observed values of pulmonary functions calculated in the female population are shown in Table 24. The residual values, indicate the difference between the recorded absolute values and the reference values derived from the normal predicted formula. Of the various spirometric functions viz. VC and IMBC were significantly decreased in the symptomatic group in comparison to those observed in the symptomless female population. The mean difference between the observed and predicted values of VC was found to be —0.42 litres in the symptomatic group which was significantly greater than the mean difference of—0.05 litres recorded in the asymptomatic group ($p<0.001$). Similarly, IMBC revealed three fold greater reduction (—9.3

litres) in the symptomatic female population which was significantly affected in contrast to the mean difference of—3.8 litres noticed in the symptomless female population. Similar significant reductions in the absolute observed values of $FEV_{0.75}$, FEV_1 and PEFR were recorded in the symptomatic female population suffering from various respiratory symptoms. Thus the $FEV_{0.75}$ revealed a mean value of 1.75 litres in the affected population which was significantly reduced in comparison to the mean value of 1.97 litres observed in the unaffected female population ($p<0.01$). The FEV_1 showed a mean value of 1.90 litres in the symptomatic population which was significantly decreased in contrast to the mean observed value of 2.12 litres recorded in the asymptomatic female population ($p<0.05$). Similarly PEFR revealed a significant difference between the two groups ($p<0.05$). However, FVC, FEV_1/FVC percentage and Air Velocity Index (AVI) were not significantly reduced in the symptomatic female population.

Pulmonary Function Assessment In MIC Exposed Population Affected By Respiratory Impairment

Anthropometric Details : The physical characteristics of the male and female population affected by obstructive, restrictive and the mixed ventilatory impairment are shown in Table 25. Among the male population studied, the bronchial obstruction cases were the oldest and the cases with lung restriction were the youngest. The other anthropometric details viz., height and weight were identical in the male population suffering from obstructive, restrictive and combined ventilatory defects, while in the female population the mixed pulmonary impairment cases were the oldest and the obstructive cases were the youngest. The female population with restrictive lung disorders were found to be tallest in comparison to others who suffered from obstruction and combined pulmonary defect. However, weight-wise there was no significant difference observed among the categories of pulmonary impairment cases.

TABLE—24
Lung function values in MIC exposed female population

Lung Function Parameters	Asymptomatic (n=30)			Symptomatic (n=364)		
	\bar{X}	\pm	SEM	\bar{X}	\pm	SEM
rVC	—0.05	0.09		—0.42	0.02	
rFVC	—0.25	0.09		—0.19	0.02	
FEV _{0.75} litres	1.97*	0.08		1.75*	0.02	
FEV _{1.0} litres	2.12*	0.09		1.90*	0.02	
FEV ₁ /FVC	83.9*	1.53		81.2*	0.49	
IMBC (litre/min)	—3.8	3.08		—9.3	0.94	
PEFR (litre/min)	352*	10.6		327	3.66	
AVI %	1.06*	0.03		1.04*	0.01	

r = Residual values

* = Observed values

TABLE - 25

Physical characteristics of the study population affected by pulmonary impairment on exposure to MIC gas

Characteristics	Male Population						Female Population					
	Obstructive (n=14)		Restrictive (n=54)		Mixed (n=57)		Obstructive (n=15)		Restrictive (n=50)		Mixed (n=117)	
	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	$\bar{X} \pm SEM$	
Age, years	40.4	8.9	34.6	1.7	39.2	1.7	31.0	2.6	36.4	1.6	39.9	1.0
Height,Cm	161.2	1.7	163.7	0.9	161.9	0.8	149.7	1.3	150.1	0.8	147.6	0.6
Weight,Kg	52.1	2.5	54.1	1.5	54.1	1.5	47.4	2.1	50.6	1.5	48.3	0.9
Distance from UCIL Factory (Km)	1.9	0.5	2.4	0.1	2.3	0.15	2.8	0.3	2.	0.1	2.6	0.1

Pulmonary Function Evaluation In MIC Exposed Population Suffering From Bronchial Obstruction

The mean observed and reference pulmonary function values and their differences in the male population with airway obstruction are shown in Table 26. It can be observed from the table that the mean observed lung function values were significantly decreased in comparison to their respective mean reference values in the MIC exposed male population. Thus VC revealed a significant mean difference of -0.27 ± 0.07 litres between the mean observed and the mean predicted values in the male population ($p < 0.005$). Similarly $FEV_{0.75}$ and FEV_1 also exhibited significant mean decreases of -0.38 ± 0.13 litres and -0.33 ± 0.13 litres respectively as compared to their respective mean reference values ($p < 0.05$). The FEV_1/FVC ratio expressed in percentage revealed a mean observed value of $64.0 \pm 1.2\%$ thereby indicating that these bronchial obstruction cases suffered from mild category of obstructive ventilatory syndrome induced by MIC exposure in the male population. The prevalence of bronchial obstruction was further confirmed by the impaired IMBC observed in such cases. IMBC showed a mean difference of -14.0 ± 5.6 litres/min between the mean observed and the mean reference values. The AVI index was also found to be below normal indicating a mean value of 0.92% suggesting prevalence of airway obstruction in the lungs of MIC exposed male population. However, two pulmonary tests viz., FVC and PEFR, although revealing decreased observed mean values in contrast to reference values, did not differ statistically. This is normally expected in the mild obstructive cases since PEFR has wide variability and has the inability to pick up mild bronchial obstruction within the lungs. FVC is generally normal or near normal in such cases. Thus we find that a battery of pulmonary function tests conducted in the MIC exposed male population viz., $FEV_{0.75}$, $FEV_{1.0}$, lowered FEV_1/FVC ratio ($<70\%$), the lowered AVI% (1) and IMBC revealed the presence of obstructive dysfunctioning in such cases.

TABLE—26

Pulmonary function status of MIC exposed population affected by obstructive ventilatory impairment

Lung Function	Male Population (n=14)						p value	Female Population (n=15)						p value	
	Observed $\bar{X} \pm SEM$		Reference $\bar{X} \pm SEM$		Difference $\bar{X} \pm SEM$			Observed $\bar{X} \pm SEM$		Reference $\bar{X} \pm SEM$		Difference $\bar{X} \pm SEM$			
	V C litres	3.16	0.15	3.44	0.11	-0.27	0.07	<0.005	2.29	0.11	2.52	0.05	-0.22	0.1	<0.05
240	FVC, litres	3.46	0.22	3.44	0.11	0.08	0.14	N.S.	2.58	0.13	2.52	0.05	0.06	0.12	N.S.
	FEV _{0.75} , litres	2.08	0.16	2.47	0.11	-0.38	0.13	<0.05	1.49	0.13	—	—	—	—	—
	FEV ₁ , litres	2.27	0.17	2.60	0.11	-0.33	0.13	<0.05	1.64	0.12	—	—	—	—	—
	FEV ₁ /FVC%	64.0	1.2	—	—	—	—	—	63.2	2.2	—	—	—	—	—
	IMBC litre/min	81.8	6.9	95.8	3.9	-14.0	5.6	<0.05	61.9	4.3	82.4	2.2	-20.5	4.2	<0.05
	PFR, litre/min	369	22.1	381	7.2	-12.0	21.4	N.S.	294	18.8	—	—	—	—	—
	AVI %	0.92	0.04	—	—	—	—	—	0.81	0.04	—	—	—	—	—

The female population which suffered from obstructive ventilatory impairment revealed a mean difference of -0.22 ± 0.1 litres between the observed and the reference values of VC. This was found to be decreased significantly at ($p < 0.05$) level. The FEV_1/FVC ratio revealed a mean observed value of $63.2 \pm 2.2\%$ which was found to be significantly decreased in comparison to the normal value (<70%) observed in the healthy population. The FEV_1/FVC ratio suggested occurrence of mild bronchial obstruction in the lungs which is also confirmed by the lowered observed AVI index ($0.81 \pm 0.04\%$) (normal=1) in the female population studied. Another confirmative test of bronchial obstruction is IMBC which also revealed significantly decreased mean observed value of 61.9 ± 4.3 litres/min. This was found to be 20.5 ± 4.2 litres less than the reference value calculated. Thus IMBC test was also significantly affected in the female population suffering from obstructive pulmonary syndrome ($p < 0.05$).

Pulmonary Function Assessment In MIC Exposed Population Affected By Restrictive Ventilatory Disorder

The mean values of various pulmonary functions recorded in the male and female population suffering from restrictive lung abnormality are illustrated in Table 27. It is seen from the table that the mean observed values of different lung parameters are significantly decreased in comparison to their mean reference values in the male and female population. Among the male population suffering from lung restriction, VC exhibited a mean decrease of -0.92 ± 0.03 litres and FVC revealed a mean decrease of -0.55 ± 0.05 litres in contrast to the respective mean reference values of VC and FVC calculated in these cases. Thus it is observed that the VC and FVC were significantly reduced in these cases ($p < 0.001$). Similar patterns were also marked with respect to $\text{FEV}_{0.75}$ and $\text{FEV}_{1.0}$ parameters. $\text{FEV}_{0.75}$ revealed a mean difference of -0.23 ± 0.03 and $\text{FEV}_{1.0}$ showed -0.22 ± 0.03 difference between the observed and the predicted values. Thus $\text{FEV}_{0.75}$ and $\text{FEV}_{1.0}$ parameters were statistically decreased at $p < 0.001$ level. The FEV_1/FVC percentage ratio revealed a normal value of $84.0 \pm 1.06\%$ in the male population affected by restrictive lung impairment. The Air Velocity Index showed a raised mean observed value of $1.30 \pm 0.02\%$ thereby suggesting the presence of airway restriction in such cases. Besides this, IMBC and PEFR were also significantly reduced in contrast to their respective mean predicted values ($p < 0.001$).

In the female population suffering from restrictive lung disease, the mean observed VC was found to be significantly less than the predicted value by 0.76 ± 0.04 litres ($p < 0.001$). FVC revealed a mean difference of -0.38 ± 0.05 litres between the observed and the calculated predicted value ($p < 0.001$). The ratio FEV_1/FVC was found to be within the normal range. Air Velocity Index was characteristically found to be raised ($1.21 \pm 0.03\%$) thereby confirming the presence of restrictive pattern of lung disease in the female population studied.

Pulmonary Function Assessment In MIC Exposed Population Affected By Combined Ventilatory Impairment

Mean lung function values and their differences between the observed and the predicted values recorded in the male and female population are shown in Table 28. Among the male population, the mean observed values of VC and FVC were found to be significantly decreased in contrast to the respective mean calculated reference values. The VC revealed a mean difference of 1.20 ± 0.06 litres and the FVC showed a mean difference of -1.19 ± 0.22 litres between their observed and the predicted values respectively. These differences in VC and FVC were found to be statistically significant ($p < 0.001$). Similar trends were also recorded with respect to $\text{FEV}_{0.75}$ and $\text{FEV}_{1.0}$ parameters. The $\text{FEV}_{0.75}$ and $\text{FEV}_{1.0}$ showed significant differences of -0.91 ± 0.06 litres and -0.84

TABLE—27

Lung function values in MIC exposed population with restrictive lung disease

Lung Function	Male Population (n=54)			p Value	Female Population (n=50)			p Value						
	Observed $\bar{X} \pm SEM$	Reference $\bar{X} \pm SEM$	Difference $\bar{X} \pm SEM$		Observed $\bar{X} \pm SEM$	Reference $\bar{X} \pm SEM$	Difference $\bar{X} \pm SEM$							
VC, litres	2.74	0.05	3.59	0.05	-0.92	0.03	<0.001	1.81	0.05	2.57	0.03	-0.76	0.04	<0.001
FVC, litres	3.10	0.06	3.65	0.05	-0.55	0.05	<0.001	2.18	0.05	2.56	0.03	-0.38	0.05	<0.001
FEV _{0.75} , litres	2.44	0.05	2.67	0.05	-0.23	0.03	<0.001	1.79	0.03	—	—	—	—	—
FEV _{1.0} , litres	2.60	0.06	2.86	0.05	-0.22	0.03	<0.001	1.82	0.05	—	—	—	—	—
FEV ₁ /FVC%	84.0	1.06	—	--	—	—	—	85.0	1.1	—	—	—	—	—
IMBC, litre/min	97.6	1.94	103.7	1.85	-6.0	1.1	<0.001	71.0	2.4	81.2	0.8	-8.8	1.6	<0.001
PFR, litre/min	457	8.9	398	3.6	60.3	9.6	<0.001	337	10.8	—	—	—	—	—
AVI%	1.30	0.02	—	—	—	—	—	1.21	0.03	—	—	—	—	—

TABLE—28
Pulmonary function values in MIC exposed population affected by restrictive-cum-obstructive syndrome

Lung Function	Male Population (n=57)						p	Female Population (n=117)						p
	Observed $\bar{X} \pm SEM$	Reference $\bar{X} \pm SEM$	Difference $\bar{X} \pm SEM$	Value		Observed $\bar{X} \pm SEM$	Reference $\bar{X} \pm SEM$	Difference $\bar{X} \pm SEM$	Value					
VC, litres	2.28	0.07	3.48	0.05	-1.20	0.06	<0.001	1.58	0.03	2.50	0.13	-0.91	0.03	<0.001
FVC, litres	2.54	0.08	3.50	0.06	-1.19	0.22	<0.001	1.79	0.04	2.50	0.02	-0.69	0.03	<0.001
FEV _{0.75} , litres	1.62	0.04	2.52	0.06	-0.91	0.06	<0.001	1.28	0.03	1.39	0.03	—	—	
FEV _{1.0} , litres	1.83	0.08	2.64	0.08	-0.84	0.08	<0.001	1.39	0.03	—	—	—	—	
FEV ₁ /FVC %	70.7	1.6	—	—	—	—	—	76.7	0.89	—	—	—	—	
IMBC, litre/min	65.2	2.8	98.7	2.0	-33.6	2.2	<0.001	50.6	1.4	79.2	0.48	-27.6	1.16	<0.001
PFR, litre/min	354	13.3	382	4.1	-23.2	11.9	N. S.	288	6.3	—	—	—	—	
AVI %	1.01	0.02	—	—	—	—	—	1.02	0.02	—	—	—	—	

± 0.08 litres respectively between their observed and predicted values ($p < 0.001$). Like other pulmonary functions IMBC also exhibited a significant mean decrease of -33.6 ± 2.2 litres/min between the observed and the predicted mean values ($p < 0.001$). While PEFR although reduced did not indicate significant reduction with respect to the mean predicted value.

The female population affected by mixed ventilatory defect showed similar pattern of various lung functions as described earlier in the male population. Here also the observed VC and FVC were significantly decreased in contrast to their respective mean reference values. The VC and FVC revealed significant reductions of -0.91 ± 0.03 litres and -0.69 ± 0.03 litres respectively between their observed and predicted mean values ($p < 0.001$). Similarly, mean observed IMBC was also tremendously decreased in contrast to the mean reference value thereby showing a mean difference of -27.6 ± 1.16 litres/min ($p < 0.001$). Air Velocity Index was found to be raised ($1.02 \pm 0.02\%$) in these cases.

Discussion

The present study revealed that Bhopal population, both male and female, exposed to MIC gas due to accidental leakage from the Union Carbide factory on 2nd/3rd December, 1984 still suffered from various types of ventilatory impairment even after 90 days when this respiratory morbidity and pulmonary function evaluation study was carried out in the months of February and March/April, 1985. The overall prevalence of respiratory impairment was found to be 44.1% in the female population in contrast to the 33.9% observed in the male population examined. Thus the female population revealed significantly higher prevalence of pulmonary abnormalities induced by the MIC gas inhalation.

The three categories of pulmonary impairment recorded in the exposed population were obstructive, restrictive and the combined or mixed restrictive-cum-obstructive ventilatory disorder. It is seen from the results that in the majority of the cases, males or females suffered from mixed pulmonary disturbance (15.3% and 28.4%) respectively followed by restrictive pattern of the lung disease (14.8% in the male and 12.1% in the female population), while bronchial obstruction was recorded only in 3.6% female and in 3.7% male population.

The results of the pulmonary function studies confirmed that it is the mild form of pulmonary impairment which was mostly observed in the male and female population studied. This was evidenced by the FEV/FVC ratio which showed a mean value of 63.4% in the male population while female population exhibited a mean value of 64.3% thereby suggesting presence of mild bronchial obstruction. Thus Bhopal population exhibited mild mixed, restrictive and bronchial obstruction as a result of exposure to MIC gas. Thus the study showed that there were only 2 cases of severe bronchial obstruction in the 783 cases studied, 1 in the female and 1 in the male population.

Similarly there were only 5 severe cases detected out of 50 cases of lung restriction in the female population studied whereas in male population of 55 cases of restrictive ventilatory defect none developed severe form of lung restriction. All the 55 cases revealed mild lung restriction. Out of the 117 mixed pulmonary defect cases in the female population only 10 revealed severe mixed pulmonary impairment whereas in the male population out of 57 cases of mixed lung impairment only 8 cases suffered from severe mixed ventilatory disturbance.

The prevalence of various respiratory impairment was also analysed age-wise in the male and female population. None of the types of pulmonary impairment revealed any definite trend with

the various age groups in which male or female population was classified. This shows that the respiratory system of population of different age groups was equally affected by the inhalation of MIC vapours.

The prevalence of respiratory impairment was also analysed statistically with respect to various distance groups in which the study population lived at the time of MIC release as well as at the time of the study. Our study failed to derive any correlation between the prevalence of various types of pulmonary impairment observed in the male or female population and the various distance groups showing thereby that the study population living near the UCIL plant (0-1 Km) or staying far (4-5 Km) from it developed respiratory impairment of similar magnitude.

Pulmonary function study conducted in the asymptomatic and the symptomatic male or female population revealed that a battery of tests were significantly affected in the population which suffered from various respiratory symptoms. The spirometric parameters viz., VC, FVC, FEV_{0.75}, FEV_{1.0}, FEV₁/FVC ratio and IMBC revealed mean decreased values in contrast to their respective reference values calculated from the predicted equations prepared for healthy Indian population thereby indicating the presence of bronchial obstruction and lung restriction in the symptomatic male or female population. On the contrary, the population which did not complain of respiratory problems at the time of this study revealed normal spirometry.

It can thus be concluded on the basis of this study that the MIC gas which was accidentally released from the UCIL plant revealed its toxic effect on the respiratory tract of exposed population as indicated by high prevalence of respiratory impairment and decreased pulmonary function values in the symptomatic male and female population. The mechanisms responsible for causing lung impairment by the MIC gas are not yet very clear. Some investigators believe that MIC has an acute irritating effect on the respiratory tract resulting in the bronchospastic reactions (Munn, 1965., Peters, 1970., Baur et al, 1979). While others proposed that isocyanate induced respiratory disease may be immunologically mediated (Karol et al, 1978). While a third hypothesis has been suggested that the isocyanates are pharmacologically active (Butcher et al, 1979). They proposed that the chemically active hydrogen atoms are attached to oxygen, nitrogen or sulphur, therefore, it is not unexpected that inhaled isocyanates may react with components in the lung, leading to changes or to the inhibition of biological function. Dewair et al (1983) suggested a biochemical mechanism which acted through the inhibition of cholinesterase inhibitor enzymes by isocyanates since the broncho-constrictor responses to stimulation of vagus nerves are known to be potentiated by cholinesterase inhibitors leading to the development of respiratory disorders. Trevisan and Moro (1981) also reported on the role of AChE inhibition in TDI induced broncho-constriction. They observed a small but significant decreases in the AChE activities of the erythrocytes of workers experimentally challenged by the isocyanate vapours. They suggested that inhalation of isocyanates may lead to a gradual accumulation of inhibited enzyme (s) and/or other components in the respiratory systems to an extent which eventually exceeds the capacity of reactivation mechanism. This capacity may differ from one person to another, leading to the observed individual differences in the susceptibility to isocyanate sensitization. Rye (1973) has proposed two types of pulmonary responses to isocyanate exposure. One is direct irritant response which is governed by the total dose of exposure in direct relationship and the second is the allergic response which is controlled by host reaction. Direct irritant or toxic response is due to triggering of normal protective mechanism of the upper respiratory tract and mimics that of other respiratory irritants. The second type of response is host generated or controlled and is truly allergic. It is not to be expected on initial exposure but usually develops after a reasonable time.

RADIOLOGICAL STUDIES

Since exposure to methyl isocyanate resulted in very severe pulmonary involvement such as pulmonary oedema and chemical pneumonitis, examination of respiratory system of the surviving population was required. For this purpose apart from the clinical examination, haematology, pulmonary function studies etc. radiological examination of the exposed population was also conducted. A full sized (12" x15") chest X-ray posteroanterior view was taken in all the cases using a portable X-ray plant, and was read by a panel of three experts of the following disciplines: a radiologist, a chest diseases specialist and an industrial medicine specialist and salient features of MIC exposed lungs pointed out.

The radiological findings are given in the following table :

Radiological findings of 903 X-ray chest

I. NORMAL	739
II. ABNORMAL	164
Group A	48
Group B	17
Group C	8
	73
Pneumonitis	7
Pulmonary Tuberculosis	55
Primary Complex	7
Chronic Bronchitis	4
Bronchiectasis	2
Emphysema	1
Cardiac abnormalities	11
Collapse	2
Effusion	1
Tension Bullae	1
	91
Total	903

739 subjects (81.8%) out of a total of 903 subjects studied radiologically showed no abnormality in their X-ray. X-ray picture of 91 subjects (10.1%) showed radiological changes suggestive of definite pathology like pulmonary tuberculosis, pneumonitis, chronic bronchitis, emphysema etc. Specific radiological changes were observed in 73 subjects (8.1%). These subjects have been classified as below :

Group A	X-ray showing radiological changes due to MIC	= 48 subjects
Group B	Radiological changes suggestive of old pathology but symptoms appearing only after MIC exposure (In this category old pathology is aggravated by MIC exposure)	= 17 subjects
Group C	Radiological findings not definitely related to MIC	= 8 subjects
<hr/>		Total = 73 subjects

The subjects have been divided according to the positive findings in respect of symptomatology, X-ray findings, PFT values, and findings on the clinical examination as follows :

History	X-ray	PFT	Clinical Examination findings
—	N	N	N
+	N	N	N
+	+	N	N
+	+	Low	N
—	+	Low	+
—	N	Low	+

—denotes negative, + denotes positive, N denotes Normal

To screen out malingeringers, the findings of symptomatology, clinical examination, X-ray and pulmonary function tests were correlated. Those subjects whose chest X-ray did not show any abnormality and whose lung function values were normal and where no abnormality was detected on clinical examination were very strongly suspected to be malingeringers giving a false statement of being suffering from respiratory symptoms like cough, breathlessness, pain and/or tightness in chest etc. for the lure of getting compensation or otherwise their symptoms are psychogenic in nature consequent to the severe tragedy witnessed by them. Such cases need to be studied in greater detail during follow-up studies.

Sixty two (6.8%) subjects showed definite radiological findings of tubercular infection. Out of these, 55 subjects (6.1%) showed findings of pulmonary tuberculosis and 7 subjects (0.77%) showed findings of primary complex. The incidence of tubercular infection (6.8%), is much more as compared to National Tuberculosis Survey finding of 1.8%. Moreover, most of the X-rays where findings are suggestive of pulmonary tuberculosis showed that they are healed cases. There is a strong possibility that probably the active tuberculosis cases could not withstand the toxic effects of MIC and could not survive and those with healed tuberculosis could survive.

The other pulmonary and cardiac abnormalities observed in the MIC exposed population are similar to such abnormalities in any group of Indian population. Seven cases showed presence of pneumonitis in their X-rays. Out of these cases, involvement of the right lower zone was seen in 5 subjects, left lower zone in 1 subject and both lower zones in 1 subject, while left sided pleural effusion was observed in 1 subject only. Tension bullae on right lower zone, lung collapse on right lower lobe and middle lobe was observed. 73 subjects (8.1%) showed radiological abnormalities which are suspected to be related to MIC exposure. Out of these, in 48 subjects, the radiological changes observed appear to be caused by MIC exposure. The radiological findings of these cases are given in Table 1. The radiological changes observed in these X-rays are definitely abnormal findings but they do not conform to any definite diagnosis. These findings are haziness seen in different zones of the lungs, hilar prominence, fine mottling, reticulation etc. The changes are more marked in right lung as compared to left lung. Haziness is more commonly seen in lower zone (40 X-rays out of 48 showed haziness of right lower zone, whereas, 11 out of 48 X-rays showed haziness of the left lower zone). One case showed haziness of the upper zone on right side, whereas on left side no case showed haziness of the upper zone. Comparing the middle zone on right and left side it was observed that 3 cases showed haziness of the middle zone on right side, whereas, 6 cases showed haziness of the middle zone on left side. Preponderance of abnormalities *i.e.* haziness, hilar prominence etc. on the right side is probably because of the anatomical configuration of the right and left bronchus. The right bronchus being wider probably permitted more of MIC gas to enter the right lung and hence more abnormalities were observed on the right side.

Although haziness was observed in almost all the X-rays in this group it was surprising to note that hardly a few subjects presented with fever also.

Hilar shadows were prominent in 47 out of 48 cases in this group. Prominence of the right hilar was more common (47 out of 48) whereas left hilar was prominent in 41 out of 47 cases. Costophrenic angle, heart size and trachea did not reveal any significant abnormality.

There was no correlation between radiological picture and clinical presentation. The cases with clear cut pneumonitis had no evidence of toxæmia.

Out of these 48 cases, 37 subjects were within 2 km distance from the Union Carbide factory at the time of exposure and 10 subjects were at a distance of 2-4 km while only one person was at a distance of more than 4 km. As 37 out of 48 subjects were within 2 km from the factory they are likely to have been exposed to a significant amount of gas, and the resultant radiological change in their X-rays is due to high exposure.

Group B :	Cases showing radiological changes suggestive of old pathology which was aggravated by MIC exposure :	
	Tuberculosis	7
	Chronic bronchitis	6
	Pneumonitis	4

	Total	17

The radiological findings of 17 subjects reveal the old pathology as tuberculosis, chronic bronchitis and pneumonitis. These old pathologies seem to be aggravated by MIC exposure as the symptoms in these subjects appear only after the gas exposure. Pneumonitis is more commonly seen in the right lower zone similar to the observation in group A subjects.

TABLE—1
Radiological changes suspected to be due to MIC exposure

No.	Right Lung						Left Lung						Heart size	Trachea	Remarks
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
2	N	N	N	P	N	N	N	N	H	P	Clear	N	Central		
26	N	H	H	P	N	Linear markings	N	N	N	P	Clear	N	Central		
44	N	N	H	P	Clear	N	N	N	P	Clear	N	Central			
54	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	Chronic bronchitis C bronchiectasis		
87	N	N	H	P	Clear	N	H	N	P	Clear	N	Central	Few calcified shadows		
156	N	N	N	P	Clear	N	H	N	P	Clear	N	Central	Fine mottling		
123	N	N	H	P	Clear	N	N	N	N	Clear	N	Central	Increased bronchial markings		
133	N	N	H	P	Clear	N	N	N	P	Clear	N	Central			
201	N	N	H	P	Clear	N	N	H	P	Clear	N	Central			
207	N	N	H	P	Clear	N	N	N	N	Clear	N	Central	Increased bronchovascular markings		
219	N	N	H	N	Clear	N	N	H	N	Clear	N	Central	Increased vascular markings		
315	N	N	H	P	Clear	N	N	N	P	Clear	N	Central			
316	N	N	H	P	Clear	N	N	H	P	Clear	N	Central	Calcified shadows C fibrosis		
357	N	N	H	P	Clear	N	N	H	P	Clear	N	Central			
365	N	N	H	P	Clear	N	N	H	P	Clear	N	Right	Scattered calcified shadows		
430	N	H	H	P	Clear	N	N	N	P	Clear	N	Central	Congenital deformity of 3rd rib right side		
446	N	N	H	P	Clear	N	N	N	N	Clear	N	Central			
484	N	N	H	P	Clear	N	N	N	N	Clear	N	Central	Cystic shadows in right base		

(Contd.)

No.	Right Lung						Left Lung						Heart size	Trachea	Remarks
	Upper	Middle	Lower	Hilar	Costoph.		Upper	Middle	Lower	Hilar	Costoph.				
	1	2	3	4	5	6	7	8	9	10	11	12			
463	N	N	H	P	Clear		N	N	N	N	Clear	N	Central		Scattered calcified shadows Č surrounding Pneumonitis along Rt hilam
476	N	N	H	P	Clear		N	N	N	N	Clear	N	Central		Left border of heart straightened
495	N	N	H	P	Clear		N	N	N	P	Clear	N	Central		Right dome of diaphragm is raised due to collapse right side
509	N	N	H	P	Clear		N	N	N	P	Clear	N	Central		Scattered calcified shadows
519	N	N	N	P	Clear		N	N	N	P	Clear	N	Central		Fine mottling both lung fields
548	N	N	N	P	Clear		N	N	N	P	Clear	N	Central		Rt hilars prominent Č surrounding haziness
561	N	H	N	P	Clear		N	N	H	P	Clear	N	Central		Fine mottling
608	N	N	H	P	Clear		N	N	H	P	Clear	N	Central		
623	N	N	H	P	Clear		N	N	N	P	Clear	N	Central		
627	N	N	N	P	Clear		N	N	N	P	Clear	N	Central		Scattered calcified shadows Č Rt dome of diaphragm raised
651	N	N	H	P	Not well defined		N	H	N	P	Clear	N	Central		
701	H	N	H	P	Clear		N	N	H	P	Clear	N	Central		
868	N	N	H	P	Clear		N	N	N	P	Clear	N	Central		Fine mottling in both lungs. Old fractures 8th and 9th rib post part left side
871	N	N	H	P	Clear		N	N	N	P	Clear	enlarged	Central		Calcification left infraclavicular region

	882	N	N	H	P	Clear	N	N	H	P	Clear	N	Central	Scattered calcified shadows
	897	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	Fine mottling \bar{C} scattered calcification
	905	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	Scattered calcified shadows
	936	N	N	N	P	Clear	N	N	N	P	Clear	N	Central	Scattered calcified shadows \bar{C} fine mottling
	971	N	N	N	P	Clear	N	H	N	P	Clear	N	Central	Scattered calcified shadows \bar{C} mottling
	1034	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	
	1011	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	
	1019	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	Surrounding consolidation around Rt hilar region
251	1025	N	N	H	P	Clear	N	H	N	P	Clear	N	Central	
	1070	N	N	H	P	Clear	N	N	H	P	Clear	N	Central	Scattered calcification
	1105	N	N	H	P	Clear	N	N	H	P	Clear	N	Central	Fine mottling \bar{C} old fracture of 4th, 5th and 6th rib left side
	1128	N	N	N	P	Clear	N	N	N	P	Clear	N	Central	Increased bronchovascular marking \bar{C} fine mottling and scattered calcification
	1157	N	N	H	P	Clear	N	H	N	P	Clear	N	Central	Scattered calcification
	1165	N	N	N	P	Clear	N	N	N	P	Clear	N	Central	Fine mottling \bar{C} calcification
	1204	N	N	H	P	Clear	N	N	N	P	Clear	N	Central	Left dome of diaphragm raised, fine mottling.

N = Normal H = Hazy P = Prominent

HAEMATOLOGICAL STUDIES

Standard haematological tests were done on all the subjects using the routine clinical methods in haematology and the results are summarized below.

Estimation of Haemoglobin

The majority of the population (67.1%) had haemoglobin values higher than 12 gm% while one-third of population (32.5%) had values between 8 to 12 gm %. The percentage of population having haemoglobin level less than 8 gm % was 0.4.

When haemoglobin count was correlated with different age groups, no significant pattern could be observed. The percentage of population having haemoglobin more than 12 gm% ranged from 61.9 in the 26-35 years age group to 75.3 in the 16-25 years age group (Table 1).

There was also a direct relationship between haemoglobin level in the individuals residing at different distances from the Union Carbide Factory.

Out of the total population residing within 2 km from the factory, 65.5 per cent revealed a haemoglobin level of over 12 gm% and a similar trend was observed in 80% of the population living beyond 4 km (Table 2).

Red Blood Cell Count

The red blood cell count was more than 4 million/cmm in majority of the population (77.8%). Age-wise distribution pattern was 87.1, 82.9, 77.1, 74.3, 70.1 and 72.0 per cent respectively in subjects in age groups less than 15, 16-25, 26-35, 36-45 and more than 56 years (Table 3).

Total RBC count of less than 3 million/cmm was observed in a very small percentage of population. The percentage of population in different age groups which had RBC count between 3 to 4 million per cmm was between 12.9 to 28.0 per cent. No significant effect of the distance from UCIL factory was noted on the red blood cell count.

Total Leucocyte Count

The total leucocyte count (TLC) was high (more than 10,000) in 11.6 per cent of overall population. It was almost similar in males and females being 10.3 and 12.6 per cent respectively. The percentage of population having total leucocyte count less than 5000 was 6.4. The total leucocyte count (less than 5,000) was more in females (8.2%) than males (4.6%). The total leucocyte count (more than 10,000) has similar distribution in each population group residing between 2 km, 2-4 km, 4-6 km and more than 6 km from the factory (Table 4). Leucocytosis was maximum (28.0%) in age group over 56 years. The percentages in the age groups less than 15, 16-25, 26-35, 36-45 and 46-55 were 6.4, 8.2, 16.6, 8.6 and 8.8 respectively (Table 5).

TABLE—1

Haemoglobin values in relation to age and sex

Age Group (years)	Haemoglobin (gm/%)												
	<8			8-12			>12			Total			
	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total	
253	≤ 15	—	—	—	3 (27.3)	6 (30.0)	9 (29.0)	8 (72.7)	14 (70.0)	22 (71.0)	11	20	31
	16-25	—	—	—	17 (29.9)	25 (25.2)	42 (24.7)	54 (76.1)	74 (74.8)	128 (75.3)	71	99	170
	26-35	—	1 (0.9)	1 (0.6)	20 (26.7)	46 (45.6)	66 (37.5)	55 (73.3)	54 (53.5)	109 (61.9)	75	101	176
	36-45	—	—	—	24 (13.5)	29 (43.9)	53 (37.8)	50 (67.5)	37 (56.1)	87 (62.2)	74	66	140
	46-55	—	1 (4.2)	1 (1.7)	8 (24.2)	9 (37.5)	17 (29.8)	25 (75.8)	14 (58.3)	39 (68.5)	33	24	57
	≥ 56	—	—	—	5 (27.8)	3 (42.8)	8 (32.0)	13 (72.2)	4 (57.2)	17 (68.0)	18	7	25
Total		2 (0.6)	2 (0.4)	77 (27.3)	118 (37.2)	195 (32.5)	205 (72.7)	197 (62.2)	402 (67.1)	282	317	599	

Figures in parenthesis are the percentages of population studied

TABLE —2

Haemoglobin values in relation to distance from the factory (sex-wise)

Distance from the factory (km)		Haemoglobin (gm%)											
		<8			8-12			>12			Total		
		Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total
	<2	—	1	1	50	74	124	121	117	238	171	192	363
			(0.5)	(0.3)	(29.2)	(38.5)	(34.2)	(70.8)	(61.0)	(65.5)			
254	2-4	—	1	1	26	37	63	71	61	132	97	99	196
			(1.0)	(0.5)	(26.8)	(37.3)	(32.2)	(73.2)	(61.7)	(67.3)			
	4-6	—	—	—	1	4	5	9	14	23	10	18	28
					(10.0)	(22.2)	(17.8)	(90.0)	(77.8)	(82.2)			
	>6	—	—	—	—	3	3	4	5	9	4	8	12
						(37.5)	(25.0)	(100.0)	(62.5)	(75.0)			
	Total	—	2	2	77	118	195	205	197	402	282	317	599
			(0.6)	(0.4)	(27.3)	(37.2)	(34.5)	(72.7)	(62.2)	(67.1)			

Figures in parenthesis indicate percentage of population studied

TABLE—3

Age-wise distribution of R. B. C. count among population

Age Group (years)	≤15	16—25	26—35	36—45	46—55	≥56	Total
R. B. C. Count in million/cmm							
<3	0	3	5	4	3	0	15
	(0.0)	(1.8)	(2.9)	(2.8)	(5.3)	(0.0)	(2.5)
3—4	4	26	35	32	14	7	118
	(12.9)	(15.3)	(20.0)	(22.8)	(24.6)	(28.0)	(19.7)
>4	27	141	135	104	40	18	465
	(87.1)	(82.9)	(77.1)	(74.3)	(70.1)	(72.0)	(77.8)
Total	31	170	175	140	57	25	598

Figures in parenthesis show percentage

TABLE—4
Total leucocyte count in relation to distance from the factory

Leucocyte count	Distance from the factory (km)														
	<2			2-4			4-6			>6			Male	Female	Total
	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total
<5000	4 (2.3)	14 (7.3)	18 (4.9)	8 (8.2)	7 (7.1)	15 (7.7)	1 (10.0)	4 (22.2)	5 (17.8)	0 (9.1)	1 (4.6)	1 (8.2)	13 (6.5)	26	39
5000-10000	148 (86.5)	151 (78.6)	299 (82.4)	81 (83.5)	80 (80.8)	161 (82.1)	7 (70.0)	13 (72.2)	20 (71.4)	4 (90.9)	6 (85.1)	10 (79.1)	240 (81.9)	250	490
>10000	19 (11.1)	27 (14.1)	46 (12.6)	8 (8.2)	12 (12.1)	20 (10.2)	2 (20.0)	1 (5.6)	3 (10.8)	— (0.0)	— (10.3)	0 (12.6)	29 (11.6)	40	69
TOTAL	171	192	363	97	99	196	10	18	28	4	7	11	282	316	598

Figures in parenthesis are the percentages of the row totals

TABLE—5
Age and sex-wise distribution of total leucocyte count

Age group (years)	Total Leucocyte Count														
	<5000			5000-10000			>10000			Male	Female	Total	Male	Female	Total
	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total	Male	Female	Total
≤15	—	—	—	11 (100.0)	18 (90.0)	29 (93.5)	—	2 (10.0)	2 (6.4)	11	20	31			
16-25	1 (1.4)	9 (10.1)	10 (5.9)	61 (85.9)	85 (85.8)	146 (85.9)	9 (12.7)	5 (5.0)	14 (8.2)	71	99	170			
26-35	5 (6.7)	8 (8.0)	13 (7.4)	60 (80.0)	73 (73.0)	133 (76.0)	10 (13.3)	19 (19.0)	29 (16.6)	75	100	175			
36-45	4 (5.4)	6 (9.1)	10 (7.1)	67 (90.5)	51 (77.2)	118 (84.3)	3 (4.0)	9 (13.7)	12 (8.6)	74	66	140			
46-55	3 (9.1)	3 (12.5)	6 (10.5)	27 (81.8)	19 (79.2)	46 (80.7)	3 (9.1)	2 (8.3)	5 (8.8)	33	24	57			
≥56	—	—	—	14 (77.8)	4*	18 (72.0)	4 (22.2)	3*	7 (28.0)	18	7	25			
TOTAL	13 (4.6)	26 (8.2)	39 (6.5)	240 (85.1)	250 (79.1)	490 (81.9)	29 (10.3)	40 (12.6)	69 (11.6)	282	316	598			

Figures in parenthesis are the percentages of row totals

* Percentages were not worked out as denominator was less than 10

Differential Leucocyte Count

All the cases studied were divided in to two groups, i.e. those having polymorphs less than 70% and those with more than 70%. Increased polymorphonuclear leucocytosis was found in 71 subjects (11.9%) of the overall population. Similarly, the cases were divided in two groups having less than or more than 40% lymphocytes. The number of subjects showing lymphocytosis more than 40% was found to be 188 (31.6%). Eosinophils were found to be more than 6% in 171 subjects (28.7%) (Table 6).

The percentage of cases showing increased polymorphonuclear leucocytosis was almost similar in different age groups, i.e. 16.1, 11.1, 11.4, 14.4 and 12.0 per cent in age groups up to 15, 16–25, 26–35, 36–45 and more than 56 years respectively, except in age group 46–55 years where only 7.1% subjects showed polymorphonuclear leucocytosis (more than 70%).

TABLE—6
Age and sex-wise distribution of differential leucocyte count

Age Group (years)	Polymorphs		Lymphocytes		Eosinophils	
	<70	>70	<40	>40	<6	>6
≤ 15	Male	8	3	10	1	7
	Female	18	2	14	6	12
	Total	26	5	24	7	19
16-25	Male	64	7	48	23	49
	Female	87	12	60	39	70
	Total	151	19	108	62	119
26-35	Male	68	7	51	24	53
	Female	87	13	70	30	74
	Total	155	20	121	54	127
36-45	Male	64	10	54	20	59
	Female	53	10	47	16	43
	Total	117	20	101	36	102
46-55	Male	31	2	24	9	26
	Female	22	2	11	13	14
	Total	53	4	35	22	40
≥ 56	Male	17	1	12	6	11
	Female	5	2	6	1	6
	Total	22	3	18	7	17
Total	524	71	407	188	424	171

Lymphocyte count of more than 40% was found in 22.6% and 26.3% of subjects up to 15 and 36–45 years age group. High lymphocyte count in age groups 16–25, 26–35, 46–55 and more than 56 years was found to be 36.4, 30.8, 38.6 and 28.0 per cent respectively.

The maximum number of cases showing eosinophil count more than 6 per cent was found in age group up to 15 years (33.8%) as compared to 30.0, 26.5, 20.2 and 32.0 per cent in age groups 16–25, 26–35, 36–45, 46–55 and more than 56 years respectively.

The differential leucocyte count was not found to be significantly affected in groups of population residing at different distances from the factory.

Erythrocyte Sedimentation Rate

Erythrocyte Sedimentation Rate (ESR) was found elevated (more than 20 mm in females and more than 10 mm in males) in 36.4% of the overall population. It was raised in 39.2 and 33.8 per cent males and females respectively. The distance from the factory had no significant effect on ESR values in the study population. ESR values were raised in 36.9, 38.2, 17.8 and 33.3 per cent population residing less than 2, 2–4, 4–6 and more than 6 km from the factory respectively. The age group more than 56 years had maximum number of persons (48.0%) having elevated ESR. This was followed by 42.1, 37.7, 35.4, 35.1 and 29.1 per cent prevalence of elevated ESR values in age groups 36–45, 26–35, less than 15, 46–55 and 16–25 years respectively (Table 7).

TABLE—7
ESR values in relation to distance (sex-wise)

Distance (km)	Erythrocyte Sedimentation Rate (ESR)					
	Males		Total	Females		
	<10	>10		<20	>20	Total
<2	100 (58.4)	71 (41.6)	171	129 (67.2)	63 (32.8)	192
2–4	60 (61.8)	37 (38.2)	97	61 (61.7)	38 (38.3)	99
4–6	8 (80.0)	2 (20.0)	10	15 (83.3)	3 (16.7)	18
>6	2*	0	2*	4*	3*	7*
Total	170 (60.7)	110 (39.3)	280	209 (66.1)	107 (33.9)	316

Figures in parenthesis are percentages of row totals

*Percentages were not worked out where denominator was less than 10

TABLE—8

Age and sex-wise distribution of ESR values

Age group (years)	ESR mm /1st hr (Wintrobe)					
	<10	Males >10	Total	<20	Females >20	Total
≤15	7 (63.6)	4 (36.4)	11	13 (65.0)	7 (35.0)	20
16-25	45 (65.2)	24 (34.8)	69	74 (74.7)	25 (25.3)	99
26-35	46 (61.3)	29 (38.7)	75	63 (63.0)	37 (37.0)	100
36-45	41 (55.4)	33 (44.6)	74	40 (60.6)	26 (39.4)	66
46-55	23 (69.7)	10 (30.3)	23	14 (58.3)	10 (41.7)	24
≥ 56	8 (44.4)	10 (55.6)	18	5*	2*	7
TOTAL	170 (60.7)	110 (39.3)	280	209 (66.1)	107 (33.9)	316

Figures in parenthesis are percentages of row totals

*Percentages are not worked out where denominator is less than 10

Estimation of blood urea

The majority of cases with raised blood urea values (blood urea more than 40 mg%) were found in persons in age group 36-45 years followed by age group 16-25 (25.0%) and 26-35 (21.2%). The overall prevalence of raised blood urea was found to be 20.5 per cent in males and 12.7 per cent in females with an average of 16.3 per cent subjects showing elevated values (Table 9).

The distance from the factory did not have any significant effect on the pattern of abnormal blood urea values (Table 10).

TABLE—9
Age and sex-wise blood urea levels

Age group (years)	Blood urea (mg %)								
	<40			>40			Total		
	Male	Female	Total	Male	Female	Total	Male	Female	Total
≥15	9 (100.0)	20 (95.2)	29 (96.7)	0 (0.0)	1 (4.8)	1 (3.3)	9 21	21	30
16-25	50 (81.9)	78 (89.6)	128 (86.6)	11 (18.1)	9 (10.4)	20 (13.5)	61 87	87	148
26-35	38 (82.6)	78 (89.7)	116 (87.2)	8 (17.3)	9 (10.3)	17 (12.8)	46 87	87	133
36-45	52 (76.5)	39 (78.0)	91 (77.1)	16 (23.5)	11 (22.0)	27 (22.9)	68 50	50	118
46-55	20 (76.9)	14 (82.3)	34 (79.1)	6 (23.1)	3 (17.7)	9 (20.9)	26 17	17	43
≥56	9 (64.3)	5 (83.3)	14 (70.0)	5 (35.7)	1 (16.7)	6 (30.0)	14 6	6	20
Total	178 (79.5)	234 (87.3)	412 (83.7)	46 (20.5)	34 (12.7)	80 (16.3)	224 268	268	492

Figures in parenthesis are the percentages of row totals

TABLE—10
Blood urea levels of the population according to distance from the factory (sex-wise)

Distance from factory (km)	Blood urea (mg %)								
	<40			>40			Total		
	Male	Female	Total	Male	Female	Total	Male	Female	Total
<2	111 (77.1)	125 (81.2)	236 (79.2)	33 (22.9)	29 (18.8)	62 (20.8)	144 154	154	298
2-4	58 (81.6)	94 (96.9)	152 (90.5)	13 (18.4)	3 (3.1)	16 (9.5)	71 97	97	168
4-6	5* (88.2)	10 —	15 —	— 2	— (11.8)	2 —	5* —	12* —	17
>6	4* —	5* —	9* —	— —	— —	— —	4* —	5* —	9*
Total	178 (79.5)	234 (87.3)	412 (83.7)	46 (20.5)	34 (12.7)	80 (16.3)	224 268	268	492

Figures in parenthesis are the percentages of row totals

*Percentages are not worked out as the denominator is less than 10

BIOCHEMICAL STUDIES

A highly reactive substance like MIC could interact with the functional groups of a wide variety of biomolecules like nucleic acids, carbohydrates, proteins, etc. affecting their natural functions. Such reactions in the upper respiratory passages could be a factor in pulmonary toxicity directly and in other tissues indirectly. Interaction of MIC with body water and possibly small biomolecules, especially in the presence of ions, could also lead to toxic intermediates, or to deprivation of vital molecules. These effects could be reflected in blood and urine, as is the case with most stress factors. Therefore, explanatory biochemical studies were conducted on MIC exposed cohorts and controls.

RESULTS

Initial Phase

The estimation of ammonia and urea in serum, urine and sputum was performed in 35 male and 26 female patients who were admitted to hospital immediately after MIC exposure. The results of the analysis (Table 1) revealed that more than 50% of the patients had raised values of ammonia and urea both in sputum and serum. A similar pattern was observed in the urine but the levels of ammonia and urea were not much higher than the reported higher limit. In general, it was found that the male population was more affected than females.

Follow-up

In a separate study, the following investigations were conducted in patients exposed to MIC four months after its exposure.

Biochemical Parameters in whole Blood and Serum

Glutathione level was significantly reduced in 30% of the population (Table 2). Serum GOT (EC 2.6.1.1), GPT (EC 2.6.1.2), and Gamma glutamyl transpeptidase (EC 2.3.2.2) and total bilirubin were found to be almost normal in these populations (Tables 3&4). However, the ceruloplasmin content was significantly raised in more than 45% of the population examined (Table 4). In some cases (35%), it was even more than one-and-a half to two folds higher than the highest normal value reported in literature (50 mg%), (Oser, 1965). In 10% population, the value was raised only by 5 to 14%. The elevated ceruloplasmin levels were found in both the sexes with a more prominent change in female population. Changes in ceruloplasmin, (an acute phase/reactant protein) may be related to inflammatory disorders and to Fe, Cu transport and related functional alterations (Frieden, 1981). It is also responsible for the incorporation of iron into transferrin which is ultimately taken up by bone marrow for the synthesis of haemoglobin. Significant increase in the ceruloplasmin content observed among 40% of the MIC exposed population surveyed, may be an indication of inflammation and possible changes in haemopoietic system (Goodle, 1950; Nriagu, 1980).

Examination of the Urine in MIC Patients

Among the surveyed population of the MIC exposed area, both females and males have been found to have a relatively high value of creatinine in their urine samples compared to the control subjects (Table 5). It ranges from 2.20 to 5.04 gm/24 hrs in males and 1.99 to 3.89 gm/24 hrs in females with an average value of 3.30 gm/24 hrs and 2.95 gm/24 hrs respectively. Apparently, no change was observed in GPT activity of MIC exposed patients after 4 months. Release of creatinine in the urine sample of MIC exposed patients indicates an increased breakdown of creatine phosphate as a result of muscular distress produced after MIC exposure (Oser, 1965).

TABLE—1

**Estimation of urea and ammonia in sputum, serum and urine
of MIC exposed population**

S. N.	Group	Sputum Urea mg %	Sputum Ammonia mg %	Serum Urea mg %	Serum Ammonia mg %	Urine Urea mg %	Urine Ammonia mg %
1.	Control	5—10	0—5	14—40	0.06—0.12	0.02—4	upto 50mg
2.	Male	4.89 (35)* (0.68—15.76)	9.63 (1.55—27.94)	55.61 (36.5—101.86)	2.38 (0.24—35.7)	2.31 (0.42—4.06)	33.08 (14.9—55.9)
		18.8%	64.7%	86.4%	81.8%	12.5%	13.6%
3.	Female	3.17 (26)* (0.5—8.65)	10.50 (0.93—23.3)	75.92 (38.0—100.2)	0.93 (0.311—3.11)	2.63 (0.23—4.55)	34.48 (9.32—59.0)
		Nil	56.3%	76.9%	66.7%	22.2%	16.7%

Values in parenthesis denote the range

()* denote number of subjects

Values in % represent the percentage of the population (surveyed) exhibiting higher value than the maximum limit of the control

TABLE—2
Examination of whole blood of 'MIC' exposed population

Age group (in years) and Sex	Number of Subjects	Glutathione u mole/100 ml
Control value		M = 100—140 F = 100—140
10 — 20		
Male	22	100 (73 — 140) 12%
Female	38	91 (60 — 135) 15%
21 — 40		
Male	82	90 (54 — 130) 35%
Female	103	94 (57 — 129) 25%
41 — 65		
Male	42	91 (54 — 125) 30%
Female	40	89.0 (65 — 124) 40%
Average		
Male	146	94 (54 — 140)
Female	181	91 (57 — 135)

Values in parenthesis denote the range

Values in % represent the percentage of the population (surveyed) exhibiting lower values than the minimum limit of the control

M = male

F = female

TABLE - 3

Biochemical examination of serum of MIC exposed population

Age group (in years) and sex	Number of Subjects	G P T I. U./ml	G O T I. U./ml	r—G T P I. U./ml
Control		5-35	5-40	upto 500
10—20				
Male	10	9.38±0.44 (7.0 — 15.4)	9.54±0.54 (4.0 — 15.4)	145.65±19.23 (26.9 — 403.5)
Female	12	10.44±0.23 (8.6 — 13.0)	10.68±0.45 (5.4 — 15.4)	169.57±20.71 (87.0 — 260.9)
21—40				
Male	40	11.2±0.5 (6.0 — 32.3)	10.0±0.27 (4.02 — 18.4)	148.87±14.44 (43.5 — 521.7)
Female	58	10.48±0.17 (6.0 — 17.4)	10.0±0.20 (5.4—17.4)	162.74±9.19 (60.9 — 347.8)
41—65				
Male	23	10.32±0.29 (7.0 — 15.4)	9.90±0.35 (6.0—18.4)	160.68±22.38 (43.5 — 434.8)
Female	14	12.26±0.38 (7.0 — 19.0)	12.06±0.53 (5.4 —17.4)	144.85±17.02 (43.5 — 217.4)
Average				
Male	73	10.30±0.41 (6.0 — 32.6)	9.82±0.39 (4.0 — 18.4)	151.73±18.68 (26.9 — 521.7)
Female	84	11.03±0.26 (6.0 — 19.0)	10.92±0.46 (5.4 — 17.4)	159.05±15.64 (43.5 — 347.8)

Values in parenthesis denote the range

TABLE—4
Biochemical examination of serum of MIC exposed population

Age group (in years) and Sex	Number of Subjects	Bilirubin mg%	Ceruloplasmin mg%
Control		0—1.5	25—50
10—20			
Male	10	0.52±0.12 (0.2 — 0.8)	57.61±10.33 (23.7 — 125.6) 55.6%
Female	12	0.40±0.04 (0.2 — 0.8)	43.13±5.20 (19.0 — 75.8) 27.3%
21—40			
Male	40	0.65±0.07 (0.2 — 1.5)	44.45±3.40 (19.0 — 90.1) 36.6%
Female	58	0.49±0.05 (0.2 — 1.3)	48.31±2.82 (19.0 — 113.8) 68.5%
41—65			
Male	23	0.74±0.11 (0.2 — 1.4)	45.14±4.28 (21.3 — 106.7) 30.4%
Female	14	0.52±0.17 (0.1 — 1.1)	49.61±5.54 (26.1 — 92.4) 21.4%
Average			
Male	73	0.64±0.10 (0.2 — 1.5)	49.1±6.00 (19.0 -- 125.6) 37.0%
Female	84	0.47±0.09 (0.1 — 1.3)	47.02±4.52 (19.0 — 113.8) 54.4%

Values in parenthesis denote the range

Values in % represent the percentage of the population (surveyed) exhibiting higher value than the maximum limit of the control

TABLE—5

Biochemical examination of urine in MIC exposed patients at Bhopal

Biochemicals parameters	Control	MIC exposed patients	
		Male	Female
1. Glutamate pyruvate transaminase (G. P. T.) (EC 2.6.1.2) (u mole pyruvate/ min/100 ml urine)	18.83 ± 0.74 (14.63—22.61)	21.45 ± 0.80 (14.83—25.27) [20]	20.85 ± 0.75 (18.62—26.60) [27]
2. Creatinine (gm/24hrs/1.5 litre urine)	1.71 ± 0.156 (1.1—2.39)	3.30 ± 0.23 (2.20—5.04) [20]	2.95 ± 0.24 (1.99—3.89) [27]

Values in parenthesis indicate the range

Values in square bracket indicate the number of subjects

IMMUNOLOGICAL STUDIES

Immunological tests are among the most sensitive indicators in predicting or detecting the toxicity caused by chemicals. Therefore, immunological studies were conducted in methyl isocyanate (MIC) exposed victims of Bhopal, to ascertain whether or not, MIC has altered the natural defence or immune system of the host.

Immunoglobulin Estimation

The quantification of immunoglobulins was performed by Radial Immuno Diffusion (RID) technique, using tripartigen plates supplied by Hoechst Pharmaceuticals Ltd India.

Immunoglobulin G (IgG) is the most common and predominant immunoglobulin present in serum. It enhances phagocytosis and helps in neutralization of toxins. IgG was studied in 389 MIC exposed cases and the mean value was found to be 1242 ± 12.28 mg% out of which 4% of the cases showed higher IgG values; mean 2847.46 ± 0.99 mg% with a range of 2334 mg% to 3474 mg%. In 7% of the cases the IgG levels were below the normal value (Table 1 A and Table 3) with a range of 300mg% to 620mg%. Immunoglobulin A (IgA) was estimated in 312 MIC exposed cases. The mean value was found to be 213.95 ± 4.40 mg%. Among these, 7% of the cases were of low IgA values i.e. 70.83 ± 5.82 mg% with a range of 20.00 to 118.90 mg% (Table 1 B and Table 3).

In 309 MIC exposed victims, the value of Immunoglobulin M (IgM) was found to be 177.00 ± 5.00 mg%. In 8% cases, IgM was raised (390.95 ± 10.43 mg%) with a range of 294.74 to 436.79 mg%. Lower values were observed only in 2% of the cases with a mean value of 39.24 ± 0.10 mg% (Table 1 C and Table 3).

C-reactive protein (CRP)

CRP was estimated in 168 cases. It was not found elevated in any of the cases.

Rheumatoid factor (RF)

It was estimated in 168 cases out of which only two cases showed raised levels.

Anti-Streptolysin O (ASO)

Among 168 gas exposed cases, none of them showed high levels of ASL in sera.

CRP, rheumatoid factor and ASO were determined by Slide Agglutination method.

Cell-viability

Cell viability was determined by Trypan Blue Exclusion method. The cell viability of MIC victims was found to be normal (mean 94.36 ± 0.46 %).

Phagocytosis

Phagocytosis study was conducted at Bhopal to find out whether or not MIC has altered the ability of peripheral blood mononuclear cells to engulf and process the microorganisms. Our studies showed that 40% of the cases had suppression in phagocytic ability (Table 2).

Clotting time

The range of blood clotting time in 111 cases was found to be 3.0 to 9.0 min.

COMMENTS

Alterations in immunological processes could be an outcome of MIC exposure, which may have a bearing on the health of the victims in future.

TABLE—1A

Immunoglobulin Profile

IgG

MIC Exposed Group

Mean value \pm SE (mg%)	1242 \pm 12.28
Range	(300—3474)
No. of cases studied	389

Control Group

Mean value \pm SE (mg%)	1184 \pm 88.96
Range	(600—1726)
No. of cases studied	10

Normal Indian Values

Mean value \pm SD (mg%)	1130 \pm 417.39
Range	(626—2304)

TABLE—1B
Immunoglobulin Profile
IgA

MIC Exposed Group	
Mean value \pm SE (mg%)	213.95 \pm 4.39
Range	(20—364)
No. of cases studied	312
Control Group	
Mean value \pm SE (mg%)	216.90 \pm 22.83
Range	(90.90—338.40)
No. of cases studied	10
Normal Indian Values	
Mean value \pm SD (mg%)	181.51 \pm 62.18
Range	(103—365)

TABLE—1C
Immunoglobulin Profile
IgM

MIC Exposed Group	
Mean value \pm SE (mg%)	177.00 \pm 5.004 §
Range	(39.00—436.79)
No. of cases studied	309
Control Group	
Mean value \pm SE (mg%)	111.47 \pm 12.97
Range	(40.00—192.05)
No. of cases studied	10
Normal Indian Values	
Mean value \pm SD (mg%)	117.39 \pm 53.91
Range	(44—289)
Significance (t-test)	§ p <0.001 in comparison to control group p <0.05 in comparison to normal Indian values

TABLE—2

**High/Low Immunoglobulin values in MIC exposed population of Bhopal
in comparison to normal Indian Values**

	IgG	IgA	IgM
High			
Mean \pm SE (mg%)	2847.46 \pm 0.99	—	390.95 \pm 10.435
Range	2334—3474	—	294.74—436.79
Percent of cases	4%	—	8%
Low			
Mean \pm SE (mg%)	407.38 \pm 22.81	70.83 \pm 5.82	39.24 \pm 0.107
Range	300—620	20—118.9	39.0—39.48
Per cent of cases	7%	7%	2%

TABLE—3

Phagocytosis of SRBC by peripheral blood mononuclear cells

	MIC Exposed Group	Control Group
Percent phagocytosis Mean \pm SE	17.23 \pm 3.05	32.50 \pm 0.90
Range	0.0—39.21	29.10—38.05
Per cent suppression in phagocytosis in MIC exposed group	46.98%	—
Significance (t-test)	p < 0.001	—

CHROMOSOMAL STUDIES

The present cytogenetic study was conducted by the Department of Anatomy, GSVM Medical College, Kanpur in collaboration with Industrial Toxicology Research Centre, Lucknow in MIC victims at Bhopal. A thorough clinical examination revealed congestion and degenerative changes in conjunctivae, decreased lung function, tenderness of liver and colon, congestion in throat, dermatitis, impairment of sexual desire and impotency, insomnia, sluggish deep jerks and raised reaction time.

Andersen *et al* (1980) in a standard Ames' test found that toluene di-isocyanate (TDI) and 4, 4-methylenediphenylisocyanate (MDI), were mutagenic in the presence of a conventionally prepared microsomal fraction (S9). This study itself calls for a thorough *in vivo* studies so that any genetic and carcinogenic potential can be quantitatively assessed. Moreover, the massive exposure of MIC gas to the residents of Bhopal, raised the vital question of any long term genotoxicity. Therefore, chromosomal aberrations in the peripheral blood lymphocyte culture of the subjects exposed to MIC gas were studied to assess its mutagenic and carcinogenic potential.

Materials and Methods

The study was done in 31 subjects of either sex and of random age group who attended our temporary outpatient clinic at Bhopal. 5 ml of peripheral venous blood was drawn in a heparinized disposable syringe. The buffy coat lymphocytes were obtained by incubating the blood at 37°C in the syringe as such keeping the syringe at a inclination of 70° for 45 minutes. These lymphocytes were cultured in media TC199, at 37°C for 68 hours, using phytohaemagglutinin-P (PHA-P, Difco) and homologous patients serum. Three hours before harvesting, 8 drops of colchicine (0.01%) was added. The cultured lymphocytes were treated with 0.56% hypotonic saline for 20 minutes and fixed in 3:1 methanol-glacial acetic acid for 15 minutes at 37°C. The air dried slides were prepared and stained with 4% buffered giemsa for 30 minutes and Trypsin-G banding was done. One hundred well spread metaphases from each case were studied for chromosomal aberrations. The results were compared with 31 control cultures set in the normal residents of Bhopal who were not exposed to the MIC gas.

RESULTS

Metaphases were observed for presence of breaks and gaps. Number of breaks and gaps in 100 metaphases of each case were noted (Table 1).

't' test was applied to find out the significance of difference in means of chromosomal aberration data. The mean data in the exposed group was compared with the control group after ascertaining the assumptions of normality and homogeneity of variance.

When breaks in test group is compared with the control group, the results indicate that the difference was observed at 0.001% of level of significance (Table 2). The same level of significance was found with the gaps, i.e. $p < 0.001$ (Table 3).

DISCUSSION

The present study shows that MIC exposure has caused very significant degree of chromosomal aberrations among the patients followed. This study was done 4 months after the MIC exposure when the clinical signs and symptoms were still well marked. In our view, a follow-up should be done when the clinical signs and symptoms apparently subside, so that residual effects of the MIC exposure on chromosomes may be ascertained and indications for genotoxicity determined.

TABLE—1
Breaks and gaps in 100 metaphases

S.No.	Test subjects		Control subjects	
	Breaks	Gaps	Breaks	Gaps
1.	12	15	5	6
2.	12	26	5	7
3.	13	27	6	6
4.	11	13	6	5
5.	12	13	5	6
6.	13	12	6	6
7.	13	12	6	6
8.	13	13	6	7
9.	14	15	7	6
10.	14	16	4	6
11.	13	15	4	5
12.	16	17	4	7
13.	14	15	7	6
14.	18	18	7	5
15.	14	18	6	5
16.	17	17	7	5
17.	17	20	6	7
18.	16	18	5	6
19.	19	20	6	5
20.	17	17	7	5
21.	15	16	6	5
22.	16	17	5	5
23.	17	18	5	6
24.	14	17	6	5
25.	17	15	7	6
26.	19	20	5	7
27.	17	18	4	5
28.	19	17	4	4
29.	15	18	5	4
30.	17	16	6	5
31.	17	19	6	7

TABLE—2
Statistical analysis of chromosomal breaks

	Control	Test	't'
N =	31	31	
Mean (\bar{X})	5.61	15.19	20.82***
S.D. (σ)	0.99	2.30	

TABLE—3
Statistical analysis of gaps

	Control	Test	't'
N =	31	31	
Mean (\bar{X})	5.68	16.23	23.44***
S.D. (σ)	0.87	2.29	

*** $p < 0.001$, i.e. highly significant

BEHAVIOURAL-PSYCHOLOGICAL STUDIES

The signs and symptoms observed in many of the MIC exposed population suggested likely effects on central and peripheral nervous systems. Therefore behavioural studies on the exposed population to assess the degree of involvement of the nervous system due to MIC exposure were undertaken.

Objectives

1. To study the visual perception/memory, auditory memory, perceptual motor speed, attention/response speed and manual dexterity of MIC exposed population of Bhopal.
2. To evaluate the exposed population on a standardized subjective questionnaire.

Methodology

In this study only those psychological tests which are recommended by W. H. O. (1984) have been taken. Most of these tests are developed by the Institute of Occupational Health, Helsinki, Finland (1979) and are accepted world over as standard behavioural test battery for toxicopsychological studies.

Research Design : The research design was ex-post-facto type. The independent variable was exposure of MIC gas and dependent variables were different psychological parameters, viz, auditory memory, visual perception/memory/perceptual motor speed, attention/response speed and manual dexterity. Cohorts were randomly selected from different locations of the affected area of Bhopal. With the help of research design the effect of independent variable on dependent variable, i.e. exposure response relationship, was assessed.

From the cohorts chosen for the ITRC study, 350 subjects were selected randomly for conducting various psychological tests. This sample included subjects from both the sexes and represented different socio-economic groups and were also drawn from different age groups. The children were excluded from the study.

The subjects of control group were equally distributed according to age, sex and socio-economic status, comparable to the exposed population, the only difference being that the subjects of this group were not exposed to methyl isocyanate or any other toxic or irritant gas.

Psychological Testing

The necessary precaution of testing the subjects in a quite, calm and comfortable place having proper light and ventilation without any disturbances from any source was taken. The

exposed and control subjects were studied in the same surroundings. Free conversation with the subjects was done so that his motivation and cooperation could be ascertained. The tests were presented in a definite order.

TOOLS

A Behavioural Tests

Standard behavioural tests used in toxico-psychological studies were employed. Applicability in this local situation, was the criteria of selecting particular tests for maximum information. Both central nervous system and peripheral nervous system functions were evaluated on the basis of these tests. The following core tests were used to test the various psychological parameters :

FUNCTIONAL DOMAIN	CORE TESTS
a. Auditory Memory	Digit Span Test
b. Visual Perception/Memory	Benton's Visual Retention test, Raven's Progressive Matrics
c. Perceptual Motor Speed	Digit Symbol test, Bourdon Wiersma Vigilance test
d. Attention/Response Speed	Simple Reaction Time a. Auditory b. Visual
e. Manual Dexterity	Santa Ana Dexterity Test
f. Attention/Vigilance	Other tests of attention or vigilance / time sharing tasks
g. Affect	E.P.I. / Subjective questionnaire

B Questionnaire on Subjective Symptoms

The test was performed individually with the help of a subjective questionnaire which was used by Hanninen et al (1976) in their studies on solvent exposed workers at Institute of Occupational Health, Helsinki. The questionnaire consists of 47 items grouped according to the factor analysis into four scales, measuring general lability, general fatigue with somatic complaints, lack of extroversive activity and neuroticism.

METHODS

1 Auditory Memory

Digit Span—Subtask of Wechsler Adult Intelligence Scale (WAIS) and of Wechsler Memory Scale (WMS) has been widely used in neuropsychology and also in behavioural toxicology. The subject is requested to recall digit series forward and backward immediately after hearing them. It is a test of immediate auditory memory.

2 Visual Perception and Visual Memory

Visual memory tests measures visual pattern recognition (visual organization) and memory for visual pattern. These tests are either recognition tasks where the subject has to match alternative figures in usually-short term memory or visuo-practical tasks where the subject has to reproduce figures from memory. Performance in visual memory tests depends on pattern recognition as much or even more than the memory per second.

Benton Retention Test —It is a well known visual memory test comprising of 10 tasks with one or three geometric figures to remember in each. In addition to memory, attention and visual or spatial ability contribute to the performance. The number of correctly drawn figures is used as the score.

3 Perceptual Motor Speed

Classic methods for perceptual motor speed and accuracy are paper and pencil tests where the subject has to scan a test sheet row by row or column by column, searching for and marking certain target characters as fast and as accurately as possible. These tasks require visual selectivity and high speed repetitive motor responses and the capacity for sustained concentration.

Digit Symbol Test (DST) : It is a subtask of Wechsler Adult Intelligence Scale. The test sheet gives a list in which numbers are associated with certain simple symbols and a list of random digits with blank spaces below them. The subject is asked to write the correct symbols in the blank spaces as fast as possible. Digit Symbol Test is generally considered to be one of the most valid detectors of cerebral dysfunctions.

Bourdon—Wiersma Vigilance Test : The test has a sheet having groups of three, four and five dots in successive rows. The task is to strike over all the groups of four dots as accurately and as quickly as possible. The performance time allowed for full test is only 5 minutes. The number of omissions and errors are calculated and with the help of a standard formula a score is obtained. This score represents perceptual accuracy in percentage.

4 Attention/Response Speed

Simple Reaction Time (SRT) —It is the length of time between the onset of a stimulus and the execution of the motor response. SRT, thus has both, a sensory and a motor component. In behavioural toxicology, SRT has been measured for visual and auditory stimuli; however visual SRT is the most common method. In addition to the mean or cumulative reaction time, the changes in reaction time over a space of time provide a sensitive indicator of toxic effects.

5 Manual Dexterity

Coordination visual perception and motor performance is required for this test. The degree to which either perception or motor performance is prominent varies from test to test. In this test the quality of psycho-motor performance is the dominant variable.

Santa Ana Test —It originates from the psychomotor test battery of Fleishman and has been modified and standardized for the purposes of behavioural toxicology at the Finnish Institute of Occupational Health. The test has a base plate with square depressions and each depression contains an accurately fitting peg with a cylindrical upper part. The task is to take one peg in succession, lift it from the depression, turn it around 180 degrees and put it back. The score consists of the number of pegs turned in two 30-seconds trials. Separate measurements are taken for the preferred hand, the non-preferred hand, and for both hands at the same time.

6 Attention/Vigilance

It includes other types of tests of attention or vigilance and time sharing tasks.

7 Affect

Different personality tests are included in this series like, Rorschach Inkblot and Eysenck Personality Inventory (EPI) and questionnaire for subjective symptoms.

STATISTICAL TECHNIQUES USED

The following statistical tools were used for the analysis of data pertaining to memory, perceptual motor speed, attention/response speed and manual dexterity.

(1) *Analysis of Variance*—In order to test the significance of the variations among three different groups, viz. control, exposed male and exposed female, the analysis of variance as suggested by R.A. Fischer, was worked out.

(2) *t-Test* — In order to find out the significance of difference between the two groups, this test is applied. The expression standard error (SE) of the difference between the two groups is represented by :

$$SE \text{ (diff)} = EMS \left(\frac{1}{n_1} + \frac{1}{n_2} \right)$$

where EMS=mean square within groups

n_1 and n_2 =denote the number of subjects in the two groups

INTERPRETATION AND RESULTS

Memory

(a) *Auditory Memory (Immediate)*— Immediate memory scores in females were significantly lower as compared to controls, however, no significant difference was observed in males. Overall immediate memory score (male and female) in the exposed population was significantly lower as compared to controls. This shows that the effect of exposure in reducing the auditory memory is likely to be more in case of females than in males (Table 1a and 1b).

(b) *Visual memory*— Immediate memory (visual) is significantly reduced in the exposed population ($p < 0.001$) as compared to controls. When males and females were compared it was found that immediate memory is more affected ($p < 0.05$) in males as compared to females (Table 1b). Overall group results show that immediate visual memory was affected due to MIC exposure. Delayed memory (visual) was also significantly reduced in exposed population ($p < 0.01$) as compared to control whereas no significant difference between male and female was observed indicating that both are equally affected by MIC gas exposure.

Perceptual Motor Speed—Both Digit Symbol Test and Bourdon-Wiersma test measure the perceptual motor speed. The latter test also includes attention/vigilance as an additional parameter. In the Bourdon-Wiersma test the changes were significant ($p < 0.001$) while in the Digit Symbol test no significant changes were observed (Table 2a and 2b). The analysis of the questionnaire and results of interviews with the exposed subjects revealed that these subjects were having a lack of concentration and a poor attention. The study also revealed that attention/vigilance was significantly impaired in the population affected by MIC gas.

TABLE I (a)
Analysing variance (ANOVA)

Sources of variation	Immediate Memory (Auditory)			Immediate Memory (Visual)			Delayed 10 sec. D.F.	Memory for (Visual) M.S.	F
	D.F.	M.S.	F	D.F.	M.S.	F			
Between group	2	15.045	4.61*	2	176.80	44.42***	2	117.785	25.02***
Within group	453	3.265		368	3.98		362	4.71	

TABLE I (b)
Mean memory scores and test of significance of different comparisons

Characters	Groups	Sample size (n)	Mean	S.D.	Comparisons	Diff. of means	S.E.D.	t	Level of significance	
278	IAM	Control	100	8.96	1.75	Control vs Exposed	0.44	0.2044	2.153	*
		Exposed	356	8.52	1.83	Control vs Male	0.25	0.2232	1.120	NS
		Male	190	8.71	1.78	Control vs Female	0.66	0.2287	2.886	**
		Female	166	8.30	1.87	Male vs Female (Exposed)	0.41	0.1920	2.135	*
	IVM	Control	100	6.92	1.35	Control vs Exposed	2.13	0.2335	9.122	***
		Exposed	271	4.79	2.20	Control vs Male	2.37	0.2546	9.309	***
		Male	159	4.55	2.20	Control vs Female	1.79	0.2745	6.521	***
		Female	112	5.13	2.16	Male vs Female	0.58	0.2461	2.357	*
	DVM	Control	100	5.35	1.93	Control vs Exposed	1.80	0.2547	7.067	***
		Exposed	265	3.55	2.25	Control vs Male	1.84	0.2780	6.619	***
		Male	156	3.51	2.29	Control vs Female	1.74	0.3005	5.790	***
		Female	109	3.61	2.20	Male vs Female	0.10	0.2709	0.369	NS

IAM = Immediate auditory memory

*p<0.05

IVM = Immediate visual memory

**p<0.01

DVM = Delayed visual memory for 10 seconds

***p<0.001

N. S. = Not Significant

D. F. = Degrees of Freedom

M. S. = Mean Square

TABLE—2,a)
ANOVA table of perceptual motor speed tests

Sources of variation	B.W. Vigilance Test			Digit Symbol Test		
	D.F.	M.S.	F	D.F.	M.S.	F
Between group	2	1394.045	10.58***	2	55.74	0.325 (NS)
Within group	387	131.790		371	171.580	

TABLE—2(b)
Table of means and test of significance of different comparisons

Character	Group	Size	Mean	SD	Comparisons	Diff. of means	SE (D)	t	Level of significance
Vigilance	Control	100	51.00	8.06	Control vs Exposed	6.12	1.3313	4.597	***
	Exposed	290	44.88	12.42	Control vs Male	6.26	1.4725	4.251	***
	Male	155	44.74	12.10	Control vs Female	5.95	1.5146	3.928	***
	Female	135	45.05	12.82	Male vs Female	0.31	1.3515	0.229	(NS)
Digit Symbol Control Test	Control	100	44.52	12.85	Control vs Exposed	(NS)			(NS)
	Exposed	274	43.37	13.17	Control vs Male				
	Male	157	43.57	13.37	Control vs Female				
	Female	117	43.11	12.94	Male vs Female				

*** significant at $p < 0.001$

(NS) = Not significant

TABLE—3 (a)
ANOVA table of attention/response speed

Sources of variation	Simple Reaction Time (Light)			Simple Reaction Time (Sound)		
	D.F.	M.S.	F	D.F.	M.S.	F
Between group	2	0.0400	4.166*	2	0.0397	7.065***
Within group	424	0.0096		424	0.0056	

TABLE—3 (b)
Table of mean and test of significance of different comparisons

Character	Group	Size (n)	Mean	SD	Comparisons	Diff. of mean	SE (D)	t	Level of Significance
280 Simple reaction time (SRT) (light)	Control	70	0.27	0.05	Control vs Exposed	0.035	0.0128	2.734	**
	Exposed	357	0.31	0.11	Control vs Male	0.030	0.0137	2.190	*
	Male	190	0.30	0.10	Control vs Female	0.040	0.0139	2.878	**
	Female	167	0.31	0.11	Male vs Female	0.010	0.0104	0.962	(NS)
Simple reaction time (SRT) (sound)	Control	70	0.18	0.04	Control vs Exposed	0.035	0.0098	3.571	***
	Exposed	357	0.22	0.08	Control vs Male	0.030	0.0105	2.857	**
	Male	190	0.21	0.08	Control vs Female	0.040	0.0107	3.738	***
	Female	167	0.22	0.08	Male vs Female	0.010	0.0079	1.266	(NS)

* Significant at $p < 0.05$

** Significant at $p < 0.01$

*** Significant at $p < 0.001$

NS=Not significant

Attention/Response Speed—This was studied by using the Reaction Time Test. It was found that with light stimulus the exposed male group was significantly different with the control at 5 per cent level and in the same group with sound stimulus the difference was significant only at one per cent level. Exposed female group was significantly inferior to the control for both the stimuli. It was also found that the overall exposed group was significantly inferior to control group. Moreover, exposed males and females did not show any significant difference (Table 3a and 3b). Exposure to MIC equally affected the reaction time (attention/response speed) for both the stimuli in both males and females. The results of Reaction Time Test showed that exposure to MIC increased the attention/response speed of the affected persons.

Manual Dexterity—The effect of exposure on manual dexterity in comparison groups, namely, control, exposed male and female were insignificant as 'F' value was found to be less than one. It was concluded that exposure to MIC did not affect manual dexterity in the exposed population.

B Results on Subjective Questionnaire

When males and females were separately compared the results indicated that generally females are more affected than males, however, no statistical evidence was established ($p > 0.05$).

TABLE—4

Number of bad cases for categories of subjective questionnaires

	Exposed n = 289	Male n = 154	Female n = 135
I	230 (79.58)	117 (75.97)	113 (83.70)
II	256 (88.58)	133 (86.36)	123 (91.11)
III	165 (57.09)	93 (60.9)	72 (53.33)
IV	13 (4.50)	4 (2.60)	9 (6.67)

DISCUSSION

The surviving population from Bhopal gas disaster has not only faced the ill effects of MIC exposure on their physiologic system but also have witnessed the tragic scenes, where the nearest and dearest ones were dying helplessly and nothing could be done to save them. Such ghastly scenes have left very deep impacts on the minds of the surviving population. The effect obviously is more pronounced in young people, in women, in elderly persons and those who are emotionally sensitive by nature. This impact has not only affected their thinking and emotions but also has resulted in a significant effect on their behavioural functions as described above. Many symptoms like nervousness, headache, palpitation, loss of appetite, insomnia, impotency, menstrual disturbances etc. observed in the exposed population may be due to the effects of MIC, but there is strong likelihood that a significant proportion of such symptoms may be only psychogenic in nature caused or precipitated by the unfortunate experiences after the gas tragedy.

Our results on the psychological tests revealed that the effect on visual perceptual memory (immediate and delayed) as measured by Benton Visual Retention Test was seriously affected. The auditory memory was also affected but to a lesser extent. This fact was also confirmed by the subjective symptoms questionnaire where a significant number of individuals were found to be suffering from poor memory.

Attention/response speed was also affected due to exposure to MIC. For measuring perceptual motor speed Digit Symbol Test did not show any significant findings, whereas, Bourdon-Wiersma Vigilance Test showed significant differences as compared with control. The reason seems to be that this test measures the attention/vigilance as an additional domain along with perceptual motor speed. Attention/response has shown significant difference as compared to control in reaction time study. The analysis of the subjective questionnaire has also revealed, lack of concentration in the exposed population. Thus it seems that attention-vigilance was dominating over perceptual motor speed performance.

The results of behavioural toxicological tests revealed that memory, mainly visual, perceptual and attention / response speed along with attention/vigilance were severely affected in population exposed to MIC.

The subjective complaints noted were difficulty in concentration, confusion, poor memory, headache, irritability or depression. Difficulty in concentration was the commonest complaint, causing problems at work and at home. Patients, generally students, found that they were unable to read a book or concentrate on finer work. They also complained of forgetfulness viz. forgetting, where they had put a particular thing, telephone number or address or why they had gone for shopping. Generally symptoms were at their worst during the first month after the gas exposure. At the time of testing they were all improving.

A significant change in the behaviour of family members was noted by several housewives. Both physical and mental factors operating together viz. breathlessness on exertion and difficulty in concentration forced many a people to a restricted work schedule. Lack of energy and physical capacity to work coupled with mental trauma have resulted in majority of population being turned into mental and physical cripples. The "gas phobia" or "carbide phobia" has made the entire population so sensitive that any smell resembling the odour of MIC gas produces a number of psychosomatic symptoms in the population, especially those who are more vulnerable like children, women and the aged. It remains to be seen how long it will take to restore the mental and physical faculties of the affected persons to normalcy.

CASE REPORTS

A team of toxicologist, neurologists, and pathologists from Industrial Toxicology Research Centre, Lucknow, K.G.'s Medical College, Lucknow, and Gandhi Medical College, Bhopal, undertook detailed clinical examination of patients, exposed to MIC (22 males and 11 females; mean age 38.3 years; range 8-60) for possible ocular and neurological symptoms. The patients were present within three kilometres from the Union Carbide plant at the time of the accident, and they belonged to low or middle socio-economic status. Around midnight most of these patients woke up because of severe burning in the eyes, irritating cough, dyspnoea and suffocation which soon became intolerable. Some of the patients, because of anxiety and panic, ran for a safer place and medical help (14 patients), while the others stayed in their houses and waited for the crisis to pass over (19 patients). Ophthalmological and respiratory involvement dominated the clinical picture and in the severely affected patients neurological involvement was also observed as reported below.

OBSERVATIONS

Ophthalmological Manifestations

All the patients experienced severe burning in the eyes which was associated with watering and redness. 73% patients complained of diminution of vision and photophobia, and 24% had pain in the eyes. At the time of examination, all the patients had marked congestion of the eyes. Keratitis was present in 6 cases and was bilateral in 2. The corneal opacity was of a macula grade in 4 patients and leucoma grade in 2. Characteristically, only the exposed portion of the cornea was affected being directly exposed to MIC. On fundus examination, superficial flame shaped haemorrhages were observed in 2 cases, in both of them, they were in the superior temporal quadrant. In majority of the cases, the symptoms improved by the third day (range 2-7), except in 2 in whom they persisted till second week due to severe keratitis.

Respiratory Manifestations

All the patients had severe cough, irritation and dryness of throat, rhinorrhoea, suffocation and breathlessness. Eighty one per cent of the patients complained of chest pain because of tracheitis and 73% had excessive frothy expectoration. Ninety one per cent of the patients were markedly dyspnoeic. Pharyngitis and laryngitis were present in 12% patients and were associated with difficulty in swallowing and hoarseness, respectively. Crepitations and rhonchi were present bilaterally in 94% patients. In 64% patients dyspnoea improved by the fourth day (range 2-7) but in spite of symptomatic treatment 46% patients were dyspnoeic at rest in the second week.

Neurological Manifestations

Severe cough and dyspnoea were followed by fainting in 55% patients. The duration of unconsciousness ranged from 30 minutes to 3 days. One patient had prolonged unconsciousness; he also had myoclonic jerks localised to the right upper extremity and generalised hyperflexia. His clinical picture was suggestive of toxic encephalopathy. Three patients who had prolonged unconsciousness (more than 12 hours) had brisk deep tendon jerks and extensor planter response. Weakness of the legs was present in 2 patients, it was more marked in the proximal muscles; one patient had difficulty in getting up from the squatting position and the other had difficulty in

walking. In both these cases, the deep tendon jerks were absent and sensations were normal. Mild to moderate headache (55%), giddiness (46%), burning sensation in hand and feet (9%) and hypoesthesia (3%) were also noted.

Miscellaneous Manifestations

Shortly after exposure to MIC, 64% patients had 1-4 vomitings, 15% had 1-2 loose motions and 6% complained of pain in abdomen. The patient with toxic encephalopathy, developed gastric haemorrhage on the fourth day of MIC exposure. Liver enlargement (3 cm) was present in a patient but he did not have jaundice. Of all the cases, 91% patients had sinus tachycardia which persisted in the first week. Generalised bodyache and fever were also present in 12% patients during the first week.

By the end of the second week, 3 patients were free of symptoms and were discharged, 29 patients had varying degree of illness and were still in the hospital. One patient died on the eighth day of MIC exposure; his lung biopsy was done and subjected to histopathological examination.

To study the effect of extent of exposure to MIC on the clinical picture, the physical activity undertaken by the patient at the time of the accident was assessed in relation to the severity of the clinical picture. Dyspnoea at rest on the seventh day and history of loss of consciousness were taken as the indicators of the severity of the clinical picture. The statistical analysis was done by the chi-square test. The proximity of the patient to the accident site was found to be significantly associated with the severity of the clinical picture, i.e. to dyspnoea at rest ($p<0.1$) and loss of consciousness ($p<0.05$).

Seventy seven per cent of the patients had polymorphonuclear leucocytosis. Blood urea was raised in 67%, SGOT in 26% and alkaline phosphatase in 33% in the first week. The chest X-ray films of 19 patients were examined. Bilateral patchy consolidation suggestive of pneumonitis was present in 15 patients while bilateral airspace consolidation suggestive of pulmonary oedema and prominent bronchovascular markings were present in 2 cases in each group. Left sided pneumothorax in addition to pneumonitis was present in one patient. Light microscopy of the lung tissue revealed the necrosis of the lining of respiratory bronchioles which was covered by fibrous hyaline exudate. Marked destruction of alveoli and areas of pneumonitis were present. The alveoli were replaced by fibrinous, or haemorrhagic exudate containing red blood cells, polymorphs, lymphocytes and in some of the alveoli, the predominant cells were macrophages. The alveolar septa were damaged and were replaced by irregular hyalinised fibroconnective tissue. The damaged alveolar capillaries were seen as reminiscences of the vessel wall around the collection of red blood cells. At places the features were suggestive of interstitial pneumonitis, characterised by accumulation of lymphocytes, proliferation of fibrocytes and macrophages along with fibrinous material in varying amount.

Case Report

L. D. P., a 20 year male resident of Ibrahim Pura, Bhopal, woke up at 1 a.m. on 3rd December because of burning, redness and watering from eyes. This was associated with irritating cough, suffocation and dyspnoea. He ran around to search his relations and fainted because of exhaustion in the Military Hospital. On regaining consciousness on 6th, he experienced weakness in the legs and was unable to stand. He was treated in Hamidia Hospital and improved by 13th December, 1984, but again developed weakness on 26th December and hence he was admitted on 10th January in the Department of Neurology.

On examination, the patient was of average built and nutrition, had flaccid quadriplegia with grade IV power, the weakness being more marked proximally. The superficial reflexes were normal, deep, reflexes were just present. No abnormality was detected in sensory system. Bowel and bladder functions were normal.

His hemoglobin was 13 gm%, white cell count 18000/mm³ with 60% polymorphs and 40% lymphocytes. Urinalysis was normal; ESR was 4 mm for the first hour; blood WR, VDRL was negative and CSF and liver function tests were normal. X-ray film of chest showed heavy bronchovascular marking. X-ray lumbar spine showed spina bifida. His nerve conduction velocity was normal. Electromyography of quadriceps, biceps and deltoid muscles showed normal pattern without any spontaneous activity. His action potentials were normal, amplitude, duration and interference pattern was normal. Muscle histology was normal on light microscopy but there were ultrastructural changes in the myofibrils showing irregular 'Z' bands, dilated endoplasmic reticulum and small and spare mitochondria.

The patient was given injection of ACTH for 20 days and then followed by tablets of Prednisone. The patient showed marked improvement, could walk normally and was discharged on 2nd March 1985.

Follow-up Studies

Three months after the initial examination, 24% of these patients could be followed up. By this time, all the patients were discharged from the hospital but most of them 88% still required medical supervision and treatment. Rawness in throat and dyspnoea (62.5%), cough (37.5%), reduction in visual acuity (62.5%), headache (50%), burning in hand and feet (37.5%), depression and irritability (75%) were the commonly reported symptoms.

COMMENTS

The respiratory involvement in the patients of the present study seemed to be due to the irritation of the upper respiratory tract, bronchitis and pneumonia. The radiological picture was also suggestive of bilateral patchy pneumonia (79%) and pulmonary oedema (10.5%). The histological picture of lung revealed extensive damage to the lining of respiratory bronchioles, alveolar capillaries and patchy pneumonitis. These observations are generally in agreement with the findings in the follow-up study presented elsewhere.

Alteration of sensorium was the commonest neurological manifestation. Alteration in consciousness ranged from 30 min to 3 days and 3 patients who had prolonged unconsciousness had hyperreflexia and extensor planter response. One patient had clinical features suggestive of toxic encephalopathy. Neuromuscular weakness was also observed in some patients. ACTH and prednisone treatment apparently helped recovering from neuromuscular weakness, which suggests need for further follow-up.

DISCUSSION

The results contained in this report are the outcome of a planned, systematic study carried out by ITRC during Phase-I and Phase-II in February-March, 1985, to investigate the after-effects of methyl isocyanate exposure on the population of Bhopal. As stated above, systematic investigations for studying 10 different parameters involving history taking, clinical examination, chest X-rays, lung function tests, haematological studies, behavioural studies, immunological studies, biochemical studies and chromosomal studies were undertaken. The subject group studied during this investigation comprised of Muslims, about 81%, and Hindus about 19%, belonging to the age group 15 years and above. A large percentage of the entire subject group was in their mid-twenties and thirties. The majority of the people was in the low socio-economic group.

Complaints related to the respiratory functions and ocular systems constituted the majority. Symptomatology involving the various physiological systems was analysed in reference to the distance from the factory. The average number of complaints per subject showed a declining trend with increasing distance. The prevalence of symptoms pertaining to respiratory and gastrointestinal systems was significantly higher in the population group residing within a distance of 4 km as compared to those residing beyond that distance.

Lung function tests were carried out using eleven different parameters. Those who could not perform the correct technique in spirographic tests were not included in this study. The prevalence of ventilatory impairment was found to be 34% in the male population as against 44% in females. In case of restrictive lung disease prevalence was 34 per cent. The combined obstructive-cum-restrictive ventilatory impairment was observed in 22% of the cases out of 783 cases who could perform spirometry. Pulmonary function impairment was predominant in this subject group. This was evidenced by the FEV/FVC ratio which showed a mean value of 63% in male population and 64% in female population, thereby suggesting the presence of mild bronchial obstruction. Thus, this population group exhibited mild, mixed, restrictive bronchial obstruction as a result of their exposure to methyl isocyanate. From the detailed studies on various spirometric parameters, this subject group revealed impaired functional capacity of their respiratory tract and decreased pulmonary function values in the symptomatic male and female population.

The mechanism responsible for causing lung impairment by methyl isocyanate is not clearly understood. Some investigators believe that MIC has an acute irritating effect on the respiratory tract resulting in bronchospastic reactions (Baur et al, 1979). Some other authors have proposed that isocyanate-induced respiratory disease may be the effect of immunological (Karol et al, 1978) and pharmacological (Butcher et al, 1979) effects of the chemical. Dewair et al (1983) suggested that inhibition of cholinesterase by isocyanate can be related to the respiratory disorders. Support for such a concept came from Trevisan and Moro (1981) who reported on the role of acetyl cholinesterase inhibition by TDI.

Out of 739 subjects examined by chest X-ray, 73 showed radiological changes which are not expected in the general population and, therefore, could be related to their exposure to MIC. Haematological studies showed a higher value of haemoglobin in the majority (67%) of

the population studied. There was also an increase in red blood cell count in 78% of the subject group studied. About 12% of the overall subject population showed an elevated total leucocyte count. ESR (erythrocyte sedimentation rate) was increased in 36% of the overall subject group studied.

Glutathione level was significantly reduced in 30 % of the population. However, the ceruloplasmin content was significantly raised in more than 45 % of the population examined. A decrease in glutathione level in this exposed group indicates that the ability to detoxify toxic chemicals in this group has been impaired. An increase in ceruloplasmin content is indicative of some inflammatory processes going on within the body. This could be due to some under-current infection in these individuals or to some kind of repair mechanism in progress to repair the damage caused in the tissues. It may have resemblance also to some changes in haematopoietic systems (Goodle, 1950, Nriagu, 1980). Among the surveyed population a relatively high level of creatinine was observed in their urine samples compared to the control subjects. This increase indicates an increased rate of breakdown of creatine phosphate, possibly as a result of muscular distress produced after MIC exposure (Oser, 1965).

A variety of immunological tests were performed to determine the levels of immunoglobulins G, M and A. On an average these values were similar to those of normal individuals, except for the fact that about 4 % of cases showed higher IgG values (2847 mg %). Some (7%) cases showed lower IgA values (70 mg%). In 8 per cent of the cases IgM was raised (390 mg%). Studies on phagocytosis involving peripheral blood mononuclear cells indicated that 40% of the cases had suppressed phagocytic ability. Suppression of phagocytic ability could be extremely harmful for an individual, since phagocytes render protection against primary infection and help in the elimination of toxic, unwanted chemicals or biochemicals from the physiological system. Depressed phagocytic function would mean that such a subject group would be more susceptible to infection. A great deal of care and attention, therefore, is needed to protect the exposed population by using effective measures of immunization, vaccination and nutritional supplementation etc., to increase their immunological competence to fight infection in an effective manner.

Chromosomal studies were conducted using peripheral blood lymphocytes by stimulating them with phytohaemagglutinin and examining one hundred well spread metaphases from each case for chromosomal aberration. This study, conducted in collaboration with GSVM Medical College, Kanpur, indicated that MIC exposure has caused an appreciable degree of chromosomal aberration (increased number of breaks and gaps) compared to an equal number of control individuals tested for this purpose from Lucknow, Kanpur and Bhopal.

Sophisticated behavioural and psychological studies were conducted on 350 subjects selected randomly. Many symptoms, such as nervousness, headache, perception loss, memory disturbances etc. were observed in the exposed population. The results of the psychological studies indicated that visual-perceptual memory (immediate and delayed) was significantly affected. This was confirmed by the subjective questionnaire study in which 250 out of 289 cases reported that they were suffering from poor memory. Attention/Response speed was also affected in the exposed population. The results of behavioural toxicological study revealed that visual memory, perceptual memory and attention/response speed, along with attention vigilance capacity were affected in the population group exposed to MIC. The major complaints noted were difficulty in concentration, confusion, poor memory, headache, depression etc. Difficulty

in concentration was the commonest complaint causing problems at work and at home. Forgetfulness was also a major complaint. The general symptoms were at the worst during the first month after exposure to the gas. Lack of energy and physical capacity to work was also a common complaint recorded. Thus an appreciable amount of behavioural and psychological changes was evident in this subject group investigated by us.

The above data, particularly those showing various abnormal physiological functions in the population group studied by us are indicative of various deleterious effects which appear to have been caused due to exposure to the toxic gas released in the air by the Union Carbide plant at Bhopal. All the people had complained about signs and symptoms which had quite a great degree of similarity indicating that they were exposed to similar type of toxic gas. Therefore, the signs and symptoms and after-effects recorded in the study appear to be related to their exposure to methyl isocyanate gas and any others produced and released after the run-away reaction in the storage tank of methyl isocyanate.

In order to study this toxic phenomenon in a controlled manner, we have been successful in developing a laboratory animal exposure chamber to study the deleterious effects of MIC in rats exposed to it through the inhalation route. Interestingly, many of the signs and symptoms involving histopathological, immunological, behavioural, neurological and biochemical changes observed in human patients, could be reproduced in animals exposed to MIC. This data would be compiled in a separate volume later.

In order to further follow-up the conditions still existent in the population of Bhopal exposed to MIC, this laboratory has recently carried out Phase-III studies in Bhopal in the month of January, 1986. This data is being analysed for compilation in a separate volume.

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APPENDIX-I

CHEMISTRY AND TOXICOLOGY OF METHYL ISOCYANATE

Chemistry of Methyl Isocyanate

Isocyanates ($R-N=C=O$) resemble aldehydes and ketones in their affinity for active hydrogen atoms, but also function as cumulated unsaturated systems thereby making them highly reactive. Due to this, isocyanates are useful chemical intermediates. Three isocyanates are of major commercial importance. One is methyl isocyanate (MIC), almost all of which is used to make carbamate pesticides. The other two are toluene di-isocyanate (TDI) and 4, 4,—diphenylmethane diisocyanate (MDI) both of which are used almost exclusively to make urethane and isocyanurate polymers.

TDI and MDI, like MIC, are flammable as well as reactive. MDI and TDI are essentially non-volatile, unlike MIC which is highly volatile. MIC is a colourless liquid with a sharp odour. It boils at 39.1°C (at 760 mm Hg) and has a vapour pressure of 348 mm Hg at 20°C . Furthermore, although the liquid is slightly lighter than water, the vapour is about twice as heavy as air. If released, it tends to stay close to the ground as it diffuses from the source. Thus, MIC has a much greater potential for damage than TDI and MDI.

MIC will react with many compounds. The reactions tend to be exothermic and vigorous (Fig. 1). MIC and water will react to yield methylamine and carbon dioxide. Methylamine reacts further with MIC or other reaction products to give either 1,3-dimethylurea (with excess water) or 1,3,5-trimethylbiuret (with excess MIC). A trace of acid or base will promote the reaction.

At room temperature, the MIC-water reaction starts off slowly, and is exothermic. Specifically, it produces about 585 Btu per lb of MIC or about 3700 Btu per lb of water. If sufficient quantities of both reactants are present, and if the heat is not somehow removed, the temperature will go up and the reaction rate will rapidly increase to the point that the MIC will start to boil violently. In a closed tank, the pressure could build up to the point that relief valves would open, venting both MIC vapour and carbon dioxide. If safety devices fail to operate, or if they were overwhelmed by the amount of vapours being generated, the heavy, noxious MIC vapours would escape to the atmosphere. MIC in addition to reacting with a great many other chemicals, can also react with itself. In the presence of a catalyst, pure MIC will form either a cyclic trimer (trimethyl isocyanate) or a gummy, resinous polymer. Extremely pure MIC will spontaneously form a linear polymer.

These reactions also are exothermic. Trimerization, for example, liberates about 540 Btu per lb of MIC, equivalent to 54 Kcal per mole of trimer. Any number of substances can catalyze the reaction : strong bases such as sodium hydroxide or sodium methoxide, triphenylarsine, triethylphosphine, metallic chlorides and others. However, the reaction rates and the induction periods vary widely with different catalysts. According to the literature, the time required for complete trimerization, using various catalysts, can range from 10 minutes (sodium methoxide) through one hour (ferric chloride) to four weeks (4-dimethylaminopyridine). MIC samples contain a small residual amount of phosgene which inhibits both the reaction between MIC and water and polymerization. But it also should be noted that the phosgene provides a source of chlorine and that most stainless steel alloys, although generally chemically resistant, are rather vulnerable to attack by chloride ion. In theory, at least, that could lead to production of substances that could act as catalysts.

Of the billions of pounds of isocyanates manufactured worldwide each year, the bulk consists of three key industrial materials: toluene di-isocyanate (TDI), diphenylmethane-4,4'-di-isocyanate (MDI) and a polymeric form of MDI known as polymethylene-polyphenyl polyisocyanate. These compounds are used in the polyurethane industry to make foams, elastomers, insulators and coatings.

Use

MIC is used in the production of pesticides and pharmaceuticals. There is also some application in the production of polyurethane foams and plastics. The major use of MIC is in the manufacture of N-methylcarbamate pesticides such as aldicarb, aldoxycarb, banol, baygon, butacarb, carbaryl, carbofuran, landrin, larzin, meobal, methomyl, zectran and so on.

Production

The most widely known method for the production of methyl isocyanate is the reaction of phosgene with methylamine. Phosgene is produced by reacting carbon monoxide (CO) with chlorine gas. Major producers of MIC are reportedly Union Carbide Corporation (USA) and Bayer (FRG). It is understood that Japan, the Republic of Korea, Taiwan and Israel also have firms producing MIC. Production figures are unknown.

Several companies around the world are manufacturing carbamate pesticides such as BASF (FRG), Bayer (FRG), Drexel (USA), Du Pont (USA), Maag (Switzerland), Maktechim-Agan (Israel), Mitsubishi (Japan), Nihon (Japan), Pillar (Taiwan), Schering (FRG), Sunko (Taiwan), Union Carbide (USA, Brazil, France, India). Carbaryl production is also known to take place in USSR.

Occupational and Environmental Hygiene

Severe irritation and corrosion of eyes and skin, nose, throat and the respiratory tract have been described, overexposure will cause pulmonary oedema and suffocation. Effort increases lung symptomatology up to suffocation.

Survivors may develop varying degrees of lung fibrosis and respiratory insufficiency. Sensitization to MIC and other isocyanates may occur. Eye damage such as severe keratitis and corneal ulcer may become irreversible (corneal opacity). Short-term exposures to MIC levels between 10-20 ppm have been reported to be 'unbearable'.

Very few toxicity data have been reported in the medical and scientific literature. No carcinogenicity studies have been carried out. No teratogenic effects have been reported. Metaplasia in the respiratory tract has been reported from animal studies.

Environmental Behaviour and Fate

Very little is known about the environmental behaviour and fate of MIC. In contact with humid air or water, however, rapid decomposition or polymerization to less toxic products occurs. No significant MIC residues in air, water and food can therefore be expected.

Treatment of Poisoning

No specific antidote to MIC is available. Suggested treatment upon exposure to MIC should be as for prevention or treatment of lung oedema; absolute rest and hospitalisation, administration of oxygen and positive pressure artificial respiration, administration of spasmolytics, corticosteroid containing spray, corticosteroids and antibiotics against secondary infection, treatment of eyes with antibiotics and corticosteroids.

Symptomatic treatment is needed against cardiac failure. Long-term corticosteroid treatment may help to prevent pulmonary fibrosis.

Occupational Exposure Limits/Safety Precautions

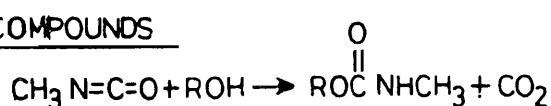
Permissible exposure limits in workshop air are set in most countries at 0.02 ppm (0.05 mg/cubic metre air; time-weighted average). Skin absorption is possible. The IDLH (Immediate Danger to Life and Health) level has been set at 20 ppm. Worker exposure should be kept to a minimum. The use of impervious clothing, gloves, face shields and eventually, respirators is prescribed. Any possibility of body contact should be as much as possible excluded.

Transport recommendations by the UN Committee of Experts on Transport of Dangerous Goods and the International Maritime Organisation do exist.

UN Number 2480 (Orange Book); packing Group I (very severe risk of poisoning; deck cargo only).

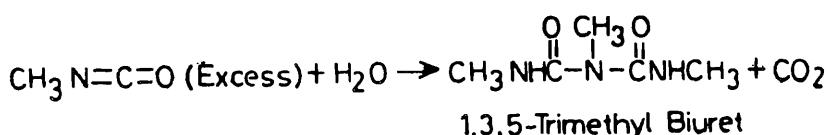
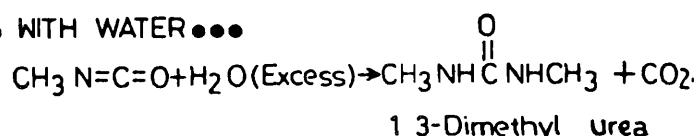
METHYL ISOCYANATE WILL REACT WITH MANY "ACTIVE HYDROGEN"

COMPOUNDS

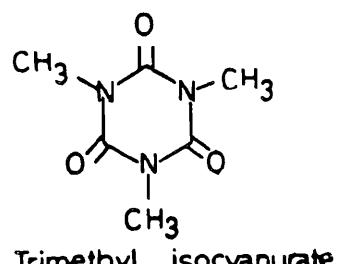
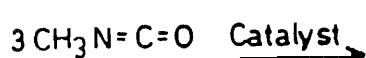


An N. Methyl carbamate.

••• WITH WATER •••



••• And with it self •••



PROCEDURES FOR THE DETERMINATION OF METHYL ISOCYANATE IN THE ENVIRONMENT

1 Chromatographic Method

(a) The method involves the collection of methyl isocyanate on an ion exchange resin, reaction with a fluorescent reagent and analysis by high pressure liquid chromatography.

(b) A previous method for determining isocyanate monomer using 1 (2-methoxyphenyl) piperazine with high performance liquid chromatography (HPLC) was modified to measure both monomer and prepolymer. A dual detection system employing electrochemical and ultra-violet detectors is used to identify isocyanate derived HPLC peaks which are then quantified by reference to a monomer standard. The precision of the method is better than 10% over the range 35-140 ug (NCO)-m³ for a 10 minute sample.

(c) The concentration of air-borne isocyanates were measured during spray painting with two component polyurethane paints. The isocyanate component hexamethylene-di-isocyanate (HDI) and its prepolymer of the biuret type were determined by high performance liquid chromatography after derivatization to stable urea derivatives with N-4-nitrobenzyl-N-n-propylamine. Samples were collected on reagent impregnated glass fibre filters, and the derivatives were eluted with the chromatographic eluant. An impregnation technique facilitates the chromatographic separation and the subsequent quantitative determination.

2 Detector Tube Method

The need for a simple method to determine the level of MIC in vessels prior to entry or to locate leaks from process equipment led to the development of a detector tube. This is based on the orange-to-yellow colour change obtained when MeNCO reacts with p-aminoazobenzene on silica gel. It is capable of detecting 1 to 30 ppm MeNCO.

3 Titrimetric Method

The isocyanates are determined by treatment with an excess of n-butylamine in dioxane to form the corresponding substituted urea and thiourea respectively. The excess of butylamine is then determined by titration with standard 0.02 N. hydrochloric acid.

4 Colorimetric Procedure

Methyl isocyanate is collected by scrubbing air through two midge impingers connected in series containing dimethylsulfoxide hydrochloric acid (DMSO-HCl) absorber solution. Air is scrubbed through the impingers at a rate of 0.1 litre per minute for eight hours. MIC collected is hydrolyzed in the absorber solution to methylamine, which is transformed to 2,4-dinitrophenylmethylamine with 1-fluoro-2,4-dinitrobenzene. 2,4-Dinitrophenylmethylamine has a yellow colour which is extractable in tetrachloroethane, the intensity of which is measured spectrophotometrically at a wave length of 366 mu.

5 Micro determination in Air using a short Chromatographic Column

Methyl isocyanate is collected by passing air through a stainless steel tube, 1/4"×10", packed with 5 per cent didecyl phthalate on C-22 firebrick. The tube is cooled with dry ice and the sample is collected at 0.5 litre per minute for two hours. Methyl isocyanate is degassed from the tube by heating into an evacuated flask containing dimethyl sulfoxide hydrochloric acid (DMSO-HCl) absorber solution. Methyl isocyanate is then estimated as in the colorimetric method.

TOXICITY OF METHYL ISOCYANATE

Methyl isocyanate is an irritant to the eyes, mucous membranes and skin and it can cause pulmonary irritation and sensitization. Exposure of humans to high concentrations causes cough, dyspnoea, increased pulmonary mucous secretion and chest pain. Isocyanate cause pulmonary sensitization in susceptible individuals. Should this occur, further exposure must be avoided, since extremely low levels of exposure may trigger an asthmatic episode. Cross sensitization to unrelated materials probably does not occur. Experimental exposure of 4 human subjects to 0.4 ppm had no effect. At 2 ppm, there was lacrimation, irritation of the nose and throat and at 4 ppm the symptoms of irritation were more marked. The symptoms became more severe including unbearable irritation, irritation of eyes, nose and throat at a concentration of 21 ppm. The TLV for methyl isocyanate is fixed at 0.02 ppm.

Since very little toxicity data on MIC *per se* is available, QSAR approach has to be applied taking data from TDI and MDI. According to Rye (1973), the larger the molecular weight of the isocyanate in question, the toxicity, volatility, vapour pressure and total exposure dose are lower. Since isocyanate compounds vary in molecular weight from the low mono to the high poly form, their volatility decreases and the exposure hazard is directly proportional to the change. The low molecular weight ethyl and methyl isocyanates are skin irritants and can cause permanent eye damage and the higher molecular weight compounds are not. The oral toxicity of the entire group is relatively minor, producing only minimal gastro-intestinal change in very high dose. There have been no reports to indicate that skin absorption occurs. Other systemic changes (i.e. renal, hemopoetic) have not been evident in routine surveillance of workers. The most common, most severe and by far the most important human response have occurred in the respiratory system.

The importance of volatility of the compounds used is extremely relevant to this response, since respiration of the fumes is necessary for exposure response to occur. Other considerations are increasing volatility with rise in temperature and rapid hydration and dissipation of fumes in high humidity.

Two types of responses, irritant and allergic, have occurred once exposure reaches sufficient magnitude (Rye, 1973). Direct irritant or toxic response is due to triggering of normal protective mechanism of the upper respiratory tract and mimics that of other respiratory irritants. The symptoms depending on total dose, appear 4 to 8 hours after onset of exposure and respond to supportive measures after removal from exposure, and persists for 3 to 7 days. The symptoms are those, associated with increased protective mechanism, with increased secretion, cough, pain on respiration, some restrictions of air movements due to combination of secretion, oedema, and pain. It is important to discern whether the type of dyspnoea involved is due to these conditions or to pure airway constriction with characteristic expiratory difficulty, as in asthma (Rye, 1973).

The allergic response in host is not to be expected on initial exposure but usually develops after a reasonable time in the work area. It may masquerade as a cold or mild hay fever until

the full blown asthmatic-like attack occurs. The mechanisms are different and the response to therapy may also be quite different. Whereas, supportive measures suffice for the irritant reaction, bronchodilator or steroid intervention is needed in allergic attack. Immediate removal from exposure applies in both types of reactions but in the case of the allergic reactions, any future exposure must be prevented since even minute exposure less than that measured with currently available methods may trigger the incident.

No epidemiological study is available in literature involving human population exposed to MIC. However, some studies had been conducted with toluene di-isocyanate and diphenyl methane di-isocyanate. The first report in the medical literature appears to be by Fuchs and Valade (1951) in which 9 cases of progressive bronchial irritation, of which 7 went on to develop an asthma-like syndrome on continued exposure to a mixture of 2, 4 and 2, 6 isomers of TDI. From Germany in 1953, 17 similar cases were reported, 13 of them severe and one ultimately fatal (Reinl, 1953). In 1959, 99 cases of respiratory illness were attributed to TDI in a single U. S. plant producing polyurethane foam (Walworth and Virchow, 1959). Williamson (1965) observed that high concentration of TDI vapour may cause chemical bronchitis with severe bronchospasm. Dernehl (1966) and Dodson (1971) have classified some of these cases as chemical pneumonitis and have followed a clinical course similar to that of broncho-pneumonia from bacterial infection. In such cases, secondary bacterial invasion of the inflamed bronchial tree and lungs is very likely to occur. Pulmonary oedema may complicate the picture. The early German literature contains many descriptions of individual cases with the above features (Reinl, 1953; Ganz and Mager, 1954; Schurman, 1955).

An implication of the work of Peters and associates (1968, 1970) and of Adams (1970) is of cumulative impairment of lung function of the workers exposed to TDI. From Canada, Mastro-matteo (1965) reported that 12 out of 24 workers in a TDI plant had developed symptoms of TDI toxicity. From 3 to 7 days after commencement of exposure, these men experienced symptoms including coryzal symptoms, laryngitis, sore throat, tracheitis, bronchitis and pneumonitis. Six required hospitalization, four patients developed anxiety neurosis, psychosomatic complaints, depression and even paranoid tendencies. One year following the incident these men had not returned to full time employment. In accidental exposure to isocyanate fumes in a group of 55 firemen in a factory in which polyurethane foam was being manufactured Mc Kerrow et al (1976) noted mainly gastrointestinal, respiratory and neurological symptoms. Fifteen men described gastro-intestinal symptoms which subsided within 2 days of onset. Respiratory symptoms were described by 31 men and were most pronounced during the 3 days after the fire, thereafter tending to improve. When the men were reviewed at 6 months there was a suggestion that some of them might have sustained long term damage to the respiratory tract, and almost four years later 20 men had permanent respiratory symptoms. Serial measurements of ventilatory capacity revealed a marked decline in the first 6 months although this was not sustained.

Maxon (1964) studied 7 men who developed acute respiratory symptoms after exposure to TDI in a plastic varnish factory. Symptoms reported were dyspnoea, chest pain and wheezing. In addition haemoptysis occurred in 4 patients. A series of timed vital capacity determinations indicated impairment in 6 out of 7 patients. Subsequent evaluations demonstrated improvements in some of the patients at first and later some deterioration. In the absence of pre-exposure baseline studies, it was impossible to assess the degree of late disabling effects of exposure to TDI.

The immunochemical response of human subjects to low concentration of di-isocyanate has been investigated. Results showed that an exposure of about 1.3 ppm/min resulted in an antibody response whereas an exposure of about 0.9 ppm/min did not. Thus demonstration of antibodies in the serum of individuals could be of diagnostic value for a recent exposure to di-isocyanate. However, the number of individuals in this study is too small to indicate that the titre of the antibody found is proportional to the exposure.

Thirty-eight workers exposed to levels of TDI below the TLV were examined for lung function at the beginning and end of a work day (Monday) by Peters et al (1968). Statistically significant decreases occurred in FVC, FEV, PEFR, PEF 50% and 25% of VC. Thirtyfour of these workers were examined on Friday and it was found that FVC had returned to base line, the FEV₁ was still depressed and the expiratory flow rate was more depressed. Diurnal variation could not account for these changes. Workers with respiratory symptoms showed greater decrease in FEV₁ than workers without symptoms. Similar results were obtained with 111 workers exposed to TDI during a workshift (Wegmen, 1974). The data showed a dose-response relationship between exposure and acute respiratory effects. Workers in a factory producing polyurethane foam have been studied at 6 month intervals for a period of 18 months, showed reduction of ventilatory capacity (Peters et al 1970). Cumulative changes exceeding those associated with aging occurred in these workers over 6, 12 and 18 months. Symptomatic workers showed a greater response to TDI than asymptomatic one's and a substantive positive correlation existed between the acute and cumulative changes in FEV₁.

Complaints of respiratory symptoms amongst workers in a factory using isocyanate to produce polyurethane foam led to a study of changes in ventilatory capacity in the course of several working days. Mean decrease of the order of 0.18 litre was observed in FEV₁ in 15 employees during each of three normal workshifts. No significant changes occurred on days when a process involving the liberation of isocyanate was stopped, or when the men were given an oral aminophylline compound prophylactically. An aerosol of isoprenaline failed to reverse the decrease in ventilatory capacity observed during a normal working day. Approximately half the subjects studied were found to show increased bronchial sensitivity to a histamine aerosol, all were smokers, whereas none of the non-smokers showed a significant (more than 10%) reduction in ventilatory capacity after histamine. Smokers and/or positive histamine reactors among polyurethane workers tended to show a greater decrease in ventilatory capacity during a working day than non-smokers and nonreactors (Gandevia, 1963).

A common response from the inhalation of MIC following acute toxic symptoms, is an asthma like syndrome that develops on subsequent exposure to even minute amounts of isocyanate. This "immediate" type of hypersensitivity resembles the "wet" allergic reaction commonly associated with hay fever or plant pollen reaction. In some workers a "delayed" type of response occurs, consisting of a low-grade-fever, headache and malaise, without a stimulation of secretions in the respiratory tract. This type of response by contrast, requires a far greater exposure to activate it than the immediate type reaction (Stokinger and Scheel, 1973).

Immunologic testing of more than 1000 sera in U.S. workers population showed 0.5% clinical cases of delayed hypersensitivity and 1.5% clinical cases of wet allergic hypersensitivity occurs upon exposure to organic isocyanates. Of the remaining 98% about 30% showed clinical signs when first exposed but became asymptomatic on continued exposure. The remaining 60% developed precipitating antibodies (Gamma globulin G) and also develop immunity without

symptoms. During the last 5 years pre-employment screening has been in effect in two plants in the USA, which manufacture isocyanates. This screening has been found to be extremely effective in reducing the number of unwanted clinical reactors (Stockinger and Scheel, 1973).

COMMENTS

Even though toxicological data on MIC *per se* is limited, analogy from the above data could be useful in appraising MIC toxicity on single acute exposure. Detailed experimental studies are needed to cover this lacunae.