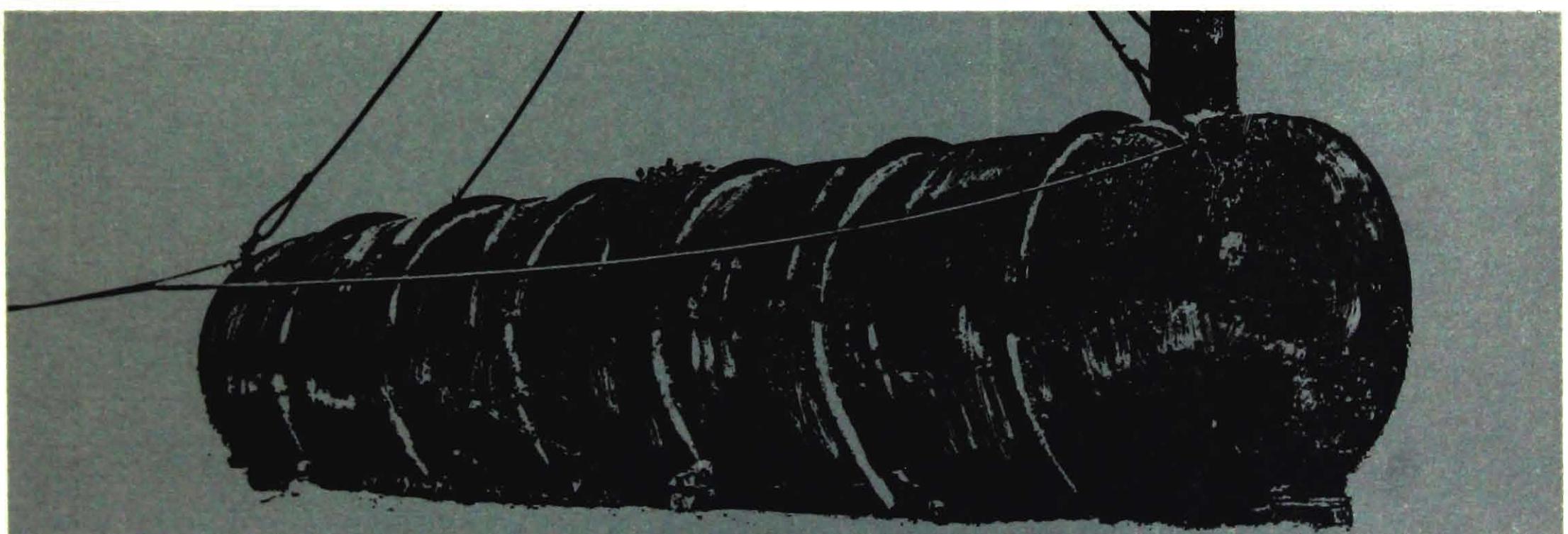
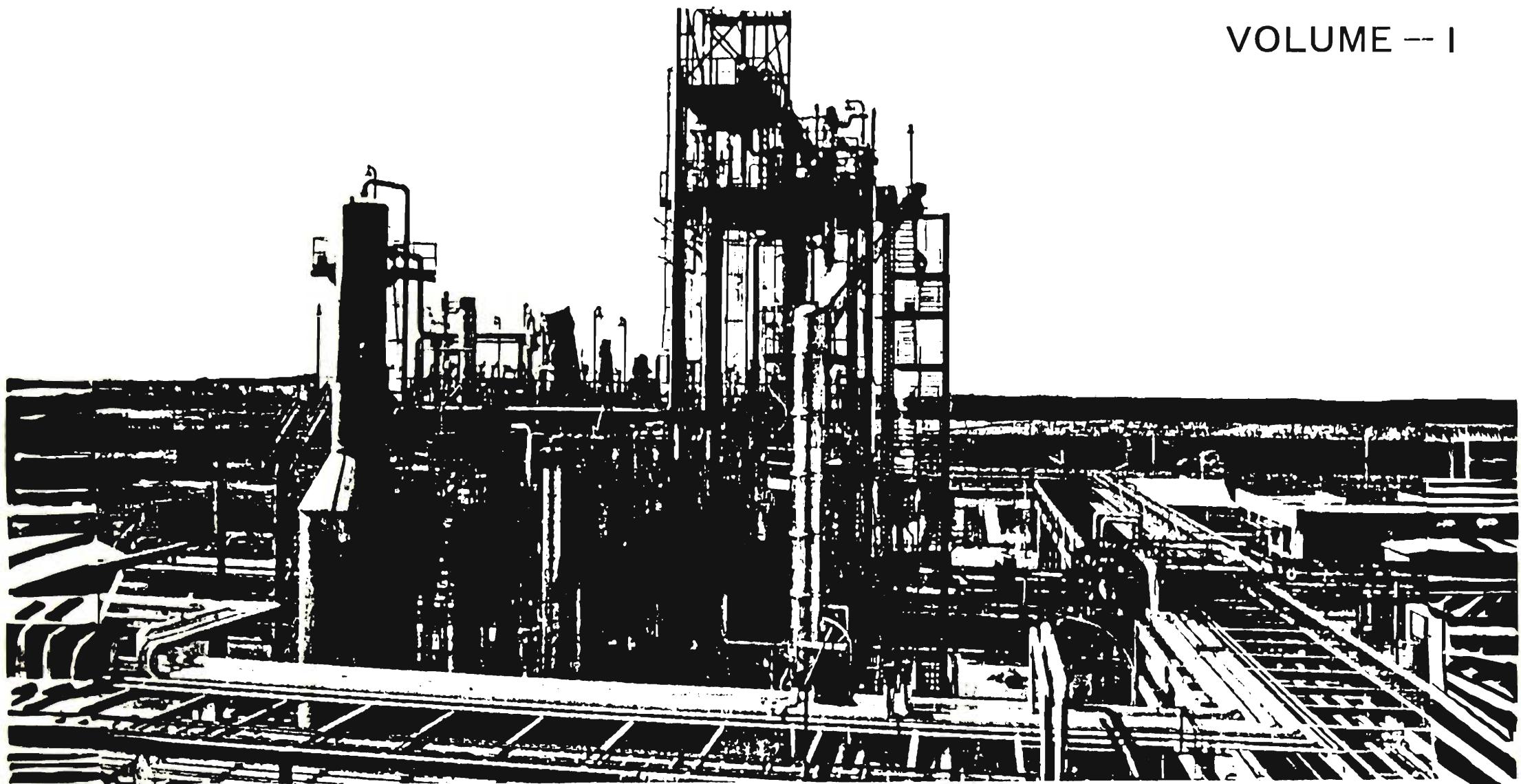


CSIR'S CONTRIBUTION TO UNDERSTANDING THE CHEMICAL PHENOMENA LEADING TO THE TRAGIC TOXIC GAS LEAKAGE AT THE UNION CARBIDE PESTICIDE PLANT, BHOPAL AND AFTERMATH

VOLUME -- I



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

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RESTRICTED

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THE TRAGIC TOXIC GAS LEAKAGE AT
THE UNION CARBIDE PESTICIDE PLANT,
BHOPAL AND AFTERMATH**

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PREFACE

December 3, 1984, saw the worst industrial disaster occurring in Bhopal. The leakage of poisonous methyl isocyanate (MIC) gas from the chemical plant of Union Carbide left in its wake over two thousand dead and countless many maimed and in a state of permanent disrepair. An industrial disaster of this unprecedented nature required a technical assessment by an expert group of the highest level of competence. The Government of India requested Dr. S. Varadarajan, the then Director General of the Council of Scientific & Industrial Research, to coordinate scientific and technological investigations of the disaster. He brought together at Bhopal a team of scientists, engineers and technologists from CSIR laboratories and other agencies/departments and industrial enterprises and supervised 'Operation Faith' and subsequent investigations on the causes and consequences of the accident. As a result, today we have a clearer understanding of the causes and circumstances leading to the accident.

Two important conditions circumscribe Operation Faith and the further work by our scientists. First, an event of this magnitude had not occurred before. A solution to the problem was not within the realm of a single unit or an agency. It was a crisis-management-situation calling for the interplay of multi-disciplinary and multi-dimensional expertise, at a national level. The magnitude of the efforts put in by the scientific team under the leadership of Dr. S. Varadarajan was immense, technically challenging and had to be completed within a short period of time. This we believe, was done. It was a tribute to Indian Science and scientists. CSIR, naturally, was in the forefront and received excellent support from all the other collaborating partners.

A special mention could be made here of the detailed documentation and information base created for future use, under the leadership of Dr. S. Varadarajan.

It is now time to bring together all the scientific and technical data and the results of investigations by CSIR laboratories. Hence these two volumes. The Bhopal tragedy has touched the conscience of every industrialized nation, struggling to maintain minimum standards of industrial safety. India has had several measures brought into force thereafter. It is believed that the information contained in these volumes will provide some scope to prevent recurrence of a similar disaster.

The responsibility of coordinating the investigations, on the basis of mutual consultation, was entrusted to a special CSIR Cell for Bhopal Affairs, comprising Dr. L.K. Doraiswamy, NCL, Dr P K Ray, ITRC, Dr A V Rama Rao, RRL(H), Dr G Thyagarajan, CLRI, and Dr M Sriram of Hindustan Organic Chemicals Ltd. To them we owe a debt of gratitude.

I congratulate Sarvashri C.V. Swaminathan and N.R. Rajagopal, Scientists of CSIR, for having compiled these volumes and Shri V. Ramachandran for printing them, in record time.

New Delhi
25.05.1987


(A.P. MITRA)
Director-General

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INTRODUCTION

How CSIR entered the scene

As a consequence of the uncontrolled release of toxic gas from the pesticide plant of Union Carbide, Bhopal, on the night of 2/3 December 1984, over a hundred people died and several thousands were injured within 24 hours of the leak, besides visible damage to the environment and immobilization of public life. There was utter confusion, chaos, and a sense of despair and disbelief everywhere. The Government of Madhya Pradesh was in urgent need of technical guidance regarding quality of air and water for preventing further panic among the people of Bhopal. They had to cope with medical relief for over twenty thousand people.

Dr. S. Varadarajan, the then Director General of CSIR and Secretary, DSIR had scheduled a visit to RRL, Bhopal on 5 December 1984. This came to the knowledge of the then Madhya Pradesh Chief Minister Shri Arjun Singh who had approached RRL, Bhopal for assistance. He was informed by the then Director of RRL that Dr. Varadarajan would be able to provide the required guidance.

Shri C.R. Krishnaswamy Rao Sahib, the then Cabinet Secretary requested Dr. Varadarajan to coordinate all scientific efforts at Bhopal in the wake of the gas leakage. Visualizing the need for multidisciplinary expertise, Dr. Varadarajan asked team of scientists and technologists with expertise in environmental protection and toxicology to proceed forthwith and assembled at RRL, Bhopal.

While these teams began an assessment of environmental damage and safety of air and water, the Director General, CSIR, on a visit to the accident site, was treated to a shocking revelation by the UCC management that bulk quantities of MIC were stored not only in the ill-fated tank E-610 but also in E-611. The frightening implications of the disclosure suddenly loomed large before the CSIR Chief. There was no time to lose; every available expert in and outside CSIR needed to be mobilized on a war footing. The CSIR involvement which at first appeared to be for a short time was extended as a deep and long term proposition.

The formidable and frightening task

With several hundred people dead, more dying and several thousands lying injured and requiring the correct medical treatment, and the air and water quality being suspect, the already exasperated Madhya Pradesh Government was told, to their utter dismay, that the Union Carbide's revelation of the presence of more MIC (approximately 15 tonnes according to UC) lying in tank E-611, posed a new danger that had equal devastating potential as the first one. The M.P. Chief Minister sought and secured the consent of Dr. Varadarajan to coordinate and manage the crisis.

The tasks before the CSIR scientists were:

- Assuring safety of the environment. Teams of scientists analyzed air and water samples and on the evening of 5th December assured the State Government that there was no more MIC in the environment and that the air was free from any cyanide. This information was broadcast to the public.

Dealing with MIC in tank 611. The Union Carbide management stated that the material in tank 611 and the ruptured tank 610 both came from the same batch of MIC produced during October 1984 and that part of the material had been transferred from 610 to 611. With a common manifold of pipelines and headers, this essentially implied that the conditions and causes which led to the toxic gas discharge from tank 610 were also obtained in 611. In other words, a second Bhopal tragedy was not to be ruled out. Regrettably the UC management was not aware of this new hazard and had no knowledge of the precautions to be observed, should tank 611 leak. They were unable to provide an acceptable procedure for determining the purity of MIC in tank 611, though it was known to them that MIC was vulnerable to explosive polymerisation in the presence of certain impurities and also when thoroughly pure. A reliable procedure had to be developed, and developed fast, before determining how to handle the content of tank 611.

It was necessary to analyze the circumstances that led to the toxic gas leak on 2/3 December. All possible avenues of ingress of foreign materials had to be identified and appropriate precautionary measures introduced (to prevent it).

A leakage from tank 611 could not be ruled out. A perplexing question was: if a leakage did occur., how to handle it, how to minimize damage to people and the environment. With the news of the chemical industry's worst ever disaster spreading around the world, Bhopal was teeming the media men, voluntary action groups, lawyers and interested parties from all over the world, apart from the necessary presence of representatives of government agencies, medical experts and service personnel.

More important and urgent than all these, a way had to be found out of a set of limited options for *quality* and *safely* disposing off MIC in tank 611.

The CSIR Chief and his team of scientists had, on their hands, a formidable, frightening and unenviable task.

How the crisis was managed

A crisis management team under the direction of the CSIR Chief came into being and it initiated several simultaneous actions. Prominent among these were:

- Experts from CSIR, the Indian Council of Medical Research (ICMR), the Indian Petrochemicals Corporation Ltd. (IPCL), the Department of Environment (DO En), Hindustan Organic Chemicals Ltd, (HOC) the Defence Research and Development Organisation (DRDO) and the University Department of Chemical Technology, Bombay conferred and analysed the likely causes of the 2/3 December gas leak. This was a prerecruisite for devising means for preventing a similar leakage.
- The pros and cons of four alternative options for disposal of MIC in tank 611 were evaluated by a team of experts. A major limitation was that any method selected had to be compatible with the facilities and experience available at the plant site since the plant belonged to Union Carbide and its personnel were to handle the physical operations. Once the choice of method of disposal was made, the required quantities of raw materials and chemicals had to be organised in the shortest possible time. A programme for organisation and monitoring of the plant operation was drawn up. The Director General, CSIR was personally in charge of its overall monitoring, while liaising and coordinating with other agencies which were provided the needed support.

- Information and guidance was provided to the State Government on the precautions to be taken for minimising damage, including evacuation of people to safer places.
- Guidance was provided to the State Government on precautions to be observed by the public (such as keeping water and wet towels closeby) in the event of any gas leakage, and how to act if a leak did occur.
- With rumours abounding and anxiety everywhere, authentic information was regularly provided to the press and the public through government channels and regular meetings with the press.
- A close and constant vigil was kept of Tank 611 for any rise in temperature or pressure. All instrumentation and control systems in the relevant plant areas were checked and defective instruments replaced.
- A crack team of scientists was assembled and specific responsibilities assigned in the overall task of safe disposal of contents of tank 611. They operated round the clock, in shifts.
- The crisis was successfully and efficiently managed. The processing operations (Operation Faith) were started on the morning of 16th December and completed on 22 December 1984. A total of 21 tonnes of MIC (as against 15 tonnes estimated by the Union Carbide) in tank 611, one tonne from tank 619 and material from a number of stainless steel drums were reacted in one tonne batch lots at the rate of 3-4 tonnes each day. Union Carbide's Bhopal plant was relieved of all MIC and there was satisfaction everywhere.

Interfacing with other agencies and organisations

Right from the time CSIR took over the responsibility of activities in the Bhopal plant on 5 December 1984, virtually every organisation, private or public, which was in a position to support and assist the endeavours was consulted and associated. The Indian Council of Medical Research, the Indian Council of Agricultural Research, the Defence Research and Development Organisation, the Department of Science & Technology, the Department of Environment, the Ministry of Chemicals & Fertilizers, the Directorate General of Technical Development, Hindustan Organic Chemicals Ltd., Indian Petrochemicals Corporation Limited, Central Water and Air Pollution Control Board, Indian Meteorology Department, Bombay University Department of Chemical Technology, All India Institute of Medical Sciences, Bhabha Atomic Research Centre, Safdarjung Hospital and the Academy of Young Scientists were prominently involved in the follow-up action at Bhopal after the gas leakage. The nature of involvement ranged from consultation or expert advice to actual participation at the site, conducting experimental investigations and providing medical assistance and material support.

During the planning and implementation of Operation Faith close interaction was maintained with Union Carbide, the relevant departments of Madhya Pradesh Government, Cabinet Secretariat, Ministries of Home Affairs, Health & Family Welfare, Law and External Affairs, Air Force, Army, Navy and Border Security Force and the media. The cooperation extended by these organisations enabled efficient and successful implementation of the task undertaken by CSIR.

Scientific studies on the factors related to Bhopal toxic gas leakage

Although the crisis was successfully managed there remained a good deal of follow-up work. It was necessary to carry out a scientific study of the chemical nature and reactions of MIC, features

of the facilities and control for its manufacture, storage, utilization and disposal. Equally important was a thorough examination of the buried tank (610) and its chemical contents, as that alone would provide the basis for outlining the factors and circumstances which led to the violent chemical reaction and rapid leakage of toxic gas; in other words - reconstruction of the event. It was thus a two-pronged approach: simulating in the laboratory as closely as possible the chemical reactions that occurred in tank 610, and analysis of the residue thereof.

A report, "Report on scientific studies on the factors to the Bhopal toxic gas leakages", containing the results of the above work carried out under the direction of Dr. Varadarajan was submitted to both the Houses of the Parliament on 20 December 1985. A copy of the report is included in the volume.

Suing UCC: Technical inputs to the Indian case

Early in 1985 the Government of India decided to sue the Union Carbide Corporation of USA for damages, costs and appropriate relief. The case being technically-intensive, CSIR has been providing assistance to the Government of India on most technical aspects. Mention may be made of:

- Association of DG's nominee in the team sent to USA headed by the Law Secretary to select a competent American Law Firm from the panel shortlisted by the Attorney General of India (March 1985).
- Extensive discussions with Robins, Zelle, Larsen and Kaplan (RZLK) (the Law Firm selected) on the technical aspects of the case. In several rounds of discussions detailed presentations were made of MIC gas leak, the chemistry, the design aspects of the plant etc. The counts on which UCC was culpable were suggested to the Attorneys. They were suitably incorporated in the 'Complaint' of Union of India vs Union Carbide Corporation before the United States District Court, Southern District of New York.
- Active conferences and discussions with RZLK in regard to the technical points in the series of developments which followed, such as UCC' response to the complaint, Union of India's interrogations and requests for admission, answers and objections to Defendant's interrogations and such other legal documents.
- Public relations visits to meet eminent scientists in USA (to apprise them of the chemical and technological realities of the Bhopal tragedy)
- Assistance to the Department of Chemicals and Petrochemicals (as and when required) on technical aspects of the case.

The above functions were performed by G. Thyagarajan on behalf of CSIR.

It would be reasonable to say that CSIR has helped substantially in establishing the culpability of UCC on technical counts.

Dr. R.A. Mashelkar of NCL, Pune acted as Assessor to the Bhopal Inquiry Commission and NCL provided technical services as and when needed by the Commission.

Technical P R Campaign

A suggestion was made to the Government of India to mount a Technical Public Relations Campaign both in India and the USA. This was felt necessary since the media reporting appeared biased and inadequately informed about the chemical and technological realities of the Bhopal gas leak tragedy. A broad plan of action was also suggested.

The Government of India reacted favourably and constituted a Group in which CSIR was represented.

On CSIR's suggestion, Mr Wil Lepkowski, Senior Editor, Chemical and Engineering News, American Chemical Society, USA was invited to visit India to see some of the CSIR laboratories and selected chemical and petrochemical industries in the private as well as public sectors. The objective was to provide an opportunity for one of the most reputed professional journals in the world to get a first hand impression of the research and design engineering capabilities of Indian scientists as well as their ability to run chemical plants safely. The visit was handled by CSIR with excellent cooperation from the Department of Chemicals and Fertilizers, the Ministry of External Affairs, the Government of Madhya Pradesh, ICMR, Department of Environment, IPCL, HOC and the National Organic Chemical Industries Ltd. Mr. Lepkowski's lengthy article in Chemical and Engineering News of 2 December 1985 (first anniversary of the tragedy), reproduced here on the assumption the publishers will not have any objection to our doing so, reflected the Indian viewpoints and commented favourably on the scientific and technological talent and imagination of Indian scientists and engineers.

G. THYAGARAJAN
Director, CLRI, Madras.

BHOPAL

Indian city begins to heal but conflicts remain

WILL LEPKOWSKI, C&EN Washington

Bhopal one year later and the images stream back. The storage tank of methyl isocyanate (MIC)—41 metric tons of it—cooking within from reactions with contaminants. Molecules polymerizing, heat rising beyond 100, then 200 °C. The contents boiling to such frenzy that the tank's concrete casing shakes and cracks. Gases and liquids bursting through a rupture disk and relief valve, then surging through vent lines toward their final release through an overwhelmed scrubber.

Worker panic in the plant, a sleeping community outside as the gas begins to spread. Bodies roused, coughing, crying out, eyes burning and watering. Thousands running, staggering through the dusty streets and alleys, many clutching their babies, not knowing where to run to escape. Unconsciousness, injury, and death by the thousands. Pandemonium in the hospitals. By daybreak, the scene of silence around those left behind: fathers, mothers, children; cows, bulls, goats, dogs, all in final repose. A peace in its eeriness never more heart wrenching. The bodies disposed of by cremation and mass burials.

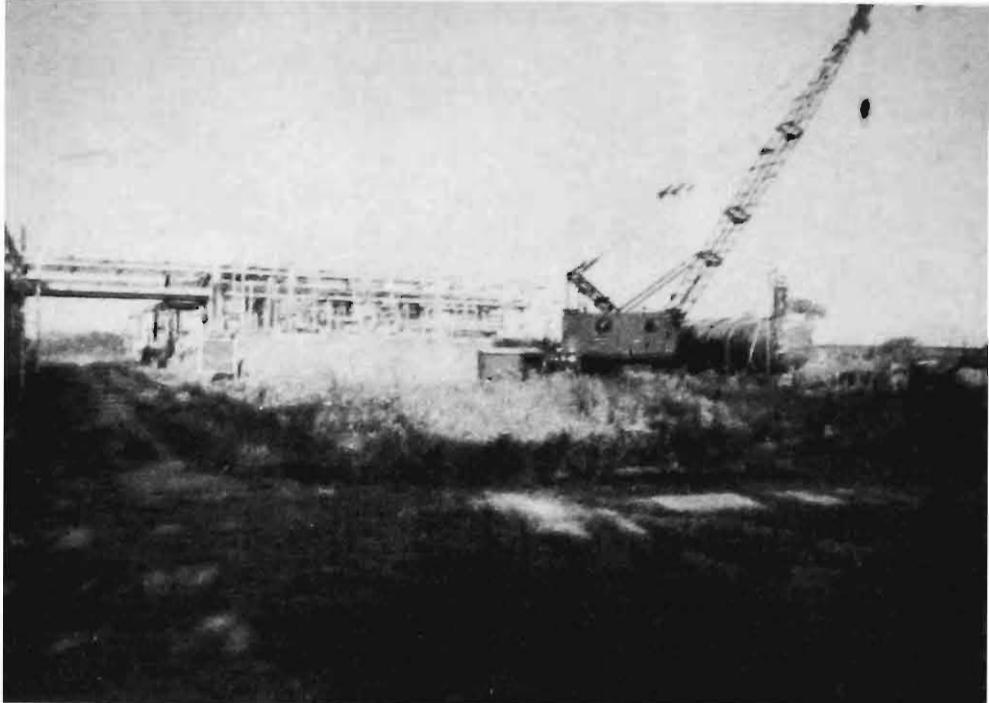
Then the local, national, and international responses. Medical supplies flown in. A planeload from the U.S. ordered back by Indian officials already thinking of compensation battles ahead. The sudden incarceration of Union Carbide officers who arrive to offer help. The dispute over the presence of cyanide in the gases. The invasion of U.S. lawyers. The overwhelming outpouring of local help. Schoolchildren, boy and girl scouts, bankers, merchants, the elderly—all transformed to paramedics and performing heroically. The visits by Prime Minister Rajiv Gandhi and Mother Theresa.

The tense, circuslike atmosphere of Dec. 16—"Operation Faith" day—when the remaining MIC in an adjoining tank is converted to its final insecticide product, Sevin. The nine-month investigation by India's Central Bureau of Investigation. The now-suspended criminal investigation by a state commission.

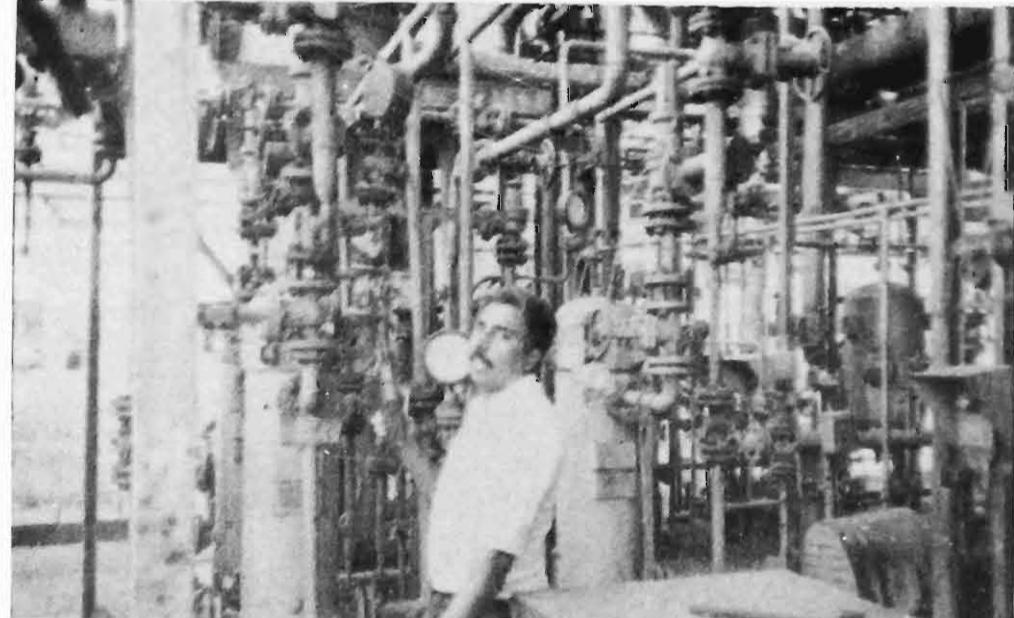
Today, Bhopal is a hotbed of unrest, reform, and rebuilding as it struggles toward a future. Mass demonstrations and memorial events are scheduled this month in commemoration of the first anniversary of the disaster. A repentant Union Carbide India Ltd. has prepared a press kit outlining its program of various relief measures. The Poison Gas Struggle Front (known by the Hindi word "morcha"), an infuriating goad to the local establishment, is staging a mass march demanding that Carbide be punished and ejected from India. The government of Madhya Pradesh—the state of which Bhopal is the capital—has scheduled a symposium with an international cast of writers and artists commissioned to deliver eulogies. Over the past year documentaries have been prepared, poems written, plays performed, paintings shown. Posters showing the misuse of technology have been circulated to science classes in schools throughout the state. In New Delhi an international symposium is being held that will announce to a world kept in the dark thus far the results of Indian investigations of the tragedy's medical effects.

Memorials, too, are being planned. One will be a research center designed along the program lines of the center in Hiroshima, which for 40 years has been following the condition of the atomic bomb victims and their progeny. Another will be attached to a Madhya Pradesh Institute of Disaster Management,

Four theories have been advanced on how water may have entered MIC storage tank



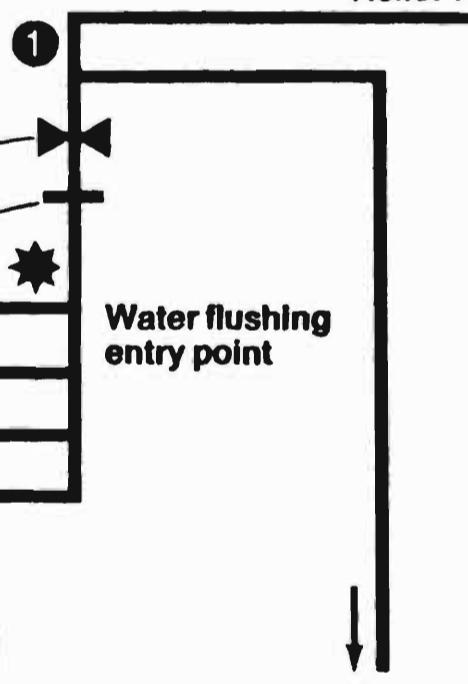
**MIC storage area viewed from MIC production unit
(tank 610 shown above ground)**



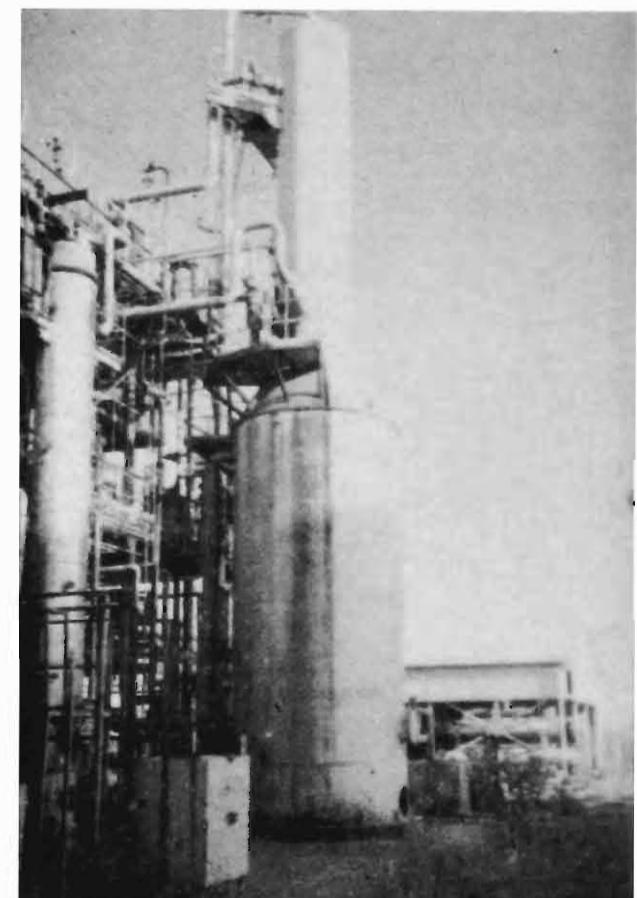
① A worker flushing out 2-inch pressure safety valve lines on the evening of Dec. 2 could have failed to insert a slip blind (a disk-shaped barrier) and thus allowed water to flow through a leaky, supposedly closed valve into an 8-inch line. The water moved through this line about 600 feet and then through a jumper line into the process vent line, which led directly to the storage tank

② Water could have entered at some point in the nitrogen line near the tank

Relief valve vent header line



Vent gas scrubber
where gases escaped



Area of pressure
safety valve
lines near MIC
production unit

expected to be an international magnet for experts in that field. A Bhopal disaster museum connected to Bhopal's stylistic art center, Bharat Bhavan, is in the works. Plans are under way to make the Gandhi Medi-

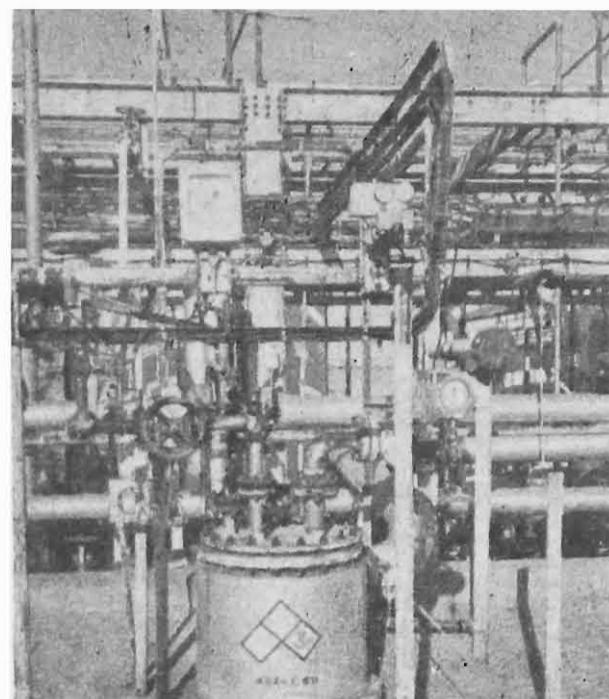
cal College a top-grade research center with particular strength in industrial pathology.

On the surface Bhopal remains today as it was before the calamity: a buzz of open air markets,

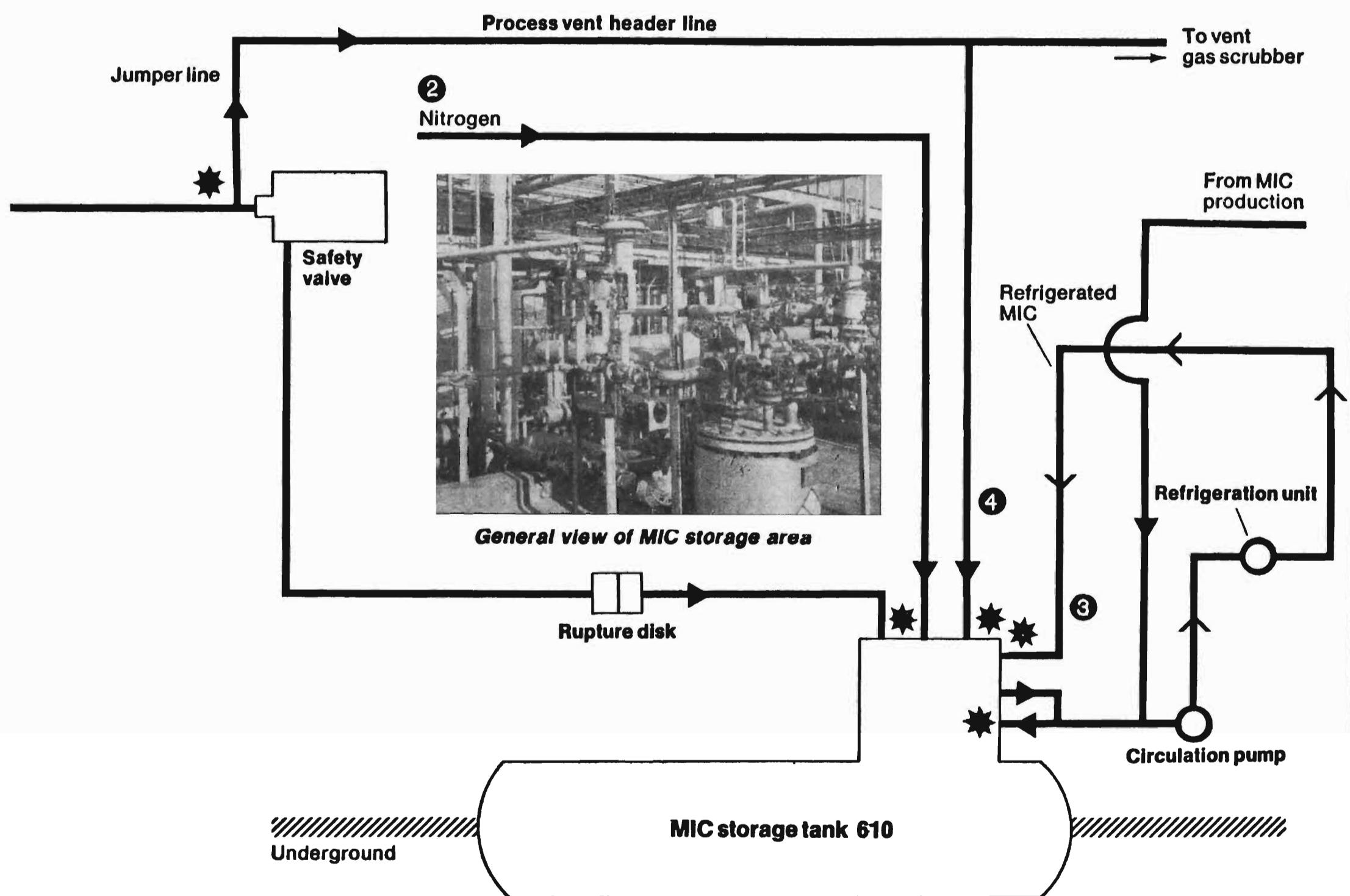
③ Water could have entered through the refrigeration line

④ Water could have entered directly through the process vent system

* Possible points of water entry



**MIC tank
611**



shops and human beings moving nonstop from dawn to hours past dusk. In one stricken area, signs of physical change stand out: a few television antennas on rooftops, new homes sturdier than the

shacks they replaced, drainage canals in place, new paving on the pathways.

The city is no longer as stunned as it was a few months ago, though thousands are debilitated and

unable to work. Mental illness as a result of the accident is one of the most serious health problems. The official government death toll is around 1800. Doctors are willing to concede that another 500 to 1000 could have died unaccounted for during the first 24 hours. Official state government figures say 320,000 persons out of Bhopal's total population of about 1 million were affected in some way, about 14,000 "seriously." About \$2.3 million has been spent on cash payments to families who lost members in the tragedy.

It is difficult, however, to measure what level of help the city needs. Officials tick off assistance figures—cash payments to families with fatalities, numbers treated for lung fibrosis, estimates of stillbirths, pounds of rice and wheat distributed, rupees handed out, the 20,000 x-rays and 35,000 clinical tests performed at Hamidia Hospital, the 1775 beds available now to gas victims.

But the numbers mean little against the magnitude of the disaster, still incomprehensible today. In any of the 30 urban wards, chats with people that were affected by the gas always reveal some unmet need. "These days, everyone is a gas victim," quips one government official. As Bhopal's current mayor Deepchand Yavad indicates, one may as well assume everyone in Bhopal was gassed. But that's a politician talking. Bhopal's pistonlike vitality makes one question claims of any urban malaise there.

Medical care, especially for lung, eye, and intestinal damage, is readily available. Every day hundreds line up at volunteer clinics, mobile treatment centers, or government outpatient facilities around the city. But an issue of high controversy is the extent to which affected persons are being actively sought. Local medical officials say that 34,000 persons have been visited by doctors inquiring about any problems. Records are being kept on everyone being treated. But to critics that isn't enough. Too many victims, they believe, are being ignored.

So there are stories in Bhopal today, and stories within stories—about the cause of the disaster, the dazzling pastiche of short- and long-term health effects, the relief measures, the controversy over the presence of cyanide in victims' bodies, the behavior of Carbide during the early hours of the disaster, the tangled legal story, the state of morality and legality in a culture as contradictory as India's.

The cause: its engineering, its implications

After a year, little is known for certain about what caused the runaway reaction in tank 610 at the Bhopal plant. What is well known, of course, is that the MIC stored in it underwent a hydrolysis reaction that, in turn, triggered a series of heat-generating polymerizations, additions, and degradations.

The resulting pressure burst the tank's rupture disk, blasted through the pressure valve just above it, and

the gases surged about 600 feet along the 8-inch relief vent line, past various branch lines, and into the scrubber. They overwhelmed the scrubber's capacity (it was designed only to handle process vent gases, not runaway reactions from storage) and the gases escaped unneutralized.

The flare tower, also designed only for process vent products and moderate flows from the storage area, was shut down for repair. Since the plant was not producing MIC or anything else that night, it made little sense to operating personnel to keep the flare burning. Moreover, a system of pressurized sprinklers that would have formed a "water curtain" over the escaping gases was itself deficient. Water pressure turned out to be too low to reach the height of the escaping gas.

Essentially three theories prevail to explain how it happened. One is sabotage (or mischief) by the insertion of water or contaminants into one of the lines leading into the tank. Carbide says its studies indicate that up to 240 gal of water could have entered this way. No other explanation but one of deliberate intent makes sense, the company says. The vast majority of Indians scorn the sabotage theory.

A second theory involves the "missing slip blind," whereby a worker, ordered to wash out a series of 2-inch pressure-safety valve lines near the MIC production unit, forgot to insert a disk meant to prevent water from rising up into the main vent line, called the relief vent header. The water, the theory goes, flowed up the line toward the MIC storage area, passed into a jumper line connected to a process vent line that led directly into the tank. This is the theory that labor, environmental, and popular activists embrace because its source is workers who claim to know what happened.

The third theory is inadvertent contamination by combinations of rust, metallic ions, chloride ion, as little as a "cupful" of water, because of lax monitoring, sloppy maintenance, and inferior technology. Indian scientists doing their investigation tend toward this view and, believing it, are warning the U.S. that until Carbide itself fully understands what happened, it could happen again wherever MIC is stored.

As the UCIL production superintendent, S. P. Choudhary, told C&EN during a tour of the Bhopal plant last month, "We just didn't know that MIC could be that reactive." Choudhary, one of the UCIL management group facing criminal prosecution by the Madhya Pradesh government, rules out all theories that would account for process contamination of lines leading to tank 610. "We do not believe that a small amount of water would have caused this runaway chemical reaction," UCIL says in a statement.

Jackson B. Browning, the parent company's vice president for health, safety, and environmental affairs, adds that the small amount of heat generated by such a small input of water would have been absorbed by the bulk of the contents.

One particular sabotage theory, advanced by Carbide during Congressional hearings after the disaster, also has been ruled out by Choudhary. According to that scheme, the "saboteur" was supposed to have attached a water hose at the source of the nitrogen line that led to the tank and simply let the water run. That scenario has several holes. For one, the source of nitrogen was at least half a mile away from the tank, in an area owned by the company that supplied nitrogen to the Carbide plant. The pressure needed to reach the MIC tank, which itself was under positive pressure, however slight, would have been too great. More telling, though, is that investigations showed no trace of water in the nitrogen line after the accident.

The slip blind theory is also illogical, he says. The reason is that a valve a few inches up from where the slip blind was to have been placed was, records show, closed. Even if the valve leaked, he says, it is improbable that even small amounts of water would have risen about 12 feet to a line that widened to a diameter of 8 inches and then continued some 600 feet to a storage tank that not only was under pressure but, by that route, closed to entry of anything (both the pressure valve and rupture disk were closed tight).

But there was another way not mentioned by Choudhary, via that jumper line between the relief valve line and process vent line. This line, open or shut by valves—how many isn't clear—led directly to the tank. Everyone who has studied the accident agrees this could be a port of contaminant entry. Contaminants might have passed along the relief valve line, across the jumper line, into the process vent line, and into the tank. The scenario assumes a lot of valves that were not just leaky but open. A third option was the nitrogen line at the area of entry into the tank. A fourth involves lines that carried MIC out to a refrigeration unit and back into the tank.

So Choudhary says there is only one option left: "Someone deliberately did it. There are lots of places in any plant where with a simple tool you can detach a linkage and add a contaminant." And a source of water existed a few feet away from the tank. But one needs a motive. Carbide hasn't really supplied the motive, except for newspaper accounts of a radical Sikh group that claimed credit for the disaster. The problem is that the existence of such a group is yet to be verified nationally.

The view of Indian scientists involved in the government's investigation of the accident is that the answer lies in contamination from corrosion. They believe the accident was just that—an accident—but that it was avoidable, and that the fault lay with the parent company, Union Carbide Corp.

"We have proof," says an Indian close to the investigation, "that the process know-how and design provided by Carbide were defective. Any other company in India purchasing foreign technology would have raised questions of why large quantities of stored MIC were necessary. UCIL could have asked something like that. But in this case, here is a plant owned by

Carbide. The detailed design was Carbide's. Approval and acceptance of the mechanics and processing were done by Carbide before commissioning."

He goes on to itemize where the Bhopal plant design was deficient. "At the Institute plant, for example, there is an intermediate storage tank between the production and storage units. This is used for continuous sampling of the product. Second, the MIC storage tank in Bhopal was not equipped with safety instrumentation. Sound alarms and flashing lights go off if the pressure and temperature increase at Institute. There was no such warning system at the storage tank area in Bhopal. In addition, the chilling system was underdesigned. At the Institute plant, the storage tank itself has refrigeration coils. The Freon is circulated inside the tank. At Bhopal, the material was taken out and then returned. So the UCIL refrigeration system was underdesigned; the cooled MIC went right back into the tank, which was probably at ambient temperature most of the time. So it probably was never being chilled, even when the unit was on. I don't think the tank could have been cooled much below 15 °C."

Indian government laboratories are attempting to simulate the reactions that might have taken place, based on their own samplings of residues as their own check on Carbide's investigation. "We have taken samples of the tank's wall," says one source. "It's almost impossible to go in the tank now because it still contains highly lachrymating mixtures—trimers, dimers, isocyanates, dimethylurea, biuret."

S. Varadarajan, India's top scientist as director-general of the Indian Council of Scientific & Industrial Research, says he is worried about the safety of those working or living in the vicinity of MIC in the U.S. today. "I think that until the exact cause of the runaway reaction at Bhopal is explained," he says, "there should be a ban on shipments."

The medical results

One year after the disaster, Bhopal is one vast experimental ground of industrial toxicology. Every patient is in some sense a toxicological celebrity.

Figures on the total number who died are becoming less controversial by the month. Some activists are still holding out for a figure of up to 10,000, but their voices have quieted. Their claim has been that thousands of bodies were dumped by Army trucks anonymously in mass graves at sites some distance from the city. But no one has located any such graves and few families have come forward to register family losses beyond those reported months ago. So the term "more than 2000" is the best anyone can say. As it is, about 15 gas-exposed persons currently die every month in Bhopal, according to official state estimates. The figure is over and above the 250 or so normal monthly deaths in the colonies that were affected.

Medical studies are showing a bewildering array of physical and psychological problems among the affected. Children under 10, when asked to make drawings, inevitably put their crayons to crude depictions

of Carbide, gas, and death. Strange sores, susceptibility to tuberculosis, persistently lowered oxygen transport are some of the complications rendered by exposure to the gases.

Some patients are classic cases, such as Dropdi Bai, a 55-year-old woman who has been hospitalized with pulmonary problems ever since the first night. Bai is special, because she is one of the few gas victims of Bhopal who has been under surveillance ever since the leak. She is likely to remain in the MIC ward of Hamidia Hospital for a long time. K. S. Gaur, the physician who administers the ward, says her major pathology is bronchiolitis obliterans—blockage of her lungs air passages. She is being given cortisone to reduce inflammations. She arrived at the hospital in a coma and showed signs of cyanosis. Sodium thiosulfate, the standard antidote to cyanide exposure, was tried twice on her, Gaur says, but with no relief.

Most of the research and treatment in the ward, he says, involves the effect of MIC on the lungs and on lung function. Other studies include the psychiatric aspects, gastrointestinal complications (varied and common), and the long-term complications of drugs such as cortisone, sodium thiosulfate, and Levamisol. "Many symptoms," he says, "can be explained by immunological disturbances."

The Indian agency in charge of continuing biomedical research on the Bhopal tragedy is the Indian Council on Medical Research, headed by V. Ramalingaswami. Located in New Delhi, ICMR has spent \$2 million in research so far involving about 150 researchers. And gradually Ramalingaswami hopes most of the followup research and continuous monitoring will be done in Bhopal itself.

The most serious overt problems researchers are investigating involve the lungs, he says. "Whereas eye effects appear to be abating, lung problems are persisting. We're looking at the nature of the disturbances induced by MIC. For those who received moderate to high exposure of the gas, lung edema developed rapidly, and scarring of the alveoli is common. These changes also have made the patients susceptible to pneumonia.

"Extensive studies have shown," Ramalingaswami adds, "that patients have an obstructed as well as restrictive element." That is, they not only absorb less oxygen but breathe in less as well. The restrictive aspect could be due to muscle spasms that constrict and narrow the lumen.

"Lung damage is the most serious and most important of our efforts," he says. Bronchodilator drugs are the most common treatment, but if the causes of the lung problems are getting increasingly subtle, other forms of therapy may be needed, he says. Breathing therapy, for example, is just being started. And it turns out that instruction in yoga breathing techniques is the form of physiotherapy chosen. Researchers are saying there is no known technique more effective for expanding lung capacity.

Results of research on Bhopal victims by India's industrial toxicology center

Total studied:

508 males, 601 females

Age groups:

50%—10 to 35 years

17%—36 to 45 years

16%—under 15 years

9%—46 to 55 years

8%—over 56 years

Average monthly income:

300 rupees (\$25)

Distance from factory:

61% less than 2 km

31% 2 to 4 km

Chest x-rays performed:

903, of which 739 were normal, 164 abnormal

91 suggested definite pathology

48 showed changes attributed to MIC

Biochemical studies:

Glutathione level reduced

In 30%, indicating hampering of detoxification mechanism and impairment of redox potential of biological system

Immunological studies:

55% showed lower phagocytic ability

Chromosomal studies:

31% showed chromosomal aberrations

Lung function tests:

39% showed ventilatory impairment

Behavioral/psychological studies:

Difficulty in concentration was most common complaint. Also confusion, poor memory, headache, irritability, depression

The immunological aspect also could be involved in explaining some of the more subtle, restrictive aspects of the lung damage, he adds. One study involving Indian scientists and Meryl Karol, an immunotoxicologist from the University of Pittsburgh, turned up detection of circulating antibodies after animal exposure to MIC—now called the MIC-specific IGE antibody. "If one detects it in the patients, the finding could lead us to believe the obstructive element could be the consequence of this immunological change."

About 3000 pregnant women were exposed to the gases, according to Ramalingaswami, and miscarriages and stillbirths were frequent. In the first 20 weeks, 436 spontaneous abortions occurred out of 2600 pregnancies. The normal rate in Bhopal is 6 to 10%. "Malformations are still being studied, although doctors are not noticing any increase of obvious birth defects," he says. "The genetic and cancer aspects of the gassing are the biggest unknowns and will have to be followed for years."

Heart surgeon R. K. Bisarya, the Bhopal mayor at the time of the tragedy and now back in full-time medical practice, takes a dour view of the medical situation in the city.

"Long-term effects are showing up now," he says. "And they are much worse than I expected. I am happy about the condition of eyes, however. I thought we'd have thousands of people needing corneal transplants. I'm glad to see that few do. But the long-range effects are bad. People's vitality is continuing to decline. Many feel they are not going to survive. There is lots of colitis, diarrhea, ulcers. A lot of female

disorders. Lots of women delivered prematurely, though the fetuses were usually normal."

Bisarya thinks the state medical establishment made a serious mistake by not taking systematic records of the affected people from the very beginning. The focus was too much on treatment and not enough on the careful recording of symptoms.

"Also, I would have expected more involvement from American scientists and physicians," he adds. "Several people I know from Los Angeles said they were willing to come and spend a year or two. They needed government grants to do that. But the U.S. provided no such help."

"Legally, it would have been beneficial to have American scientists. If the case goes to court and our Indian scientists make a claim, Carbide will send in American scientists to rebut them. If we had Americans," says. "At that time there was a lot of pressure on the medical community. Whatever supplies we gave were not acknowledged in writing. Then came the controversy over cyanide. That led some people to believe that UCIL deliberately misled the medical community. I don't know what our doctors were telling people. But the accusation that UCIL withheld information on long-term effects does not make sense. The truth is that we were unable to communicate to them what they needed to know."

Volunteer health organizations are upset with the government because they feel Madhya Pradesh physicians continue to underplay the extent of damage to women. Rani Bang, a Bombay-based gynecologist, reported in March that of 55 studies of women, 94% developed gynecological diseases like leucorrhea, 79% pelvic inflammatory diseases, and 46% menstrual bleeding. "Lactation suppression, impotence in husbands, stillbirths, and abortions have been other effects," her report stated.

Says Anil Sadgopal, leader of the Bhopal Poison Gas Struggle Front: "We were unwilling from the very beginning to accept the ways government doctors were downplaying the extent of problems. On Dec. 27 Ishwar Dass, then health secretary, was declaring that only eyes and lungs were affected. The rest of the systems he said were normal. To us activists in the field, working with the injured, the statement was shocking. Our survey teams had established that almost every organ of the body was showing one or another affliction. Gynecological disorders in various forms were observed by our doctors. And they are still showing it now."

But although medical disputes continue, especially over cyanide toxicity, much of that strident period is past. N. R. Bhandari, superintendent of Hamidia Hospital, says women need reassurance as much as anything. He believes that publicity has been so intense around dangers to newborns that anxiety is common among pregnant women. Ultrasonic fetal monitors have helped calm some women. "When they see their living baby on the screen, they feel reassured," he says.

The relief efforts

Much of the agitation that has roiled Bhopal over the past year—riots, police beatings, storming of the state government's offices, a takeover by the morcha of the Carbide factory grounds—was in response to the slowness with which the Madhya Pradesh government was responding to the needs of the victims and to Carbide's unemployed workers. A superficial look at the gas-affected area, however, leads a visitor to conclude that significant changes are taking place.

Uniformed children sit attentively in one-room shacks that serve as schools. Little assistance centers dot the colony, one providing counseling services for women, another dispensing high-protein bread. Small shops are opening with money either given by the government or loaned to the villagers by, yes, UCIL. Some new homes, built solidly of stone, are seen, contrasting sharply with the crude tin and burlap shacks that still predominate. In one sense, the gas-affected people are the new elite of Bhopal. Some of those who never had it so bad now have never had it so good and are the object of envy by the rest of Bhopal's poor.

Down Berasia Road, which divides the colony from the UCIL plant, the government has opened cottage industry training centers. In one, more than 100 women, many widowed, work at sewing machines, turning out garments that the state will distribute in the remote villages of Madhya Pradesh. A knitting operation was opened in October. Last month a hosiery production unit got started. Men are being trained in new work, including television repair.

Dass, the Madhya Pradesh first secretary in charge of all relief operations, says the government has plans to build an export-oriented business that will produce fine products for the international market. Dass is a Ph.D.-holding organic chemist who long since has abandoned the lab for government service.

A person like him was needed, for through May, the situation was getting wildly out of hand in Bhopal. A drought was threatening the area's economy. Its chief minister, Arjun Singh, had left suddenly to take up duties as governor of Punjab. Because of the lack of leadership, relief measures were in chaos. Medical treatment and record keeping was a mess. The gas-affected people, led by the morcha, were demanding more medical, nutritional, financial, and community help. And the UCIL workers were getting restive by prospects of no work. May and June were marked by demonstrations and jailings of morcha and labor leaders, as the cyanide controversy began bursting into the headlines.

By May, the central government began intervening. The chief finance minister, V. P. Singh, the most powerful general policy figure in the Gandhi government, visited Bhopal and promised to break the financial logjam. At the same time, the state's new chief minister, Motalil Vora, began paying surprise visits to the affected colonies, meeting with people to hear their grievances.

Says Dass: "The morcha was dissatisfied with the way the scientific bureaucracy failed to convey information on anything important to the people. A motley crowd led by leftists came together and took a confrontational position.

"June 25 was the watershed. Since then they haven't been able to consolidate. When I took charge, I felt that once the people see what we are trying to do, the agitational scene will lose its relevance. Such organizations do have a role to play. I told the demonstrators to try to take over the wards and take up some concrete activities like comprehensive care."

Carbide is attempting to inject a permanent presence in Bhopal's rehabilitation efforts, and Dass says its efforts are always welcome. It is funneling some money in by anonymous means and has established a trust fund of about \$200,000, made up of contributions from Carbide's Indian and U.S. employees, to be used as a source of loans to survivors who want to start businesses. Clinics funded by UCIL are in operation. A leather products business has been started, funded by UCIL. The most ambitious project is a housing project that is currently going up.

The future of the plant site is still being determined. Carbide offered to make batteries there, or reopen the pesticide formulation plant. But the government would have none of that. Carbide has a 99-year lease on the site for industrial operations at a yearly rental of \$600 a year. It has no intention of giving up the land and probably will appeal any order to depart.

"We have all our buildings and plant on the site," says UCIL's Gokhale. "There is a sizable investment there." The future of the pesticide research lab on a hill overlooking Bhopal is also unclear. Morale is poor there. Several researchers have departed. The government has suspended its tax-exempt status. It could be nationalized, or closed.

Not everyone is satisfied with the relief schemes in Bhopal. Sadgopal's morcha continues to agitate for more input for the affected people. The Rashtriya Abhiyan Samiti, another of at least a dozen public interest groups that have settled in Bhopal since the disaster, is one of Dass' sharpest critics. The group calls Dass' rehabilitation scheme a "cruel joke" on the victims.

"Only the government and its experts can explain how an aerodrome, a railway station, a botanical garden, a boating facility, and a swimming pool are related to the rehabilitation of gas victims," it says in a statement. "The government has proposed an expenditure of [\$85 million] on such irrelevant schemes. There has been no attempt to satisfy the needs of the 80% worker population of the gas-affected areas employed as railway coolies, day laborers, bidi (cigarette) makers, tailors, petty businessmen, textile and paper mill workers, railway gangmen and peons, whose health, housing, and employment have been seriously affected."

J. P. Nagar is the showcase of the affected communities. But at other areas such as Kazi Camp and Railway Colony, off the official Bhopal gas tour, the pace of recovery seems slower, though government clinics and those run by various voluntary groups keep open house in all the colonies. At the Railway Colony, stories tell of residents there being forced to pay for their own treatment and care, including trips to Bombay for special care.

The relief story in Bhopal will be a source of continuing controversy for perhaps years.

Thiosulfate/cyanide issue is most controversial

The issue over whether many of the Bhopal victims were and still are exposed to some form of cyanide poisoning is the most controversial aspect of the tragedy, and the most politically explosive. Indeed, as one Gandhi Medical College physician observes, "The cyanide issue is more sociopolitical than scientific." In the beginning, Madhya Pradesh medical officials and Carbide physicians denied any possibility of cyanide exposure among the gas-affected victims. Yet, on Dec. 6, three days after the event, scientists of India's Air Pollution Control Board were detecting cyanide at the MIC storage tank area and 50 meters downwind. At about the same time, doctors at Bhopal's hospitals were treating victims for cyanide exposure. (The presence of cyanide at the tank site is an intriguing notion, since the leakage was almost exclusively reported to be at the scrubber.)

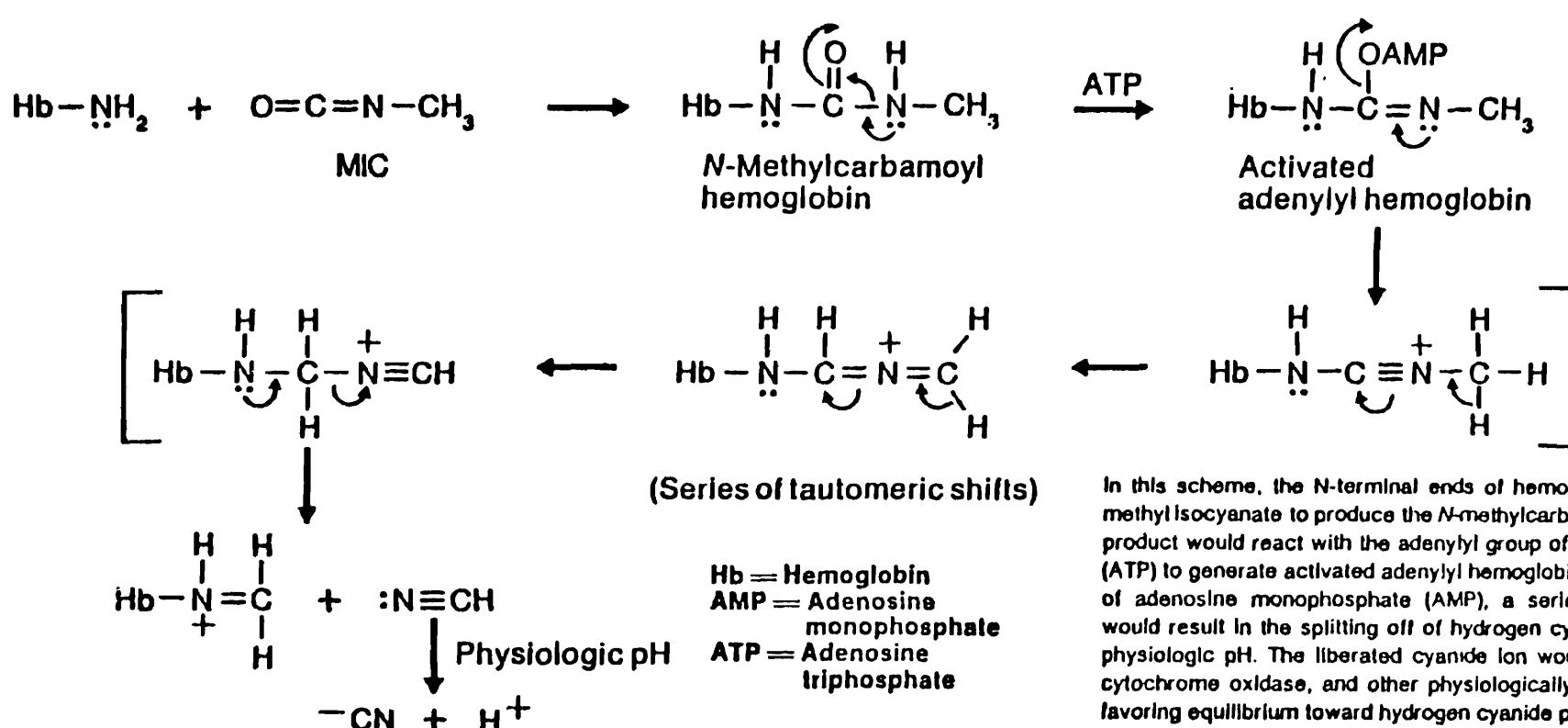
By February, the Indian Council of Medical Research finished its study of cyanide exposure and in a March report recommended continued sodium thiosulfate treatment. It said that, although there was no longer any direct exposure to cyanide, reactions involving the body's "cyanogen pool" and biochemical by-products of MIC could be accounting for the success of sodium thiosulfate treatment.

The report pointed to improved condition of treated patients and increased urinary concentrations of sodium thiocyanate after treatment, indicating the presence of cyanide in the system. Since sodium thiosulfate is a drug without appreciable side effects, the council said it would do no harm to continue treatment. Volunteer physicians were reporting permanent recovery in many cases from the treatment. But local doctors were by then opposing it, claiming that any positive results were due to psychosomatic responses. Patients, they said and say now, kept coming back for booster shots that really were doing no good.

"I feel that in the initial stages there was no doubt cyanide was present," says health services director Nagoo. "The toxin that was fixed to the tissues could well have been cyanide. But a year later it is difficult to believe cyanide is present and could be detoxified."

The issue has taken on fierce political and social overtones in Bhopal, causing riots, beatings, and jailing of both morcha demonstrators and volunteer physicians. At one point last summer, police under orders

Proposed mechanism for generation of cyanide in the body after exposure to MIC



In this scheme, the N-terminal ends of hemoglobin would react with methyl isocyanate to produce the N-methylcarbamoyl hemoglobin. That product would react with the adenylyl group of adenosine triphosphate (ATP) to generate activated adenylyl hemoglobin. Following elimination of adenosine monophosphate (AMP), a series of tautomeric shifts would result in the splitting off of hydrogen cyanide, which ionizes at physiologic pH. The liberated cyanide ion would bind to hemoglobin, cytochrome oxidase, and other physiologically critical enzymes, thus favoring equilibrium toward hydrogen cyanide production.

Source: Harold Teague, Pembroke State University

from Madhya Pradesh authorities, broke into thiosulfate dispensaries run by volunteer physicians, arrested them, and confiscated the thiosulfate supplies.

"The cyanide issue is important not merely for its biomedical/toxicological aspects," declares morcha leader Sadgopal, a biochemist who received a Ph.D. in 1968 from California Institute of Technology under James Bonner. "The real importance lies in the legal ramifications. To us it is important because a serious attempt would be made by Carbide lawyers to establish that a large portion of the lung damage can be explained by such things as endemic tuberculosis. It is at this point that the issue of cyanide toxicity would become crucial because if you can establish that so many thousands of people received clinical benefit from sodium thiosulfate injections and you have a clinical record, then you have established that they were suffering from cyanide or cyanide-like toxicity. If sodium thiosulfate gives relief, it is a specific antidote and its effect is shown by a specific chemical urine test for thiocyanate. High levels of it in urine would measure the amount of exposure."

What Sadgopal did manage to do, with the legal help of a Bombay activist lawyer, Indira Jaisingh, was to win an order by the chief justice of the Indian Supreme Court. The chief justice instructed the Madhya Pradesh government to allow the distribution of thiosulfate to volunteer groups, like the People's Medical Center, to continue their treatment. Sadgopal says his case was strengthened by Heeresh Chandra, chief pathologist at Gandhi Medical College in Bhopal. Chandra had been one of the first to detect symptoms of cyanide poisoning and to this day continues to insist that cyanide is still being generated in patients and that thiosulfate therapy is useful. What helped, too, were the March recommendations in favor of thiosulfate by Ramalingaswami's ICMR, which Madhya

Pradesh physicians refused to act upon. In a development last month, Sadgopal and Jaisingh also convinced the chief justice to appoint Sadgopal and forensic scientist Chandra to a seven-member committee with direct oversight over the entire clinical program in Bhopal.

The cyanide issue, scientifically speaking, appears to have two aspects. One is direct exposure, which could have occurred during the first hours in the areas closest to the plant. The technical book on this one is closed, although the mystery of why exposure was so vehemently denied by officialdom isn't. The second aspect is indirect exposure owing to unusual generation of toxic amounts of hydrogen cyanide in the body after exposure to MIC.

"The way the ICMR scientists have explained the mechanism of cyanide generation makes some sense," says biochemist Sadgopal. "That is the concept of the body's cyanogen pool generating cyanide-like radicals continuously in the bloodstream. When released, they could hook onto the hemoglobin, or to some other enzyme, or to cytochrome oxidase (a key respiratory enzyme). They could either block the respiratory system at the cellular level or modulate the behavior of the hemoglobin in releasing or carrying oxygen."

"Now, the sources that feed into the hypothetical cyanogen pool could be many. One possibility could be MIC linked to a peptide or amino acid, which is gradually hydrolyzed by enzyme action. Then MIC could be converted into thiosulfate by the transfer of sulfur from thiosulfate. Thiosulfate existing in equilibrium with thiocyanate is one possibility."

The scheme, though general, does make some hypothetical biochemical sense. MIC binds to hemoglobin in a carbamylation reaction. That binding was a common clinical observation at Bhopal. (The isocyanate-hemoglobin reaction is used to some advantage

clinically, too. It is a well-known treatment for sickle cell anemia, because the reaction converts the sickled hemoglobin to a more normal shape.)

A paper just submitted to the *Journal of Chemical Education* by organic chemist Harold Teague of Pembroke State University theorizes a series of reactions by which the MIC-hemoglobin combination could result in the generation of hydrogen cyanide. The reactions involve adenosine triphosphate and a series of electron shifts, resulting in the splitting off of hydrogen cyanide, which would then itself bind to hemoglobin. The success of thiosulfate therapy would then make some sense.

So scientifically, the cyanide issue is intriguing; politically it raises adrenaline levels; and legally it waits a final verdict as to its importance. Right now, it is no consideration in the current legal battle between Carbide and the government of India.

Chemical safety reform in Madhya Pradesh

If words alone are the criterion, Madhya Pradesh appears to be well along the way to cleaning up its industrial safety practices. In the aftermath of Bhopal, says Madhya Pradesh Labor Secretary S. C. Gupta, the first thing his department did was assemble a team of experts to undertake a quick survey of industries that handle chemicals in the state. The team surveyed 61 chemical units, found some deficiencies, and then suggested remedial measures.

"Another action was to give an assignment to Engineers of India Ltd., a design firm, to do safety audits of 11 industries engaged in the manufacture or use of chemicals," he says. "They inspected those units and gave interim reports and pinpointed the deficiencies that were detrimental to health and safety. We wanted to know whether they were detrimental to the health and safety of the workers and whether there could be dangers posed to localities.

"In another activity, the state has established a committee of senior secretaries to examine the question of setting down norms and procedures for ensuring the protection of villages situated in areas affected by the construction of pollution-prone industries. They have a large charter, covering steps for the approval of their operations on environmental grounds, criteria for site selection of major industrial complexes, and procedures for the regular inspection and certification of such facilities. The committee is also examining which parts of existing laws and regulations need to be modified or amended.

Gupta put together another team to examine the central government's Factories Act rules and regulations that directly relate to industrial health and safety. "We found certain lacunae," he reports. "If our inspectors were to find a certain deficiency in a unit, they had no power to suspend operations. There was also no penalty for failure to carry out the recommendations. So we are suggesting that inspectors be given the power to revoke or suspend until deficiencies are rectified. The current penalties are no deterrent. They

give three months to carry out improvements, plus a fine of only 2000 rupees."

The Factories Act does not obligate company management to keep communities informed of dangers, nor does it require preventive measures that could be taken. "Many of us did not know the UCIL factory could pose such a danger," Gupta says. "[Management] never mentioned anywhere whether any raw material was toxic. [It] had no obligation to tell us about any change in the process."

In New Delhi itself, reform of the Factories Act is under debate. The urge for reform certainly seems to exist in India, especially in the chemically developed areas around Bombay. The press is quick now to report leaks all over India. Each state has appointed independent inspection teams, trained in chemical engineering, to survey danger spots.

But although the Indian technical community is paying heed to the country's own deficiencies, it is also insisting that the West refrain from regarding the country as a technological backwater.

"Chemical accidents before and after Bhopal in the developed countries show that chemical technology is not necessarily managed more intelligently there," says chemist G. Thyagarajan, a Council of Scientific & Industrial Research laboratory director and head of the government's technical Bhopal investigation team. "Runaway reactions do not make a distinction between developing and developed countries. Did Flixborough [the 1974 chemical disaster in England] happen in a developing country? Did the Seveso poisonous gas leak occur in a poor developing country? Why did a toxic gas leak occur last August in a Union Carbide plant whose safety was said to have been beefed up by the spending of \$5 million?"

There is no lack of scientific and technological talent and imagination in India. Indian scientists point to the giant government-owned Indian Petrochemicals Ltd. (IPCL) complex at Baroda that licenses western technology, and the privately owned National Organic Chemicals India Ltd. (NOCIL) pesticide plant at rural Chiplun, south of Bombay. Managers in those plants all make the point of saying UCIL's operation at Bhopal was not representative of anything near what indigenous Indians can do. Discussions with Indian scientists, engineers, industrial management figures, bureaucrats, journalists, and activists all lead to that one point. The feeling is that Carbide bungled Bhopal badly. It was trying to push a product, Sevin, whose market potential in India was dwindling. It knew it, was hoping to sell off its Bhopal plant, and had virtually given up on it. The stage seemed set for disaster.

As far as the long-term effects of Bhopal on India's consciousness, even activists are pessimistic. Says Vijay Varma, a physicist at Delhi University, who is active in the reform of science education in Madhya Pradesh: "Bhopal happens and the general feeling is that it is an act of Providence, not likely to happen again. I think the West will learn from Bhopal more than we

Crucial court decision approaches in suits by Bhopal victims

It has been 10 months since most of the 119 lawsuits filed in the U.S. on behalf of individual Bhopal victims against Union Carbide were consolidated in the U.S. District Court for the Southern District in Manhattan. Nearly eight months have passed since the government of India sued Carbide in the same court, and more than four months have elapsed since Carbide moved to have the actions dismissed on the grounds that the U.S. was not the proper forum for the case. Now, with much of the preliminary legal work completed, the stage is set for a decision crucial to all parties.

On Jan. 3, 1986, attorneys for both sides will present oral arguments on the dismissal motion to federal judge John F. Keenan, who is presiding over the proceedings, in the Manhattan court. Judge Keenan's ruling on the dismissal motion could come on the same day or after a period of consideration. It is also possible, though not expected, that the judge could request additional information before issuing his ruling.

Whatever the timetable, the future course of the case in the U.S., and, probably, the tack of future settlement negotiations, hinges on the ruling. If the case remains in the U.S., Carbide could ultimately face American-scale damages, which are far higher than those generally awarded for personal injury in Indian courts. Therefore, legal experts believe, the company's bargaining position would be weakened and India could demand more money to settle its suit. On the other hand, a ruling for dismissal would strengthen Carbide's negotiation stance. Negotiations have been stalled, apparently awaiting the court ruling, since a reported \$300 million offer by Carbide

was turned down by the Indians last summer.

Key to the ruling is the judge's interpretation of the briefs and oral arguments in the light of *forum non conveniens*, a legal doctrine that can be used to determine whether the forum chosen by the plaintiffs is a suitable tribunal. Carbide's contention, under the doctrine, is that the actions should be moved to India because the disaster occurred there, the plaintiffs are all Indians living there, "essential" witnesses and evidence are located there, and many suits have been filed there. Underlying the company's point of view is its insistence that whatever liability may be involved should not include Union Carbide Corp., the parent firm, but only Union Carbide India Ltd. (UCIL), the company which operated the Bhopal plant and which is owned 50.9% by the parent firm.

Attorneys for the plaintiffs, on the other hand, have argued that the parent firm is responsible for the acts of its subsidiary. Acceptance of that premise, they contend, means many important witnesses and much crucial evidence on the design of the plant and control of its operation are located in the U.S. And that, they say, makes the U.S. court the proper one.

Because Carbide holds that the parent firm is not liable in the case, it wanted to shield itself from discovery inquiries until after the forum issue was decided. The plaintiffs, conversely, argued that since the liability of the parent firm was critical to their contention that the case should stay in the U.S., they needed a discovery period before final arguments on the dismissal motion were heard. Judge Keenan, looking for a middle road, allowed a limited discovery, under

which only interrogatories related directly to the forum issue were permitted.

Most of the information learned in discovery will not be made public until the briefs are filed, but Bud G. Holman, Carbide's chief attorney, says his side's inquiries uncovered "an enormous amount of information favorable to Union Carbide." He asserts, for instance, that involvement of Indian engineers in the design and construction of the Bhopal plant was greater than previously thought. Michael V. Ciresi of Robins, Zelle, Larson & Kaplan, the law firm representing India, declines to comment on what his side learned from discovery, citing a confidentiality order by the judge.

At the same time that the legal watershed grows nearer, Carbide seems to be increasingly emphasizing the theory that sabotage, rather than an inadvertent action, was responsible for the accident. Lawyer Holman admits he has no direct evidence of sabotage, but says that getting the water into the tank "was so improbably inadvertent that our conclusion is that it was deliberate." He adds that the plant library contained information that would have been useful to a saboteur and that it was open to most employees.

Ciresi scorns the sabotage theory as "the product of a runaway imagination. They have no facts to support it," he says, "and they know it."

If Judge Keenan rules in favor of Carbide on the forum issue, the plaintiffs will have the right to appeal. If the case is kept in the U.S., Ciresi says, the plaintiffs' attorneys will try to move it to trial quickly, with discovery cut off by the end of June, the summer for pretrial motions, and an opening trial date of Sept. 1, 1986.

David Webber, New York

will here. As long as the government is doing the enforcing, the process will be too corrupted. The only meaningful solution is for independent experts to take over enforcement."

Even activist Sadgopal has second thoughts. "It is amazing that we have not been able to explain the sociopolitical issues involved in the Bhopal tragedy even to the people of Bhopal—the role of the multinational, the kind of development model we

have chosen, in which the use of such pesticides and highly toxic materials is allowed, or the character of science and technology as practiced in the country, or the suppression of vital medical and scientific information by Carbide assisted by our government.

Gokhale is an especially dramatic figure, in some ways a character out of a Greek tragedy. He wants his fellow Indians to know that his company has made every effort to demonstrate that the Carbide family

cares very deeply about the plight of Bhopal's gas-affected survivors. Legally, he asserts blamelessness. He defends the management of the plant. Corporately, he stands together with the U.S. parent company. The trouble is that the parent isn't standing together with him. The managerial blame has been placed on UCIL by Carbide in Danbury. The parent firm believes that because mistakes were made in Bhopal, and because UCIL had full managerial responsibility, then the case should be shifted to India. "Fifty years of contributions to Indian society seem to have disappeared after this tragedy," Gokhale laments.

So although Carbide and UCIL both believe that the place of trial should be India, no one really wants a trial. All parties, except for various activist groups who want to punish Carbide, would prefer an out-of-court settlement. But that has complications, too, over

the worth of an Indian life. Indian government sources close to negotiations say India would accept something less than \$1 billion distributed by a formula that would ensure upfront costs and support to those suffering long-term pathologies. In addition, criminal charges against both companies would be dropped those sources say.

There is a continuing vastness to the subject of Bhopal, one year after the calamity that so rocked the conscience of the chemical industry. The lesson then, as now, is that another Bhopal cannot be allowed to happen. Safety audits are the order of the day, in India and in the rest of the world. Workshops and symposia on industrial and community safety are densely scheduled. The chemical world has learned, because industrial disasters—so enormously wasteful of money, human energy, and long-built reputations—do teach. □

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

MEASURES TAKEN AT BHOPAL

Introduction

The Director-General, Council of Scientific & Industrial Research, Dr. S. Varadarajan, had planned to visit the Regional Research Laboratory of CSIR at Bhopal on 5th December, 1984. He was asked by the Cabinet Secretary on 4th December to coordinate all scientific efforts at Bhopal in relation to situation following the leakage of toxic material on the early morning of Monday, the 3rd December, 1984.

Dr. Varadarajan and other scientists and technologists and officials from CSIR and other organisations were in Bhopal from 5th to 20th December. A list of those who were present in Bhopal at various times is given in Annexure I.

General Conditions in Bhopal

It was found that there were very considerable tragic consequences as a result of the leakage of toxic material and several deaths had been reported and many deaths continued to occur on 5th. There were also considerable worry about the safety of air and water. The factory work had been stopped and police had been posted. A case had been registered by the CBI against five officers of factory and who were also under arrest within the factory premises. Most of the factory workers were also not available. A large contingent of police occupied the factory premises. All the shops had been closed. Transport facilities were not readily available. Telecommunication facilities were extremely poor and had been disrupted. A large number of animals had also died. Disposal of the dead as well as the disposal of animal carcasses presented serious problems. With still many doubts about the toxic nature of water, air and foodstuffs, there was considerable fear among the public. A large numbers affected outside of Bhopal were being brought

to hospitals. The medical services were highly strained to meet this situation.

There were over 300 correspondents, 50 of whom were foreigners or representing foreign agencies and television teams were also present. They were also entering factory and hospitals freely.

Prior to his departure from Delhi, on 4th Dec. Dr. Varadarajan arranged for scientific teams from National Environmental Engineering Research Institute (NEERI), Nagpur, Industrial Toxicology Research Centre (ITRC), Lucknow the National Institute of Occupational Health (NIOH) of ICMR, Ahmedabad, to arrive in Bhopal on 5th December, 1984. A Central Coordinating Cell was set up on 5th at RRL, Bhopal headed by Professor P.K. Rohtagi Director of the Laboratory. Appropriate analytical and testing facilities and transport were arranged for scientists who arrived. Accommodation was also arranged for the large number of scientists and technologists arriving in Bhopal.

Following a meeting with the Chief Minister, Mr. Arjun Singh, State Government officials and Mr. Vasant Sathe, Minister for Chemicals & Fertilisers on the 5th morning, Dr. Varadarajan accompanied Mr. Sathe to the factory and had discussions with the Factory Manager and also accompanied Mr. Sathe to inspect the location of the MIC plant, MIC underground tanks, storage area and plant control room. Subsequent to the departure of Mr. Sathe, further discussions were also held with the Factory Manager and the Assistant Manager and it was found for the first time that a further 15 tonnes of MIC was present in the second tank No. 611 and this could also be involved in a further release of toxic material at any time. This further posed a new hazard to a large number of visitors, police and civil officials in the factory and in the vicinity outside the factory as well as to

general public especially as the risk of this materials was not known to them. The general public had also no knowledge of what precautions are to be observed in the event of further leakage of toxic material.

Action Taken-

- The actions taken cover the following-
- i) Examination of the environment immediately to see whether toxic material was present,
 - ii) If so what further precautions should be taken and advice given to the State Government and through them to the public,
 - iii) Action to be taken to estimate the probability of further leakage of toxic material and if possible to prevent such an event;
 - iv) In the event of leakage occurring, precautions to be taken on minimising the damage to those present in the factory and to public outside including possibility of evacuation of population.
 - v) Actions on safe disposal of the remaining MIC and any other toxic material found in the factory;
 - vi) Immediate examination of post-mortem cases, animal carcasses as well as those affected otherwise so that full scientific observations could be made at this critical time for future examination.
 - viii) Coordination of all scientific efforts and arrangements for information release so that only authoritative data is given to press, to the State and Central Governments to avoid confusion and panic.

Notes on all these are recorded below-

(i) Safety of environment

Teams of scientists analysed air and water samples as well as material from various surfaces in the factory and outside and results showed that there was no further MIC in the air or in water and no detectable material on surfaces. The State Government was immediately advised on 5th evening accordingly and this

was broadcast on the radio and press notes were also released.

(ii) Precautions to be taken

The people were advised that there was no danger in the air. Water could also be used preferably with the usual precaution of boiling the water as there was some possibility of communicable diseases such as cholera and plague spreading from undisposed bodies and carcasses. Public were also advised that they should wash all foodstuffs or boil them in water. This is because MIC reacts readily with water especially with warm water and it is converted to harmless material. Through these measures the public confidence in the environment was restored. These precautions were repeated for several days and public fears were allayed on consequences from further leakages.

(iii) Estimating the probability of further leakage

Discussions held at the factory on the morning of 5th December showed that there are three stainless steel tanks each of about 60 tonnes capacity. All pipeline connections for filling tanks with MIC from the distillation column of MIC, the pipelines for removal of MIC to reaction vessels or for filling in steel drums, the pipeline for pressurising with nitrogen, the outlet from safety valves to alkali scrubber, were all through a common system. It was also found that tank 610 from which the toxic material leaked and the tank 611 in which further material was present were both filled with varying quantities of MIC during the production of MIC and material produced upto 22nd October had been stored in both these tanks and the filling was done through common pipelines. Material from either of the tanks was taken out from time to time for further processing upto 2nd December. Thus, there was no reason to suspect the quality of the remaining material in tank 611 estimated at 15 tonnes by factory management to be any different from the quality of the material that had been stored in tank 610 and from which toxic material was released on the night of 2nd Dec. There was, therefore, no reason to believe that the hazard in material in tank 611 was any different from the hazards which had already taken place from the material from tank 610. Thus the high risk of further release of toxic material was confirmed by 11.30 hours on 5th December, It was

also confirmed that the alkali scrubber was designed to feed liquid MIC into liquid alkali solution for destruction. If gaseous emissions occur, the alkali scrubber would not at all be adequate to neutralise the material and the gas would leak out. It was also noted that MIC is a liquid under normal room conditions as it has a boiling point of 39°C. The temperature in the tank could be measured only in the portion above the liquid level and it was about 18°C. However, it was stated that the temperatures in the tanks 610 was noted at about 18°C at 2345 hrs. on 2nd December by an operator before a shift change which occurred before 0000 hours. However, the new shift operator noticed the pressure rise from 2310 hours on 2nd December and very soon after gaseous materials leaked out and this leak continued from 2315 hours on 2nd December to about 0115 hours on 3rd December. The pressure release occurred obviously due to rupture of the disc designed to withstand pressure 40 lbs. per sq. inch (just about 2 1/2 atmosphere). The safety valve would have obviously opened. It was also found that the safety valve returned to place after the gas leaked when the pressure had fallen back.

In these circumstances it was noted that there was no opportunity for a slow rise in temperature and pressure in tank 610. It was not unlikely that a similar rapid rise in temperature would occur in tank 611 and there would be insufficient time for warning being given of the impending leakage. There may not be time to feed the liquid material in the alkali scrubber for destruction also.

It was revealed during the discussions with the Factory Manager that phosgene present to the extent of 200 or 300 parts per million in MIC acted as inhibitor for polymerisation. Analysis of MIC in the tank is not normally possible because there are no facilities for drawing out samples. The analyses are generally carried out by drawing samples from pipelines for delivering MIC into the tank or for withdrawing MIC for transfer to reaction vessels.

Based on these discussions and on the general knowledge of chemistry of MIC, it was surmised that the leakage of material could occur by substantial quantity of water reacting with MIC. This is an exothermic reaction. Reaction with a part of the material could raise the temperature well above the

30°C, the boiling point and the remaining MIC could evaporate as a gas rapidly. By calculations, it was noted that 4.5 tonnes of water would be needed to react with 45 tonnes of MIC present in tank 610. However, it was pointed out by Dr. Varadarajan that 1.5 tonnes of water could be sufficient to react with one-third of the MIC and the heat produced from such a reaction could be sufficient to evaporise the remaining 30 tonnes. The reaction of large quantities of water with MIC could produce Tri-methyl Biuret (TMB) or Di-Methyl Urea. (DMU).

An alternative to the reaction with large quantities of water was polymerisation of MIC. This produces a trimer or a linear polymer depending on the condition for polymerisation. The heat generated in such polymerisation would also allow a third of MIC to polymerise and at the same time evaporate the remaining MIC as a gas. The factory staff, was maintaining that polymerisation could not occur since analysis previously carried out of MIC had always indicated presence of phosgene varying from 200 to 1200 parts per million.

Since tank 610 had been put under the control of CBI and it was considered unwise and risky to attempt opening of the tank, for examination of the material, if any, present in tank 610. In these circumstances, it was not proven whether tank 610 contained any material and if any MIC remained in the tank or if any other material was present.

Dr. Varadarajan recorded these conclusions on the probable causes of gas leakage on a note prepared at 1255 hrs. on 5th December and a copy was handed over to the Factory Manager. It was therefore concluded that there was high risk of any further toxic material being leaked from tank 611. Steps were initiated to have two operators to watch the temperature recording instrument of tank 611 on a continuous shift basis and also to watch pressures so that in the event of any indication of change, warning alarm could be activated and possible steps taken to minimise damage which would undoubtedly be large under the conditions then prevailing.

Later in the evening of the same day discussions were held in the Union Carbide Research Centre, Bhopal with Managing Director Mr. Gokhale and Vice-President Mr. Kamdar

of the Company and with Dr. Srivastava, Director of Research and other Scientific staff of the Research Centre, Dr. Varadarajan asked for some samples drawn earlier in the factory pipelines of MIC were to be analysed in the factory as well as in the Research Centre. MIC was also converted by give Trimer and Linear Polymer. Infra red spectra of these were also recorded. Data on the heat of these reactions and specific heat of MIC and the boiling point of MIC under different pressure were also obtained from literature and reports. These enabled Dr. Varadarajan to establish clearly that the reaction of MIC with large quantities of water or by polymerisation as stated in the recorded note of that morning could result in a large quantity of MIC to become gas at a temperature of 60°C which would lead to rupture of the disc and release of gas. The analytical methods for determination of phosgene were also examined.

After further detailed discussions, the Union Carbide officials stated that a team of four scientists technologists and one occupational health scientist were arriving on 6th December in Bhopal from USA. It was also found that only the factory Manager and the Assistant Manager of Union Carbide India had any knowledge of MIC and its reactions. It was felt that the team proposed by Union Carbide Management was insufficient to provide adequate information and they were finally asked to arrange for a further set of specialists of Union Carbide, USA such as those from research and chemical operation Managers familiar with Bhopal plant and the USA plant to come immediately. This team arrived on 12th December.

Union Carbide were also persuaded to bring from Calcutta one Mr. Parikh who has been previously Assistant Manager in Bhopal.

Additional information was obtained from Union Carbide officials showed that MIC is highly toxic and pure MIC polymerises readily in the presence of iron, copper and other metal catalysts. Commercial MIC was stated to be safe. It was said phosgene is present as inhibitor of polymerisation. No specifications for commercial materials could be obtained. No information was also available from the Union Carbide on even the probable causes of the conditions leading to the leakage.

Further discussions were held with the Union Carbide, USA team on the night of 6th December, 1984. They could not provide any further information on the probable causes of the accident, or of any investigation on previous small accidents wit MIC.

Furthermore, the analytical procedure of Union Carbide determination of phosgene were re-examined by Dr. Varadarajan and he found this was based on conversion of phosgene to hydrogen chloride. On the morning of 7th December, Dr. Varadarajan came to the conclusion that a small quantity of water of the order of 1 kg entering the tank 610 could react first with phosgene present at ppm level and convert it to hydrogen chloride. Hydrogen chloride could itself initiate polymerisation. Chloride can also react with stainless steel and lead to iron impurity which again could cause polymerisation. Further discussions were held on the morning of 7th with the Factory Manager and Assistant Manager and a note was recorded on Dr. Varadarajan's suggestion that the release of toxic material contained in tank 610 was due to small quantities of water. It was established that such small quantities could come from Nitrogen gas obtained by direct pipelines from a neighbouring factory or also from tube and shell condenser used for distillation of MIC in the MIC plant. He was also able to establish by further analyses, that the analytical method employed by Union Carbide could not sufficiently and clearly distinguish between phosgene and hydrogen chloride. This was also confirmed by adding quantities of hydrogen chloride to MIC and estimating phosgene. It was found that at least a proportion of the added hydrogen chloride was reported as phosgene.

The note recorded was also handed over to Union Carbide Manager immediately. It was established by these theories and experiments that adequate amount of phosgene may not necessarily be present in MIC Tank 611 to act as inhibitor and there may also be chloride which could act as initiator of polymerisation. The risk of further reaction and release of toxic gas from tank 611 was therefore very real.

iv) Action for minimising damage due to further leakage-

Since it was clear that there was potential

risk of some further leakage, the State Government was immediately informed on 5th and again on 7th December of such a danger. They were also advised that personnel including police, not needed in the factory should be removed from the factory premises and entry to the factory should be severely restricted. All entries were from then on to be made by special passes issued by Dr. Varadarajan. These measures took 3 or 4 days to become fully effective. Scientists were posted in the factory under the control of Dr. Varadarajan to ensure observance of precautions.

In cooperation with Shri P.P. Nayyar, Secretary in the Cabinet Sectt. a number of measures were devised to educate the public. All precautions to be taken were noted and a note on 'Dos' and 'DO'NTs' was prepared and handed over to the State Government. State Government was also advised to remove to enclosed buildings and structures, personnel living in slums and open areas in the vicinity of the factory. Public were informed of the risks and were also advised to use wet towels in the event of any indication of further leakage so that MIC breathing could be through wet material and MIC could be retained and destroyed by contact with water. Personnel remaining in the factory were provided towels and water bottles. Arrangements were also made to obtain 100 gas masks from the Navy for use of persons remaining in the factory in the event of further leakage.

During the meeting in Delhi of the Cabinet Committee on Political Affairs during the early hours of (Sunday) 9th December, 1984 risks of further danger to leakage were explained by Dr. Varadarajan, and various measures for protection of the public were approved. In addition for containment of material within the factory immediately several measures were introduced. Arrangements were made to cut out portion of the high level pipeline outlet of the gas in the factory and weld additional pipeline so that the outlet could be brought into a frame structure which was surrounded by a large amount of cloth on all sides. The continuous spray of large inputs of water by special pipes and by fire hoses was maintained so that in the event of any MIC escape, it can first react with water. A set of helicopters and small aircraft were also brought in for spraying water and to neutralise the gas through large quantity of water if and when

any untoward event occurred. The factory area and surrounding areas were continuously sprayed with water. The factory compound was covered up to a practical height with special stands and wet cloth material.

In addition, a special Wireless Communication System was established between the Factory, the control room at the State Sectt. Another control room established in the BHEL Guest House. A Hot line between the BHEL Guest House to the office and residence of Cabinet Secretary at Delhi was also established. A 24 hour operation Communication Cell was established in CSIR Headquarters at New Delhi. A 'No Delay Demand Telephone Service' from Bhopal to other points was also established from the BHEL Guest House Control Room.

Additional BSF aircraft and helicopters were also made available by the Cabinet Sectt. for bringing personnel and material to Bhopal.

A Special Officer was appointed by the State Government at the BHEL Guest Room Control Room to coordinate communications and for attending to emergencies. A similar Cell was established with officers of the State Government at the Sectt. Control Room.

v) Action for Safe Disposal of Material of MIC:

The following alternatives were considered for safe disposal of MIC:

i) Removal of liquid MIC under pressure using nitrogen and dumping into a very large volume of water. No arrangements for larger quantity of water in a contained environment can be made. This was therefore not feasible.

ii) The transfer of liquid MIC to the liquid alkaline solution in the alkali scrubber:

While this could be carried out, it was found that MIC contained 1% or more of chloroform and this would react to product carbene. Even a tiny quantity of carbene produces an obnoxious odour. Larger quantities will produce very undesirable odour. This might create panic exodus and stampede in the population. This method of destroying MIC could be resorted to in

an emergency if the temperature and pressure in the tank increased at any time but it was decided not desirable if other alternatives could be found. Nevertheless adequate supply of alkali was arranged to be brought to the factory and stored for use. It was estimated that the disposal of MIC through alkali scrubber might involve an operation of 6 to 8 days.

iii) Conversion of MIC Carbaryl products by reaction of alpha Naphthol:

This was considered the best procedure as factory staff were trained for this operation and facilities including instrumentation were available. Arrangements were made to release alpha Naphthol impounded by Customs in Bombay (about 30 tonnes) and brought by a convoy of lorries with Police escort to Bhopal. Adequacy of supplies of solvent catalysts and other materials was ensured.

Union Carbide, USA team as well as the Chairman of Union Carbide, USA were urging the MIC material was stable and it should be processed immediately from 6th December onwards. Through a detailed study of all factors, Dr. Varadarajan came to the conclusion that the risk of untoward leakage existed at all times and processing of MIC would involve disturbance of the tank by supply of Nitrogen. In the event of sudden reaction, precautionary measures outlined in the earlier sections available before 10 days. The public also would not be adequately informed to take precautions. It was decided by Dr. Varadarajan that it would be better to institute a number of measures within the factory, in the immediate vicinity of the factory, and for the public at large before processing is started. It was agreed with the Chief Minister that notice of seventy two hours be given before processing commenced. A series of discussions were also held with the factory management as well as Union Carbide Corporation team on the relative risks involved in the starting of processing around 7th December or a few days later. As a result, it was possible to come to an unanimous conclusion that the least risk alternative was to process the MIC for conversion to Carbaryl from the morning of Sunday the 16th December, 1984.

Prior to that date, all precautionary measures mentioned in the earlier sections could be fully completed. It was decided that every action would have the approval of Dr. Varadarajan and the team of scientists and technologists assembled by him. It also provided an opportunity for informing the factory staff and arrange for their return, restoration of confidence and completion of further measures in the factory for operations.

A formal communication from Union Carbide, USA team was accordingly recorded on 12th December, 1984 and addressed to Dr. Varadarajan, fully agreeing with the measures proposed by him. Subsequently, the Chairman of Union Carbide, USA also sent a communication to Foreign Secretary withdrawing his earlier suggestion on starting processing on 6th December and fully endorsing the actions proposed by Dr. Varadarajan namely starting operations on 16th December.

Since it was felt that the ingress of small quantities of water and metal contamination could arise from inlets into tank 611 from connections to the reactor distillation unit and from the nitrogen supply. All existing pipeline connections were closed or removed. A new Nitrogen pipeline was established. Visits were made to the Nitrogen providing factory and analytical procedure for nitrogen Institute. In the pipeline system drying agents and filters were introduced to ensure high purity. All measures were recorded and instructions issued and changes were carried out under the supervision of Scientists team.

The information on starting of these operations was provided through a Broadcast by the Chief Minister on 12th December, 1984. Those who felt it was unsafe to stay, arranged to leave Bhopal and it is estimated about 80,000 persons left Bhopal but in an orderly manner. Additional trains and transport were arranged to facilitate movement. About 6,000 to 10,000 people who were living in open areas were provided shelter in Schools and other buildings by State Government.

Detailed information on the operations proposed was provided in a Press Conference by Dr. Varadarajan on 15th December, 1984 to about 300 Press Correspondents. Two parties of Press representatives of 25 persons each were

taken to the Factory under supervision and detailed measures deployed were exhibited so that full and correct information could be provided.

Operations started on the morning of 16th December and were completed on 22nd December, 1984. All instruments were replaced by no defect instruments. At one stage the addition of phosgene to the MIC in tank 611 was considered as a method of improving the stability and phosgene was brought in by helicopter from Bulsar. At this stage an additional team from USA arrived and they were not able to give any assurance that phosgene itself acted as an inhibitor for polymerisation. Although arrangements were made for purifying phosgene so that it is metal free and provision for adding this material with due precautions to the tank were made, on receiving information of uncertainty of this acting as an inhibitor, it was decided not to proceed with the addition of phosgene.

Immediately after 5th December, arrangements were also made to establish four weather monitoring stations with the cooperation of India Meteorological Department. Two hourly observations were made in the stations on temperature, wind velocity and wind direction. With this information, it was possible to know direction of wind and on the probability of inversions occurring. Inversions tend to contain any toxic material released for long periods. With information on wind direction, it was also possible to have a system for warning specific wards and areas in the city of Bhopal in the event of any untoward release of toxic material. The same system was used throughout the period of operations of conversion of MIC into carbaryl. In addition, a system of detection of MIC in air was established in the factory so that even small release of MIC could be detected. No MIC was found throughout this period.

At one stage there were reports from some investigators, not forming part of the team, that cyanide levels in air in excess of permissible limits were detected. A large investigation was carried out to see if this could be verified by using special tubes for detection of minute amount of cyanide, flown in from IPCL Baroda along with appropriate experts. Throughout the period, no cyanide was detected in the air. The liquid level indicator in tank 611 and the

empty tank 619 were not functioning and it was learnt that these were sealed by CBI. The estimates of MIC were made from the records provided by the factory management. However, after the first day operation on 16th December, it was possible to judge quickly from the gas pressure of tank 610 that the material present in tank 611 was in excess by about 4 tonnes. Adequate arrangements were made to ensure availability of alpha naphthol for conversion of the additional material. Similarly note was taken of the MIC material (about 1.2 tonnes) stored in sealed drums. Special arrangements were then instituted for drawing material from such drums. The tank 619 was also found to contain over 2 tonnes of material. This was also withdrawn and converted. The operations had therefore to be extended by about 2 days. About 3-4 tonnes could be processed each day. The transfer of MIC from tank was done during day light hours and conversion to carbaryl was carried out throughout the night. Representatives of Scientists' team were present throughout this operation day and night and operations for each transfer of material were approved by Dr. Varadarajan and the team. Trial reactions in the factory laboratory were carried out with material in tank 611, 619 and drums separately to ensure these materials would fully react with alpha naphthol. Transferring of bulk materials were approved after such trials in each case.

Throughout this period, adequate precautions for spraying water and for test flights of aircraft for sprays were continued. Special arrangements were also made at the airport for communications so that in the event of any leakage, aircraft could be brought in for action. The entry into the factory of personnel, material and vehicles was strictly controlled throughout this period. Reports on the progress of operations were made twice a day to the press during the initial three days and subsequently once a day. As the material in tanks was used up, the level of potential damage decreased and once all the tank material was utilised, it was possible to declare that the environment would be safe. As MIC was present only in 180 Kg. steel drums. Finally all pipelines were drained off of MIC and used during the entire period, the alkali scrubber was operated.

(vi) Assistance to health and medical authorities

Scientists from All India Instt. of Medical

Sciences, Patel Chest Institute and Indian Council of Medical Research visited and stayed for substantial periods in Bhopal. They visited hospitals and had discussions with the Director of Medical Services and the Heads of hospitals and were able to monitor the treatment given for heavy toxicity affecting lungs as well as to those whose eyes were effected. A wealth of information was obtained from observations as well as from the post mortem examinations. This will be of considerable value in future. Special assistance was also given for analysis of materials drawn from patients and also during post mortem examination.

A number of foreign medical personnel had also visited Bhopal and were offering advice. Discussions were also held with such medical scientists from Germany, USA, France and Scandinavian countries.

(vii) Collection of materials for future examination

Arrangements were made for collecting material from post mortem examination and organs and tissues have been preserved along with data on symptoms and conditions of patients before death. Additional material from animal carcasses has also been collected. The histories of patients and if the dead from whom collection of samples was made, has also been recorded so that the effects of MIC over a period of exposure could be examined. Later on, there were also certain delayed effects and return of patients and observations have been made on them.

Samples have also been collected of plant specimens, leaves etc. Observations have been made to see if any deterioration has not taken place. These materials are also being analysed by ICAR as well as CSIR Laboratories.

(viii) Coordination of efforts:

As mentioned earlier a Coordinating Cell for this purpose was set up in RRL, Bhopal where a meeting of all scientific groups were held at 1400 hours daily. Written reports were made by each group every day. These have been collected and oral reports were also made in such meetings. As a result some additional tasks were also given to scientific groups.

Special arrangements were also made to

have scientific groups from ICMR, Patel Chest Institute, AIIMS, National Institute of Nutrition, Indian Cancer Research Centre, Indian Agricultural Research Institute and other institutions of ICAR, the Defence Research Laboratories in addition to those from CSIR Laboratories. Visits by Director-General, ICMR, Additional Director-General, ICMR, Adviser (Biotechnology), Department of Science & Technology, Adviser (Chemicals) and other officials from Ministry of Chemicals and Fertilizers were also arranged. Extensive investigations were also conducted by the Additional Director-General, ICMR. Special arrangements were also made for reserving certain number of seats on IAC flights between Delhi and Bhopal and for the reception of personnel accommodation and transport. Laboratory facilities were also provided at RRL, Bhopal.

The various institutes were asked to make literature surveys regarding the toxic effects of MIC and related isocyanates and a large amount of material became available. In addition material has been received from international organisations and research institutes.

Throughout this period, the Scientists of CSIR carried out a large number of analyses in the factory and in the research centre of UCIL Bhopal. These analytical results proved useful in drawing up the course of action in the processing of MIC and in estimating the risk.

Towards the end of operations for conversion of MIC, it was decided to open the safety valve and the section connected to tank 610 after taking necessary precautions. A certain amount of solid material has been replaced. The original safety valve and the ruptured disc have been handed over to CBI. The material collected from this section has been subjected to preliminary investigation in CSIR Laboratories and in the IPCL Research Centre. From this, appears there is no TUB or TMB present. Most of the material consists of trimmer and there is some amount of volatiles. No DMU or TMB has been found. The examinations are being carried out and results of which are awaited. Analysis for trace metals has also been made and presence of metals has been recorded. Small quantity of material from inside the tank 610 has also been recovered for examination which is in progress. However immediately after these

efforts, in the case of petition filed by some citizens of Madhya Pradesh, the High Court ordered that tank 610 should not be opened and no further examination be made.

From the examination made so far it appears that the incident in tank 610 took place as a result of polymerisation and not due to the input of large quantities of water. It appears that there was rapid polymerisation of a portion of the material and the temperature may have risen over 100°C, possibly 150°C. This high pressure and temperature was obviously maintained in the tank after rupturing of disc and lifting off safety valve. This could be possible because of the pipeline leading to the alkali scrubber allowed only the outflow of the gaseous material at a certain rate and the tank maintained high temperature well over 100 degrees for more than 1 to 1½ hours. It appears some thermal cracking could have also occurred because of such high temperature. This could lead to conversion of MIC to polymer and some other products such as methylamine, ammonia and dimethylamine. A strong smell of ammonia and amones was noted from the solid samples found from the safety valve section. The trimer melts at these high temperature and could have volatalised and crystallised in the tube section of the safety valve. Further hypotheses of the actual occurrence has to await fuller recovery of the material in tank 610 and determination of the total quantity of such material left in the tank.

The High Court passed orders that three lots of 5 Kg. samples from tank 611 should be preserved. Scientific reports were supplied to the Court through the State Government stating that there are no facilities for storing such large quantities and it would be unsafe to store them in glass bottles or containers. Subsequently the High Court passed orders that 5 samples of 300 gms. each should be preserved for future examination. Although the risk is there, the orders have been complied with and the material has been stored in glass bottles with covers for holding the pressure. Such material can polymerise any time and can release gaseous MIC' Adequate precautions have been taken and staff have been warned about such a risk. The High Court appears to have passed an order that detailed examination of these samples should be made in the presence of two groups of scientists one from CSIR and one from Bhabha Atemic Research Centre and these

scientists should be named by Dr. Varadarajan. Detailed information is awaited.

Since the senior factory staff were under arrest and confined to factory premises, orders for start of operations could not be issued by them. They cooperated fully with the team of the Government despite these restrictions. It was necessary that the factory operations were carried out with senior factory staff acting on their own free will. The release of these staff on bail was requested by Dr. Varadarajan and a communication was sent to Chief Secretary. The Court then arranged the release of these staff for a limited period covering the time of operations for conversion of MIC. Although factory staff was reluctant to avail of bail under such restrictions but they were persuaded by Dr. Varadarajan to accept these conditions.

Constant communications were maintained with the Cabinet Secretary and other officials of the Central Government, State Government and the Chief Minister. A meeting was also held with Mr. Soares, a Congressman from USA and the officials of the U.S. Embassy in Delhi who visited Bhopal.

Since the Chairman of Union Carbide USA had been sending messages regarding the risk of remaining material and urging processing this material from 6th, it was arranged for the Foreign Secretary to send a message to the Chairman, Union Carbide of USA asking him to send specifications of material which could be considered safe and methods of analysis of such materials. He was also informed by the Foreign Secretary that in the opinion of Dr. Varadarajan there were high risks in processing materials from 6th and precaution could not be adequately ensured for minimising the risks within the factory and to the population in Bhopal who were unprepared for such risks. No reply was received regarding specifications or tests. However, Chairman, Union Carbide USA finally sent a message endorsing actions proposed for conversion of material from 16th.

Concluding remarks

These very large set of operations would not have been possible but for the large amount of interest and cooperation and series of measures taken by the Cabinet Secretary, Ministry of Chemicals and Fertilizers, Ministry of Home

Affairs, Ministry of Health, Ministry of Law and Ministry of External Affairs. In addition ready cooperation was obtained from scientists from laboratories of CSIR, ICMR, ICAR as well as from organisations such as IPCL Baroda, Hindustan Organic Chemicals, Rasayani and Indian Drugs and Pharmaceuticals. In addition distinguished scientists such as Professor M.M. Sharma of the University Department of Chemical Technology, Bombay and Professor A.S. Paintal, Vallabhbhai Patel Chest Institute, Delhi readily agreed to visit Bhopal and have discussions and give their advice. The State Government provided a great deal of help. The authorities of BHEL at Bhopal provided unstinted support for accommodation and other facilities in their guest house and for examination at hospitals. In addition the Air Force, Army, Navy and the BSF readily gave help in various ways. The Agricultural Pesticide Spraying Service was also called into operation. The senior staff of the factory of Union Carbide Ltd. at Bhopal

gave unstinted cooperation and worked continuously for very long periods and accepted the overall supervision of the scientific team. The scientists at the UCL Research Centre also gave help in carrying out a number of analyses.

Similarly the Headquarters' staff of CSIR also maintained communication links and co-ordinating efforts at Delhi and at Bhopal. Large efforts were made by the Scientists at RRL-Bhopal. The operations of this nature could not have been carried out without the willing and sustained efforts of all those mentioned and all thanks and gratitude are due to all of them.

(S. Varadarajan)
Director General, C.S.I.R.
& Secretary to the Government of India

New Delhi, the 9th January, 1985.

List of Scientists who participated in the follow-up actions at Bhopal after the UCIL accident in December, 1984.

**Council of Scientific & Industrial Research,
Rafi Marg, New Delhi.**

Dr. S. Varadarajan
Dr. Lata Singh
Shri M.V. Ramakrishnan

Regional REsearch Laboratory (CSIR), Bhopal

Prof. P.K. Rohatgi
Dr. M. Patel
Dr. C.B. Raju
Dr. A.K. Ray
Dr. (Mrs.) M. Maheswari
Mr. Amrit Phale
Mr. B. Kujur
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**REPORT ON SCIENTIFIC STUDIES
ON THE FACTORS RELATED TO
BHOPAL TOXIC GAS LEAKAGE**

DECEMBER, 1985

This Report results from Studies

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ABSTRACT

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

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

In order to determine the conditions of formation of the chemical entities found in the residue of tank 610, a large number of experiments on the transformation of MIC from tank 611 have been carried out in open and sealed containers at different temperatures. These include heating MIC alone or reacting it in presence of water, traces of ferric salts, and chloroform. The residues have been analysed in each case. It is shown that all products found in the residues of tank 610, with the exception of DMI, DIONE and methylated amines (MMA, DMA, TMA) are found when MIC is heated in stainless steel closed tubes to temperatures upto 200°C with water and trace amount of ferric chloride. The formation of others require temperatures above 200°C. DIONE is formed only when chloroform is present in the initial mixture. The composition of residue in these trials in closest to that found in the residue of tank 610, when the sealed tube reaction mixture has been heated to 220°C - 250°C. It has also been shown that DMU and TMB which are products of reaction of MIC with water below 200°C, can be transformed to MICT, DMI, DIONE and Methylated Amines in further reactions in which MIC, trace metal and chloroform are involved. From a study of these chemical transformations and quantities of products found in the residue in tank 610, it is possible to arrive at a total materials balance. It is thus estimated that 12,087 kilograms of MIC and 595 kilograms of chloroform reacted with 512 kilograms of water to produce the residue containing 6,964 kg. of MICT, 2,675 kg. CMI, 391 kg. DIONE, 161 kg. DMU, 117 kg. TMB, 191 kg. TMU, 246 kg. DMA, 129 kg. MMA and 423 kg. TMA as well as 177 kg. of chloride. This represents

in part the chloride and fully all other materials in the residue of tank 610. From the products found in the residue, the calculated amount of heats of chemical reactions and the extent of bulging of the exhumed tank, it is surmised that the temperature in the tank rose above 250°C at the time of the accident. It has been observed, in preliminary laboratory experiments that pure MIC made by a route which does not involve phosgene or chloroform, when subjected to heating 300°C produces small amounts of hydrogen cyanide. In the presence of chloroform, hydrogen cyanide formation is not found. Further experiments at higher temperatures are planned.

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

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

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

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

The presence of sodium at levels of 50 to 90 ppm in the samples from residues of tank 610 indicates ingress of some alkali, possibly derived from the Vent Gas Scrubber Accumulator. It is known that the tank 610 could not be pressurised with nitrogen at any time after 22 October, 1984. The contents of tank 610 were virtually at atmospheric pressure from that date providing opportunities for entry of metal contaminants. From a perusal of the reports of the events of the night of 2/3 December, 1984, it appears during the cleaning of choked filters with water in the Relief Valve Vent Header, such water, perhaps mixed with alkali from Vent Gas Scrubber Accumula-

tor, could have entered the non pressurised tank and may have carried some metallic contaminants from the carbon steel portions of header pipelines. The rapid rise in temperature necessitates onset of metal catalysed polymerisation and could not result from water alone. The presence of chloroform has no influence whatsoever in initiating or accelerating the run-away reactions. The quantum of leakage is related not to the quantum of water but to the amount of MIC stored in a single container. If 42 tonnes of MIC had been stored in 210 stainless steel drums instead of a single tank, leakage by reactions or spillage would be no more than one fifth of a tonne.

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

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

1.0 INTRODUCTION

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

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

1.1 The Bhopal Pesticides Plant

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

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

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

1.1.1 *MIC manufacturing process*

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

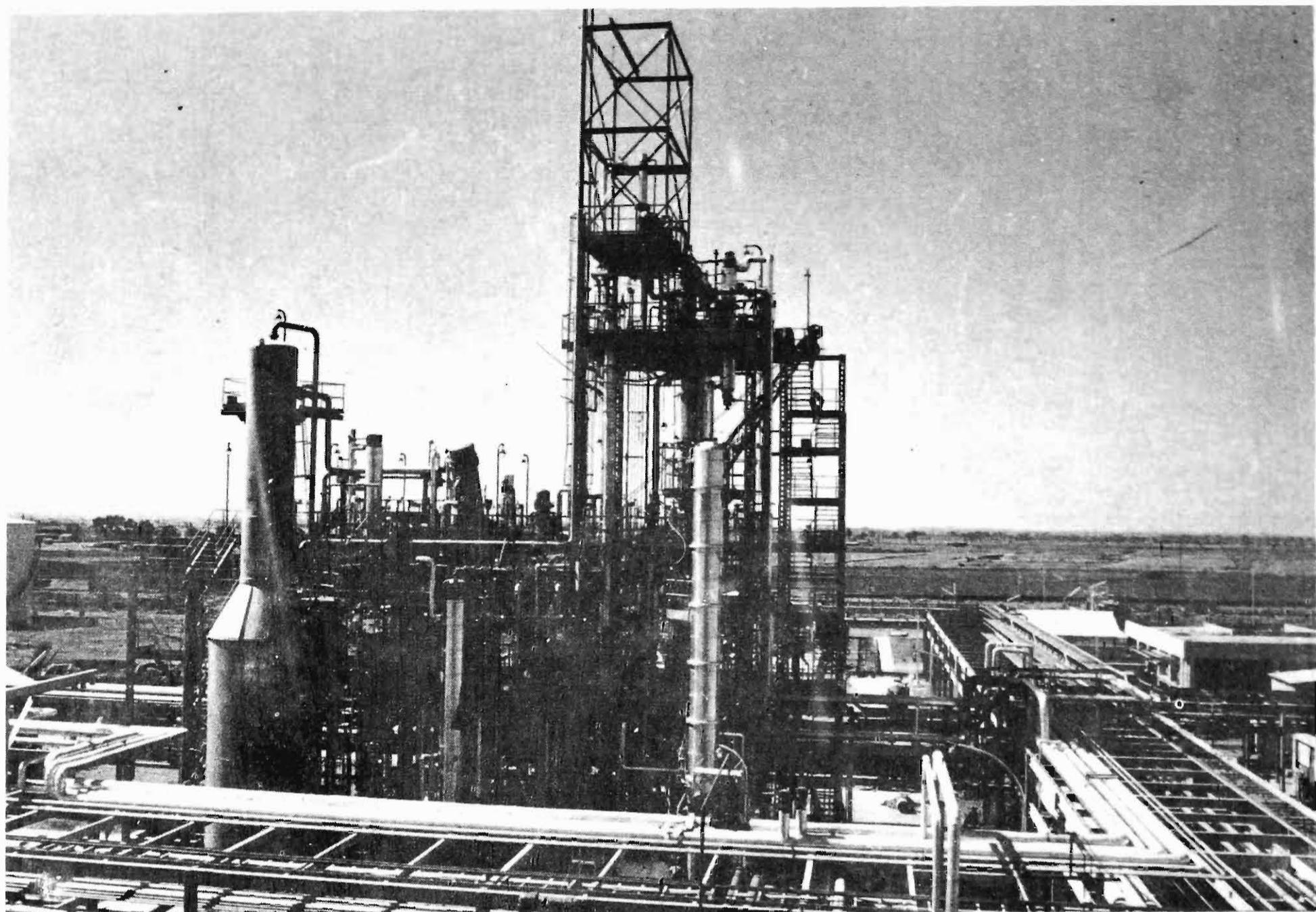
Phosgene is produced by reacting carbon monoxide and chlorine. Carbon monoxide is produced by reaction of petroleum coke with oxygen. Petroleum coke is obtained from an indigenous supplier, and oxygen is supplied from a neighbouring air separation plant. Chlorine, MMA, caustic lye and chloroform are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

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

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

1. $2C + O_2 \longrightarrow 2 CO$
2. $CO + Cl_2 \longrightarrow COCl_2$
3. $COCl_2 + CH_3NH_2 \longrightarrow CH_3NHCOCl + HCl$
4. $CH_3NHCOCl \longrightarrow CH_3NCO + HCl$

Phosgene and MMA are reacted in vapour phase to give MCC. The reaction products are then quenched in chloroform and fed to Phosgene Stripping Still (PSS). Unreacted phosgene is removed in PSS and recycled. The bottoms from PSS are fed to the pyrolyser where MCC is pyrolysed to give MIC and HCl and MIC and HCl are separated. The pyrolyser condenser feeds the MIC Refining Still (MRS). In MRS, the MIC is separated from the chloroform in the upper part and is led directly into the



MIC Plant

storage tanks. The bottoms of MRS are recycled to the process. The HCl formed is scrubbed with chloroform and extracted with water to produce aqueous HCl. Aqueous HCl is disposed off by neutralisation in a lime pit.

1.1.2 MIC storage system

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

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

The schematic layout of the three MIC storage tanks with common headers is shown

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

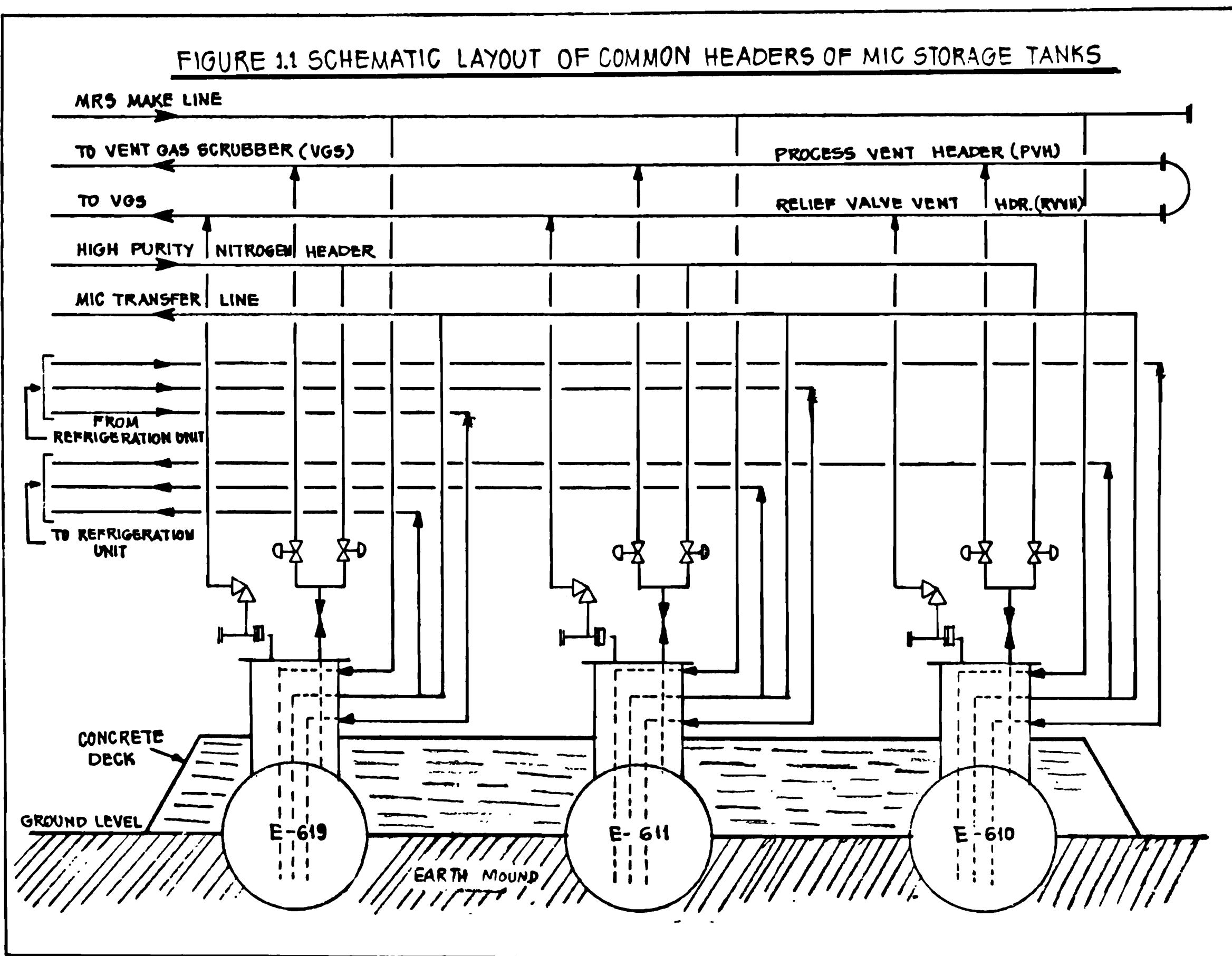
MIC is to be stored under high purity nitrogen pressure. The nitrogen is supplied to the storage tanks by a common header of carbon steel. Excess nitrogen from individual tanks is taken to a 50 mm (2") common Process Vent Header (PVH) of carbon steel. Similarly, the discharges from Safety Relief Valves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

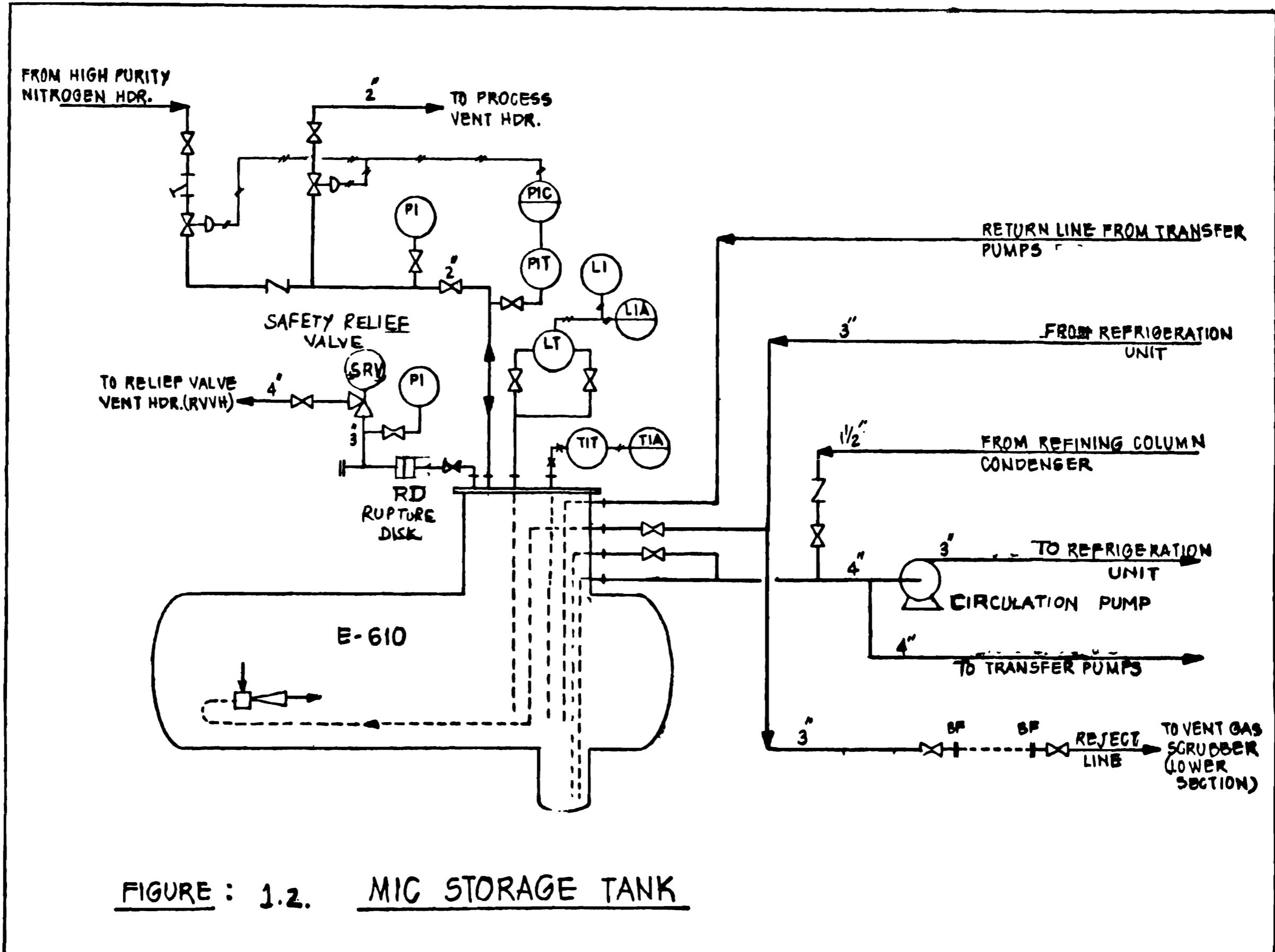
The transfer of MIC from the storage tanks to the Sevin unit is also through a common line.

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

MIC stored in the storage tanks is to be kept under an atmosphere of High Purity (HP) nitrogen. The recommended nitrogen pressure in the tanks is of the order of 1.0

FIGURE 1.1 SCHEMATIC LAYOUT OF COMMON HEADERS OF MIC STORAGE TANKS





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

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

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

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

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

1.1.3 Vent gas scrubber

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

and 2100 mm (7 feet) height. The third section comprises an accumulator, 3600 mm (12 feet) diameter and 6900 mm (23 feet) height. The capacity of the accumulator is about 80 m³ (21000 gal). The material of construction of VGS is carbon steel.

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

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

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

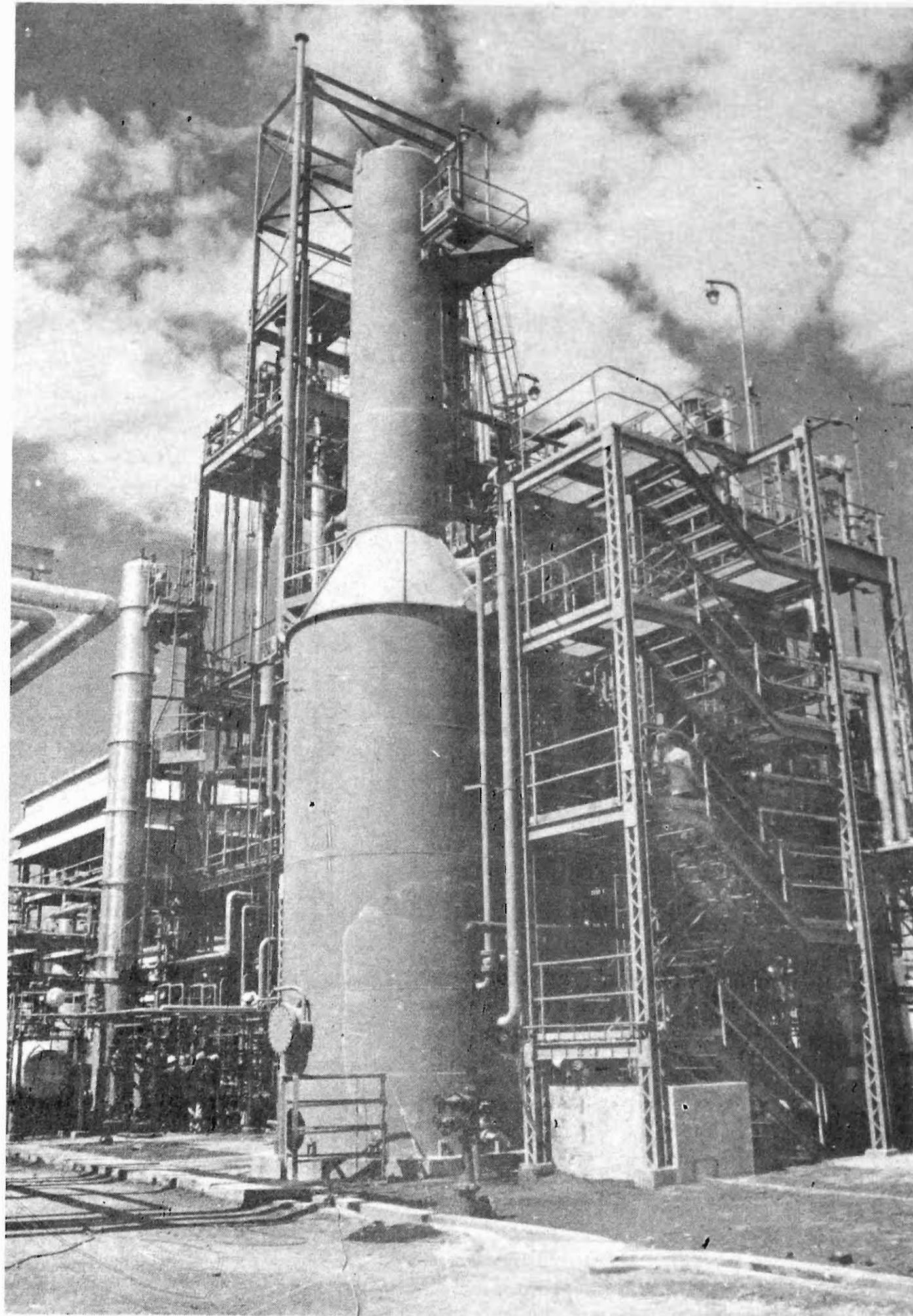
It is intended that off-specification liquid MIC from MIC storage tanks can be disposed off by neutralisation in the VGS accumulator at a controlled rate.

1.1.4 Flare tower

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

1.2 The Event

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



Vent Gas Scrubber

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

stored in tank 610. The production of MIC was stopped on 22nd October and at that time tank 610 contained approximately 42 tonnes of MIC. Tank 611 also contained MIC in quantities of the same order.

As per the operating practice, MIC in the storage tank was normally kept under nitrogen pressure of the order of $1 \text{ Kg/cm}^2\text{g}$. Reportedly till 21st October, the pressure in tank 610 was maintained at $1.25 \text{ kg/cm}^2\text{g}$. However, during the night shift (22.45 hours to 06.45 hours) of 21st/22nd October, nitrogen pressure in

tank 610 dropped to 0.25 kg/cm²g abnormally and the material in tank 610 continued to be under a low pressure of 0.1 - 0.25 kg/cm²g from 22nd October onwards. Recording of such low values is not an indication of any positive nitrogen pressure and denotes the tank contents were also nearly at atmospheric pressure.

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

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

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

On 2nd December, the first leak of MIC was noticed at 23.30 hours in the MIC structure area (MIC production facility) near VGS. The operators on the ground level in this area initially noticed some dirty water spilling from a higher level in the MIC structure. They also felt the presence of MIC in the atmosphere due to irritation of their eyes. They went up the stairs in the MIC structure and noticed that MIC and dirty water were coming out of a

branch of RVVH on the downstream side of regeneration gas cooler Pressure Safety Valve (PSV). They also noticed that the PSV had been removed and the open end of RVVH branch line was not blinded. Around 00.00 hours on 3rd December, the operators went to the control room and informed the plant superintendent and the supervisor that there was a MIC leak. They were advised to spray water around the point of leakage.

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

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

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

At this point, the operator rushed back to the control room and started the VGS circulation pump from the control room. He, however, observed that the flow indicator in the control room did not show any circulation of the caustic soda solution through VGS. In the meantime, a gaseous cloud was seen to be coming out from the stack by the field operator. Reportedly, the siren was sounded around 00.30 hours, and the plant personnel were alerted about the MIC leakage.

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

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

Gas that had escaped into the atmosphere got condensed in contact with the cold air and due to atmospheric inversion phenomenon, settled down slowly on the ground. It then evaporated and spread in the atmosphere gra-

dually due to low wind velocity, thereby affecting the population greatly.

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

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

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

1.3 'Operation Faith'

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

The teams made an examination of the environment immediately to ascertain if the presence of any isocyanate or other related materials could be detected in air water, or surfaces. They also recorded observations on any visible damages in the environment such as changes in green plants, trees, aquatic

life in the lake and the condition of animal and human population. Large number of people and animals had died by that time. Very large numbers of persons had serious irritation in eyes and breathing difficulties. The tests carried out did not show any presence of MIC or related toxic materials in the environment. Government authorities were advised accordingly. Public were advised to wash all vegetables and food articles with water and clean floors, walls and surfaces with water. These tests, collection of material and observations were continued in the next fortnight. Facilities for detection of specific toxic gaseous materials in a number of locations were established.

During the visit to the Union Carbide Plant on the morning of 5th December, 1984, the factory management provided Dr. Varadarajan a brief account of the gas leakage, the nature of facilities for storage of MIC and the associated controls. Visits to the MIC plant, storage area, the Sevin plant and VGS were made. At this stage, Dr. Varadarajan was informed that bulk quantities of MIC were stored in tanks E-610 and E-611 and the toxic gas leakage had taken place from tank E-610. It was estimated about 15 tonnes of MIC were present in tank E-611. The material in both tanks was from MIC production in October, 1984 and part of the material had been transferred from tank 610 to tank 611. It was also noted that many pipeline systems for input into the three tanks and output from these were connected to common headers. It was realised that the MIC in tank 611 could also lead at any time to a further release of toxic gases and therefore presented a serious potential hazard to large population, remaining factory staff, visitors, officials in the vicinity and to personnel providing relief and medical attention. They were not aware of this further hazard and they had no knowledge of the precautions to be observed in the event of another toxic gas leakage. The crisis warranted immediate measures and a new crisis management system, for the following:

- Estimating the probability of a further leakage.
- Analysis of circumstances that led to the leakage on 2/3 December, 1984.
- Devising means to prevent, if possible, a leakage from tank 611.

- In the event of leakage occurring, precautions to be taken for minimising the damage to those present in the factory and to the public outside through various measures, including large scale evacuation of the population.
- Safe disposal of the material in tank 611.
- Outlining of precautions to be observed within the factory and in the vicinity of the factory to neutralise any toxic gaseous material that might be emitted.
- Provision of information to the Government authorities on steps to be taken to minimise effects of such potential toxic gases.
- Provision of information on precautions to be observed by the public in the event of any gas leakage and quick dissemination of warning, if an imminent leakage is indicated.
- Provision of authentic information to the press and public continuously to avoid confusion and panic.
- Reliable communication systems.
- Mobilisation of experienced scientists, technologists for various activities.
- Institution and coordination of all scientific efforts and establishment of an organisation.
- Collection of samples, data for current needs and future studies on the nature of injuries and damage to life systems and environment, to allow for therapy, rehabilitation.

The first task, on the morning of 5th December, 1984 at the factory of Union Carbide was the estimation of probability of further leakage. Material from production was fed from a common MIC distillation unit directly, without any intermediate day or shift storage into the tanks 610 and 611 through a common pipeline. Similarly, nitrogen from a common header was supplied without storage through a pipeline to the tanks. There was no reason to believe that the hazard from material in tank 611 was in any way different from that in tank 610.

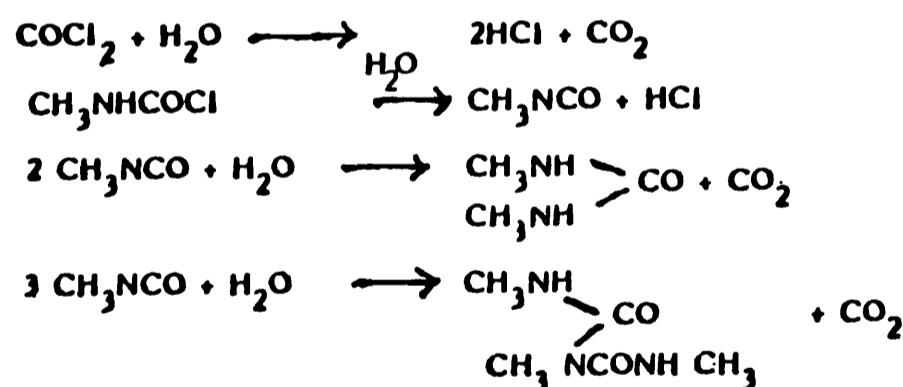
The rapid rise in temperature and pressure observed during the night of 2/3 December from tank 610 and the inadequacy of VGS to contain large releases, confirmed that any onset of reaction in material in tank 611 would lead to a rapid explosive release of toxic gases again and a repetition of the event of 2/3 December, 1984.

In the discussion on the morning of 5th December, 1984, between Dr. Varadarajan & Factory Management, it was concluded that MIC can react with water and the heat generated by reaction of about 40% of material would enable evaporation and expelling of remaining MIC as gas. About 1.5 to 2.5 tonnes of water would have been involved in the reaction in tank 610. Polymerisation or trimerisation of MIC could be initiated by traces of metal ions. In such an event, a third of the material undergoing reaction could produce sufficient heat to expel remaining material as gas. It was assumed at that time, following generation of heat by reaction with water or by catalysed polymerisation, temperature of liquid would rise to 80°C, the boiling point of MIC at 40 psig. The pressure generated by gaseous MIC as well as carbon dioxide, if any, would lead to a rupture of the graphite disc (RD) and lifting of the Safety Release Valve (SRV) and release of gas. Depending on the rate of reaction, there would be further release of gas. It was then assumed that the pipelines/ valves would have permitted free flow of gases without any obstruction through RVVH.

During further discussions on the evening of 5th December, a UCC brochure on MIC was made available, and it was stated that while pure MIC undergoes trimerisation, an exothermic reaction, without catalyst, commercial MIC of UCC does not. Phosgene present in MIC at a level of about 400 ppm acts as an inhibitor of such polymerisation and a minimum of 200 ppm of phosgene was required to ensure stability against polymerisation. These levels were prescribed by UCC in the specifications for control of quality of MIC. Phosgene was routinely estimated in MIC samples drawn from the outlet of MIC distillation unit leading to the MIC storage tanks. Such estimation of phosgene content was also made on each occasion when material from tanks was transferred to the Sevin unit. Phosgene was estimated by methods prescribed by UCC. This involved the addition of water to MIC, immediate liberation of hydro-

gen chloride from phosgene and estimation of the amount of hydrogen chloride by titration with alkali. A further modification involved addition of sodium iodide solution to MIC and estimation of iodine liberation by titration with sodium thiosulphate. The modified method was used only when abnormally high values for phosgene content were obtained.

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



From these, it appeared that relatively small amounts of water of the order of a few litres, entering 42 tonnes of MIC in tank 610, would allow all the phosgene and MCC present to react, giving HCl. Phosgene and MCC would be totally absent or reduced to low level below the minimum prescribed by Union Carbide to act as inhibitor of polymerisation. With a slight excess of water hydrochloric acid would be available and this may react with the material of the tank or with any small particle of metal which may have been present. This would produce ionisable metal chlorides. In the ab-

sence of the inhibitor, MIC could undergo polymerisation rapidly. Hydrochloric acid and metal chlorides may be expected to catalyse a violent and explosive polymerisation. The heat produced at any point, in the absence of inhibitor would promote a chain reaction, leading to a very rapid increase in temperature, vaporisation, increase in pressure and leakage of gas.

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

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

The measures introduced included of the following:

i. Ultimate safe disposal of MIC

To dispose MIC, four alternatives were considered. The first involved dumping liquid MIC into large quantities of water in a contained area near the factory. Such a facility could not be located. The reaction with cold water may take time and loss of vapour MIC into the atmosphere may not be precluded and hence this method was not practical and safe. The second envisaged dilution of MIC with carbon tetrachloride to act as a heat sink and subsequent feeding of the MIC carbon tetrachloride mixture into aqueous alkali in VGS. Carbon tetrachloride would settle in the bottom and displace alkali solution causing alkali to overflow. This was not therefore proceeded with. The third proposal was to feed liquid MIC into aqueous alkali in VGS. It was noted chloroform present in MIC would produce dichloro carbenes with highly obnoxious odour, the spread of which would create considerable

panic in the city. While such a procedure would be inevitable, in the event of any indication of onset of reaction and rise in temperature in tank 611, this was not preferred. The fourth method consisting of conversion of MIC to Sevin by reaction with alpha-naphthol was considered suitable, as staff were trained in this operation and facilities were available.

ii. Safeguards against entry of contaminants

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

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

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

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

Adequate large alkali supplies were mobilised to meet needs of neutralisation. It was realised that maximum contact with water

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

iv. Stabilisation of MIC

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

v. Disposal of MIC

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

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

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

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

iv. Since the possibility of reaction occurring in tank 611 existed, all steps have to be taken to ensure minimum damage as outlined earlier. Therefore, these steps had to be given priority and had to be completed before attempts to dispose off MIC in tank 611. These included operation of VGS, mobilisation of additional alkali supplies, erection of water curtains around the top gas outlet and around the factory perimeter, evacuation of people around the factory and those in open structures, education of the public on precautions and establishment of communication system and risk management control organisation. Additional safety equipments such as air breathing packs and helmets had to be procured. Water spray systems for extensive coverage had to be brought to position.

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

Based on these, it was decided not to embark on processing and disposal of MIC in tank 611 from 7th December, 1984, and post-

pone such operations to a later date, after all reviews, modifications and arrangements had been completed. All concerned, after full discussions, agreed with this approach.

For purposes of reaction of MIC with alpha-naphthol, a complete detailed system of organisation and review was established. Samples of alpha-naphthol and solvents were brought in. All systems were thoroughly checked and detailed written procedures were issued. Wireless communication systems were established for constant contact with control cells in the Factory and at the State Secretariat. Special communication tele-links and hot-lines with Delhi and other centres enabled the mobilisation of materials, equipment, personnel. A number of senior scientists and technologists from research organisations and major chemical manufacturing units were involved in review and checks and control of operations. Senior most officials of the Government of India and the Madhya Pradesh Government provided facilities and assistance for all these activities, and helped to restore calm and order in an environment, which exhibited constantly the acute distress of suffering of thousands of citizens. These measures motivated the staff of factories, transporters, public utilities and services to take up work in public interest within the potentially hazardous areas.

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

2.0 EXAMINATION OF TANK 610 AND ITS CONTENTS

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

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

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

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

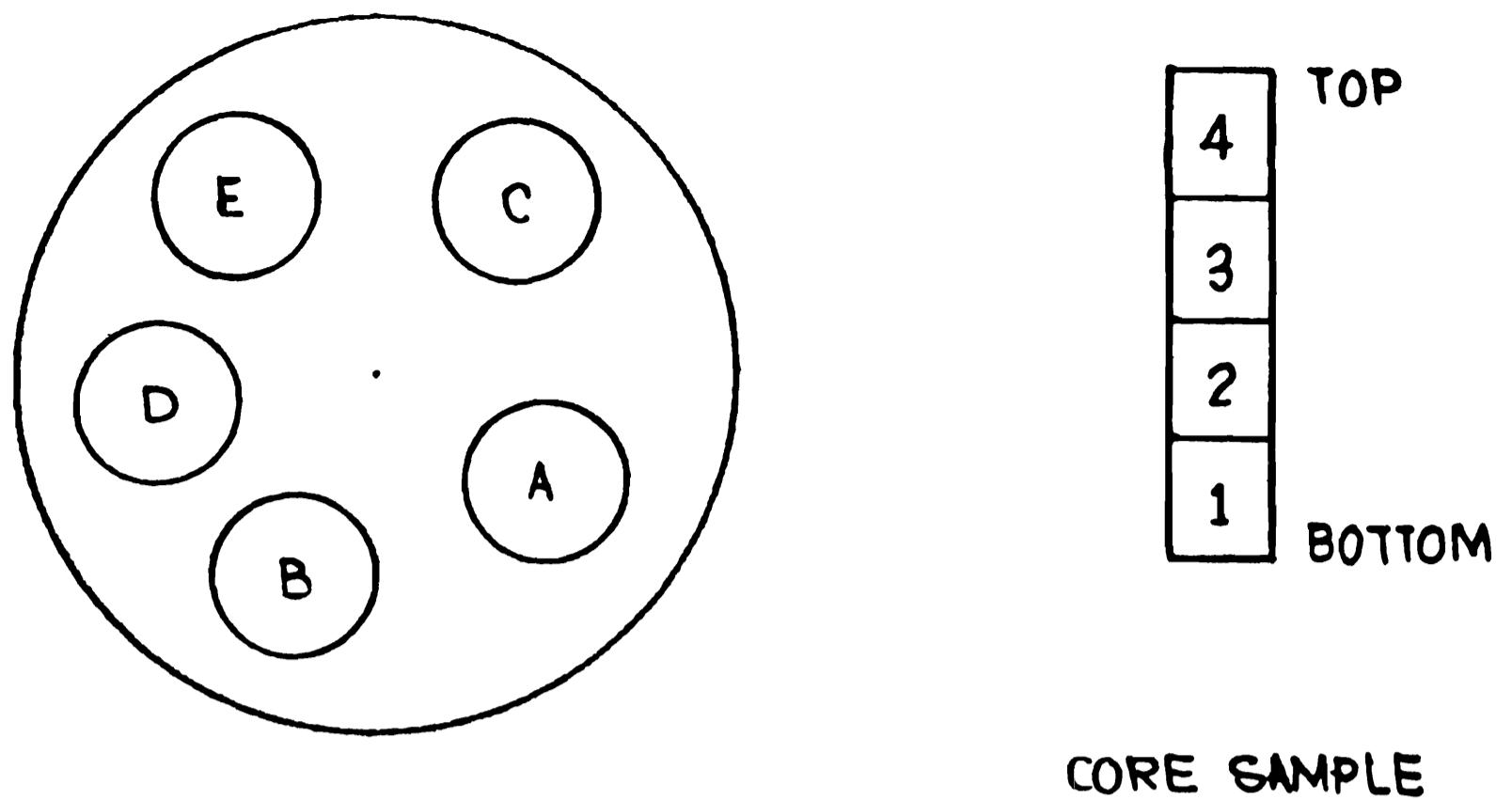
2.1. Sampling

2.1.1. *Core samples from the manhole nozzle:*

All the five nozzles located on the manhole cover were opened one after another and core samples were drawn (see Figure 2.1). A pipe 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 receiving identification number 1 of the respective series. Similarly, alphabets A to E were used for identifying the samples from different nozzles (see Figure 2.1).

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

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

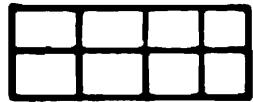


- A. SAFETY VALVE
- B. PROCESS VENT
- C. SPARE
- D. THERMOWELL
- E. LEVEL INDICATION

Fig. 2.1 Sample identification

SAMPLING SCHEDULE ON MIC TK E - 610

KEY:



SAMPLE NOS



WINDOW NOS

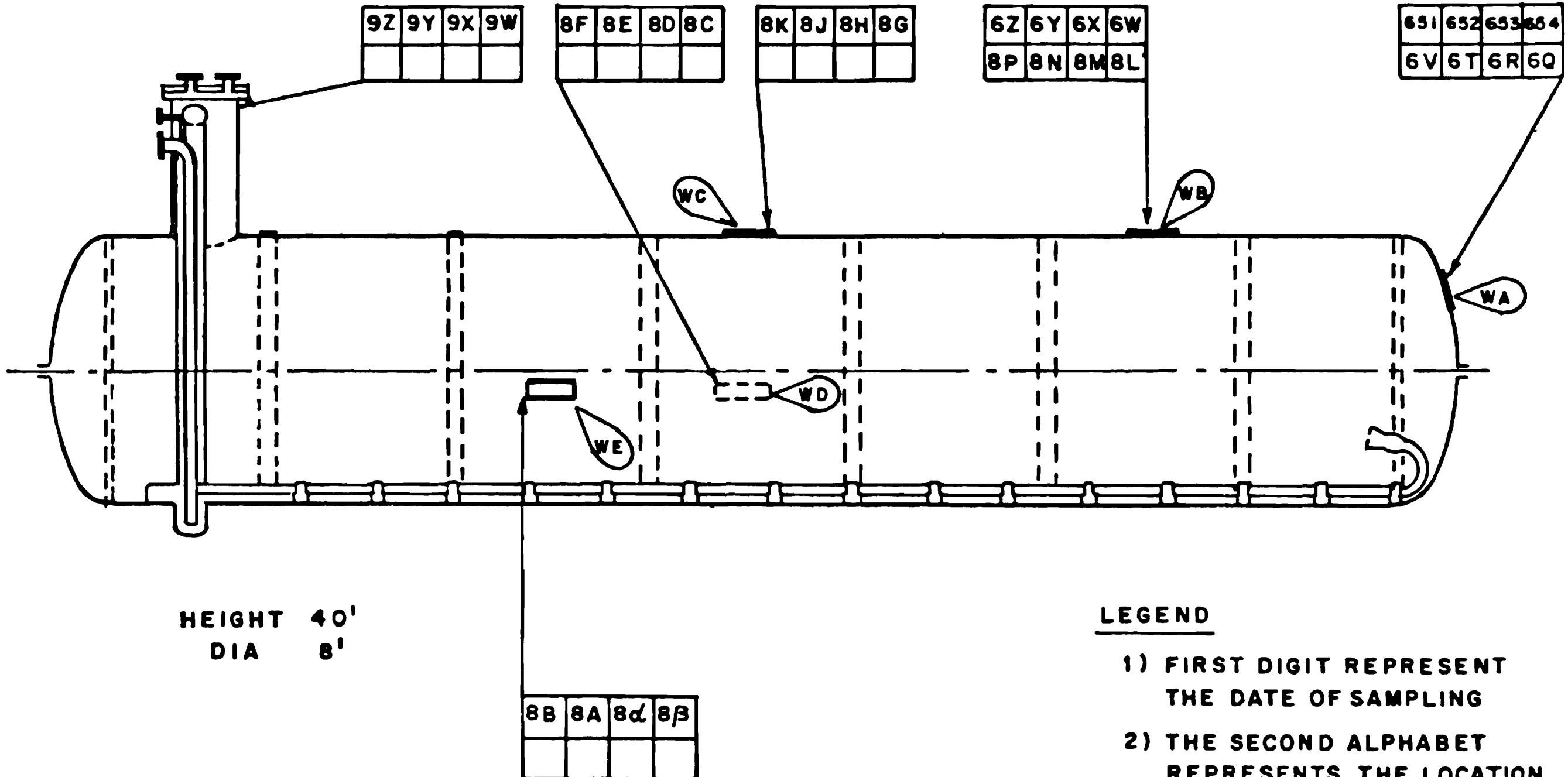


Fig. 2.2

2.1.3. Samples from pipelines:

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

2.1.4. MIC samples from tank 611:

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

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

2.1.5. Metal pieces cut from Tank 610:

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

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

2.2 Chemical Analysis

2.2.1 Physical appearance of samples of residue:

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

2.2.2. Solubility Characteristics:

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

2.2.3. Qualitative Analysis:

Smell: The samples showed a strong smell of amines.

Acidity or alkalinity: The samples were highly acidic.

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

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

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

Cyanide ions: Residue samples showed negative tests 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 column as detailed in Annexure 2. Acetone was used as the solvent for the analysis. It was found that acetone in presence of dimethyl-amine (2%) dissolved about 95% of the residue. The acetone insoluble (approximately 3-6%) showed metal chlorides (approximately 1%). It did not contain amines or other identified organic compounds. The amines could be separated using a TEPA+ KOH column on chromosorb 102. Most of the compounds were isolated from the residue using various techniques and their identity established by spectral data (IR, NMR and MS) by direct comparison with those of pure compounds. The acid present in the samples and the chloride were determined by potentiometric titration.

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

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

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

2.2.5. Analytical Results:

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

1. Methylisocyanate trimer (MICT)
2. Dimethylisocyanurate (DMI)
3. Dimethyl urea (DMU)
4. Trimethyl urea (TMU)
5. Dione
6. Trimethyl biuret (TMB)
7. Tetramethyl biuret (TRMB)
8. Monomethyl amine (MMA)
9. Dimethyl amine (DMA)
10. Trimethyl amine (TMA)

11. Chloride

12. Metallic ions (Fe, Cr, Ni, Mo, Na, Ca, Mg)

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

2.3. ‘Total representative’ sample of residue and its analysis:

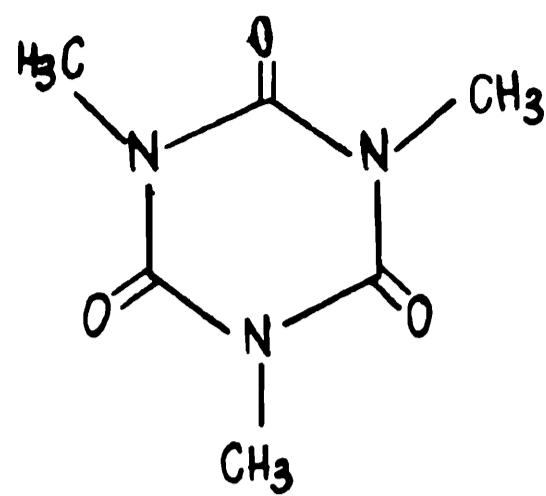
A total representative sample was prepared by mixing samples drawn from the various windows of the tank. The sample thus prepared as representative of the entire quantity of the residue was mixed and homogenised. This sample was prepared by mixing equal quantities from 22 different residue samples. These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

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

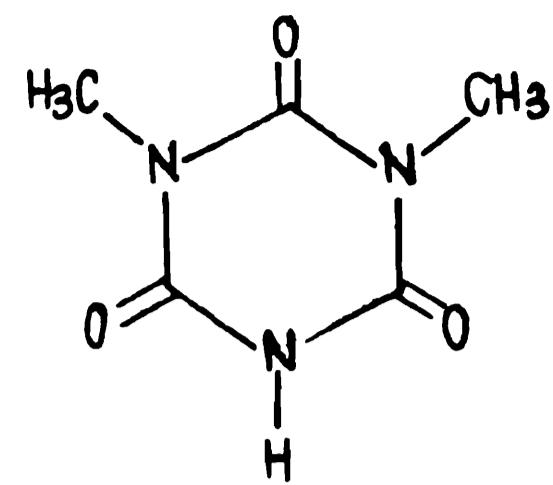
The total identified compounds in the sample add up to about 95%. As indicated earlier, the residue sample contain about 3-6% of unidentified tarry materials.

2.3.1. Product distribution:

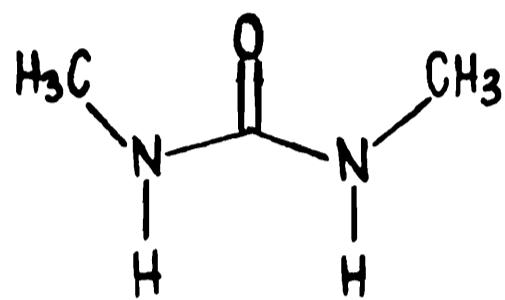
Besides the presence of various metal and chloride ions, the residue contains 10 organic compounds. These are presented as kg moles in the last column of Table 2.9. The tank residue contains 40.7 kg moles (or about 7000 kg of MIC trimer). The next highest molar concentration is that of DMI with 17.0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



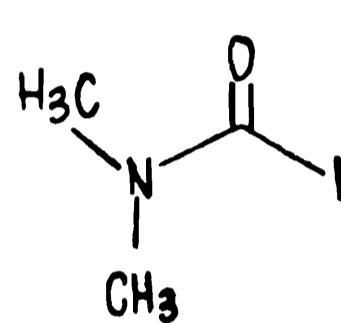
MICT
MW = 171



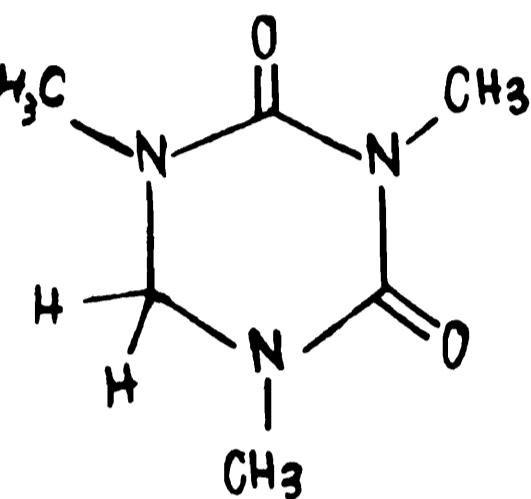
DMI
MW = 157



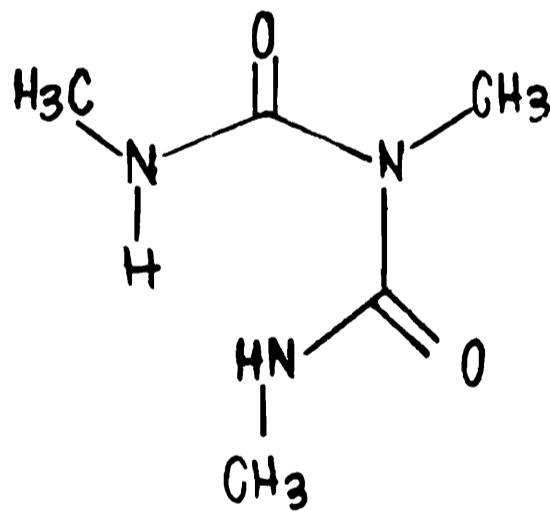
DMU
MW = 88



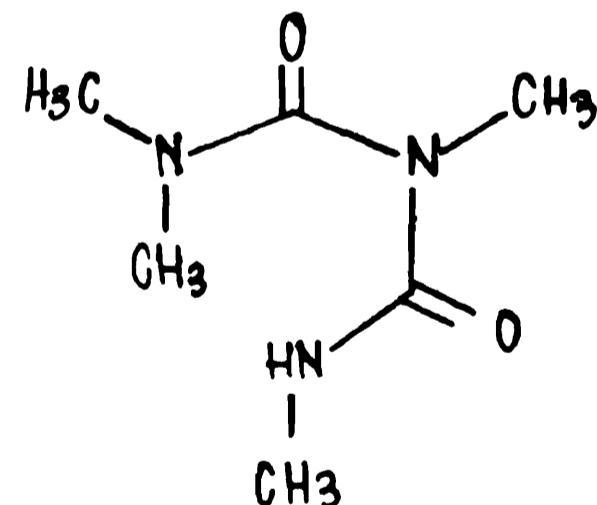
TMU
MW = 102



Dione
MW = 157



TMB
MW = 145



TRMB
MW = 159

Fig. 2.3 Structures of compounds in tank - 610

TABLE 2.1
Analysis of Liquid Samples from RVVH/PVH

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

TABLE 2.2
Analysis of MIC Samples from E-611

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

* As per Union Carbide Analytical Procedure

TABLE 2.3
Analysis of Core Samples from the Manhole Nozzles

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

TABLE 2.4
Analysis of Core Samples from the Manhole Nozzles

Sl. No.	Description of samples	Code No.	Trimethyl Urea, TMU % w/w	MIC trimer MICT w/w	Dimethyl Urea, DMU % w/w	Dione % w/w	Trimethyl biuret, TMB % w/w	Dimethyl isocynu- rate, DMI % w/w
1.	Safety valve nozzle	A-1	1.1	59.6	1.8	3.1	-	12.6
2.	Safety valve nozzle	A-2	1.9	47.9	0.9	4.4	-	16.0
3.	Safety valve nozzle	A-3	1.6	35.6	3.4	4.2	-	23.1
4.	Safety valve nozzle	A-4	1.8	34.0	3.6	4.1	-	25.9
5.	Process vent nozzle	B-1	2.0	43.3	3.6	3.2	6.5	16.8
6.	Process vent nozzle	B-2	2.0	37.3	6.4	4.1	8.2	20.6
7.	Process vent nozzle	B-3	1.9	27.1	4.8	4.2	10.7	24.4
8.	Process vent nozzle	B-4	2.5	24.9	3.8	4.2	13.5	25.0
9.	Thermowell nozzle	D-1	0.9	38.4	11.0	2.6	6.9	31.0
10.	Thermowell nozzle	D-2	0.8	38.2	3.7	2.6	9.4	31.8
11.	Thermowell nozzle	D-3	2.5	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.	Diptube bottom piece	F-1	1.3	39.2	6.2	2.8	6.5	17.7
17.	Diptube bottom piece	F-2	1.9	24.0	12.8	2.5	9.5	28.4
18.	Diptube bottom piece	F-3	1.7	23.6	10.9	6.5	13.0	20.7
19.	Diptube bottom piece	F-4	1.9	20.3	4.3	4.3	9.8	17.2

TABLE 2.5
Analysis of Samples of Tank Residues after Opening the Tank

Sl. No.	Sample No.	Acidity as HCl % w/w	Chloride Cl ⁻ % w/w	Fe ppm	Cr ppm	Ni ppm
1.	Z-1	4.5	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	Chloride Cl ⁻ % 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	4.00	0.6	35.4	5.6	6.8
M-1	1.06	62.3	0.6	2.71	-	18.6	3.7	5.8
M-2	1.64	44.8	2.2	3.82	-	27.7	5.2	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	5.7	4.7
V-3	1.2	63.4	-	2.5	-	18.3	4.3	5.3
V-4	2.38	64.0	-	3.6	-	18.9	3.5	5.2

TABLE 2.7
Analytical Results of Sodium, Calcium and Magnesium in the Core Sample

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

TABLE 2.8
Analysis of Amines by Gas Chromatographic Method

Sl. No.	Sample No.	MMA % w/w	DMA % w/w	TMA % w/w	Total % w/w
1.	M-1	0.9	1.3	1.4	3.6
2.	M-2	1.0	2.0	2.1	5.1
3.	M-3	1.0	1.4	1.8	4.2
4.	M-4	1.1	1.4	2.3	4.8
5.	H-1	1.0	1.2	2.0	4.2
6.	H-2	0.9	1.8	2.0	4.7
7.	H-3	0.9	0.8	2.9	4.6
8.	H-4	1.0	2.1	2.4	5.5
9.	X-1	1.0	1.4	2.2	4.6
10.	X-2	1.0	1.1	2.0	4.1
11.	X-3	1.0	1.6	2.1	4.7
12.	X-4	1.0	1.3	1.8	4.1
13.	A-2	1.1	2.1	3.1	6.3
14.	A-3	1.1	2.0	3.0	6.1
15.	A-4	1.0	1.9	3.1	6.0
16.	B-1	1.0	1.4	2.5	4.9
17.	B-2	1.0	1.4	2.0	4.4
18.	B-3	1.0	1.2	2.2	4.4
19.	B-4	0.7	1.3	1.5	3.5
20.	I-1	1.0	0.9	1.4	3.3
21.	I-2	1.0	1.5	2.1	4.6
22.	I-3	1.1	1.7	1.9	4.7
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	191	1.87
2.	DMU	1.29	161	1.83
3.	DIONE	3.13	391	2.49
4.	TMB	0.94	117	0.81
5.	DMI	21.42	2675	17.04
6.	MICT	55.71	6964	40.72
7.	MMA	1.02	129	4.17
8.	TMA	3.384	423	7.17
9.	DMA	1.978	246	5.47
10.	TRMB	Traces	-	-
11.	CHLORIDE	4.33	540	15.21
12.	METAL CONTENT	Fe 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 as 12.5 tonnes.

** Tarry material (4.7%) not characterised.*

Gas liquid chromatography (GLC)

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

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

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

Determination of MICT, DMI, Dione and Urea

Sample preparation:

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

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

The reliability and reproducibility of the methods were checked by analysing known standard samples. The results obtained by absolute calibration curve method are tabulated in Table 2.9. Reliability test used for the

external standard methods was the determination of standard deviation for each standard compound. The results of reliability tests using internal standard are recorded in the Tables A-2.3, A-2.4 and A-2.5.

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

Standard solutions:

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

Instruments and chromatographic conditions:

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

1. Shimadzu gas chromatograph RIA coupled with reporting integrator

GLC conditions:

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

Detector - Flame Ionisation Detector (FID)

Carrier gas - nitrogen (60 ml/min)

Column oven temperature - 180°C

Injection port temperature - 250°C

Detector temperature - 250°C

Injection volume - 0.4 μl

Total analysis time - 43 min.

Quantitation method - absolute calibration curve method 44.

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

GLC conditions:

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

Detector - Flame Ionisation Detector
(FID)

Carrier gas - nitrogen (30 ml/min)

Column oven temperature - 155°C

Injection port temperature - 250°C

Detector temperature - 300°C

Injection volume 2 μ l

Total analysis time - 15 min

Quantitation method - external standard

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

GLC conditions:

Column - FFAP 3% on chromosorb
2-HP (glass columns 2 mm ID x 100cms)

Detector - Flame Ionisation Detector
(FID)

Carrier gas - nitrogen (35 ml/min)

Column oven temperature - 190°C

Injection port temperature - 225°C

Detector temperature - 225°C

Injection volume 2 μ l

Total analysis time - 15 min

Quantitation method - internal standard

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

Standard solutions with internal standard:

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

Retention time data and order of elution:

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

TABLE A-2.1
*Retention Times of Different Compounds on FFAP
(10% and 3%) Column*

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

(Conditions as given in previous page)

TABLE A-2.2
*Retention Time of Different Compounds on
OV-210 + OV-17 3% w/w Column*

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

(Conditions as given on previous page)

Determination of amines

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

Sample Preparation

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

Standard Solutions

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

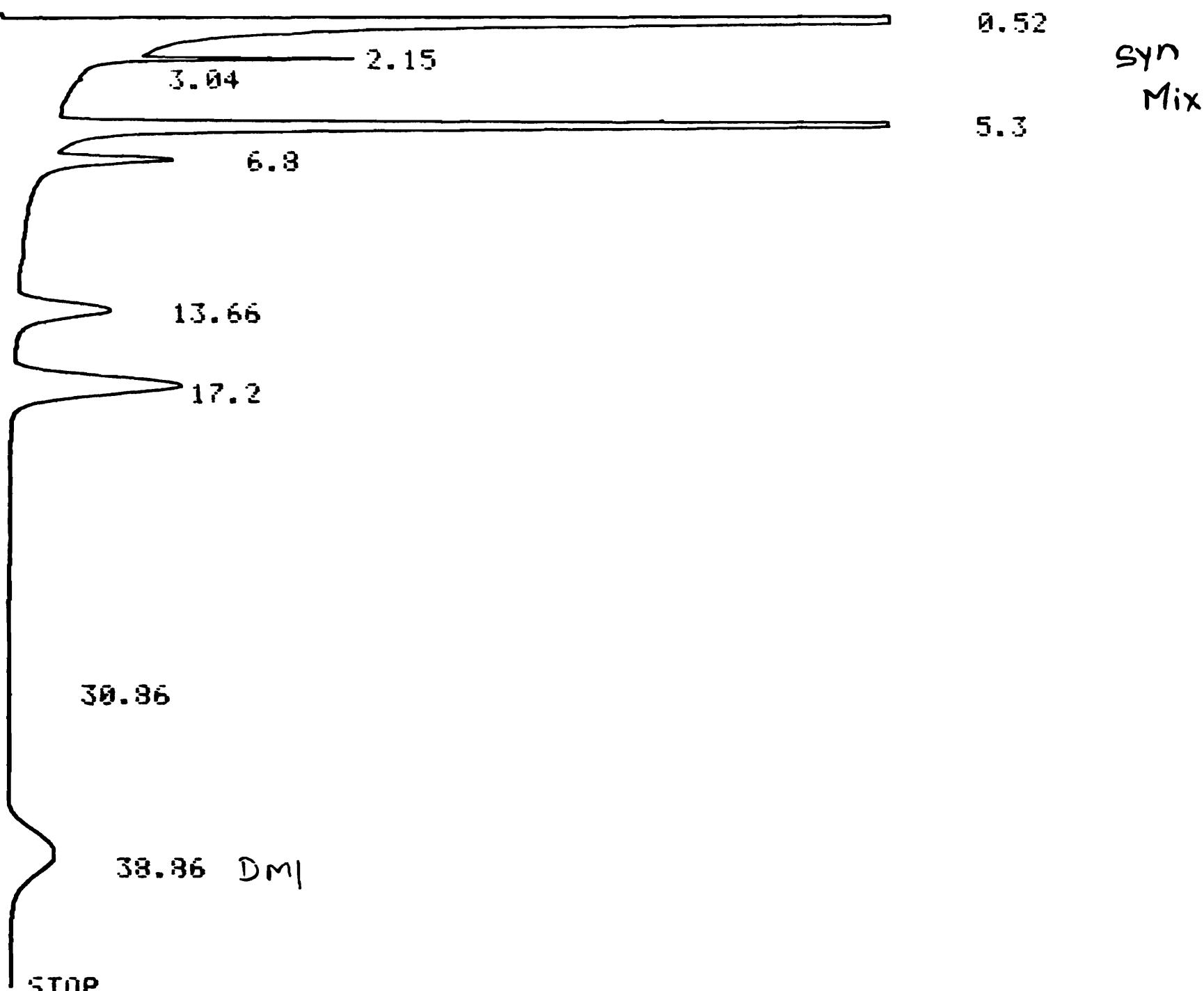
Retention times of amines were as follows:		
Monomethylamine	-	3.85 min
Dimethylamine	-	5.29 min
Trimethylamine	-	5.99 min

Reliability Test

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

FIG A-1

START 08.21.11.02.



INJECT TIME 01:31:44

FFAP - 3X

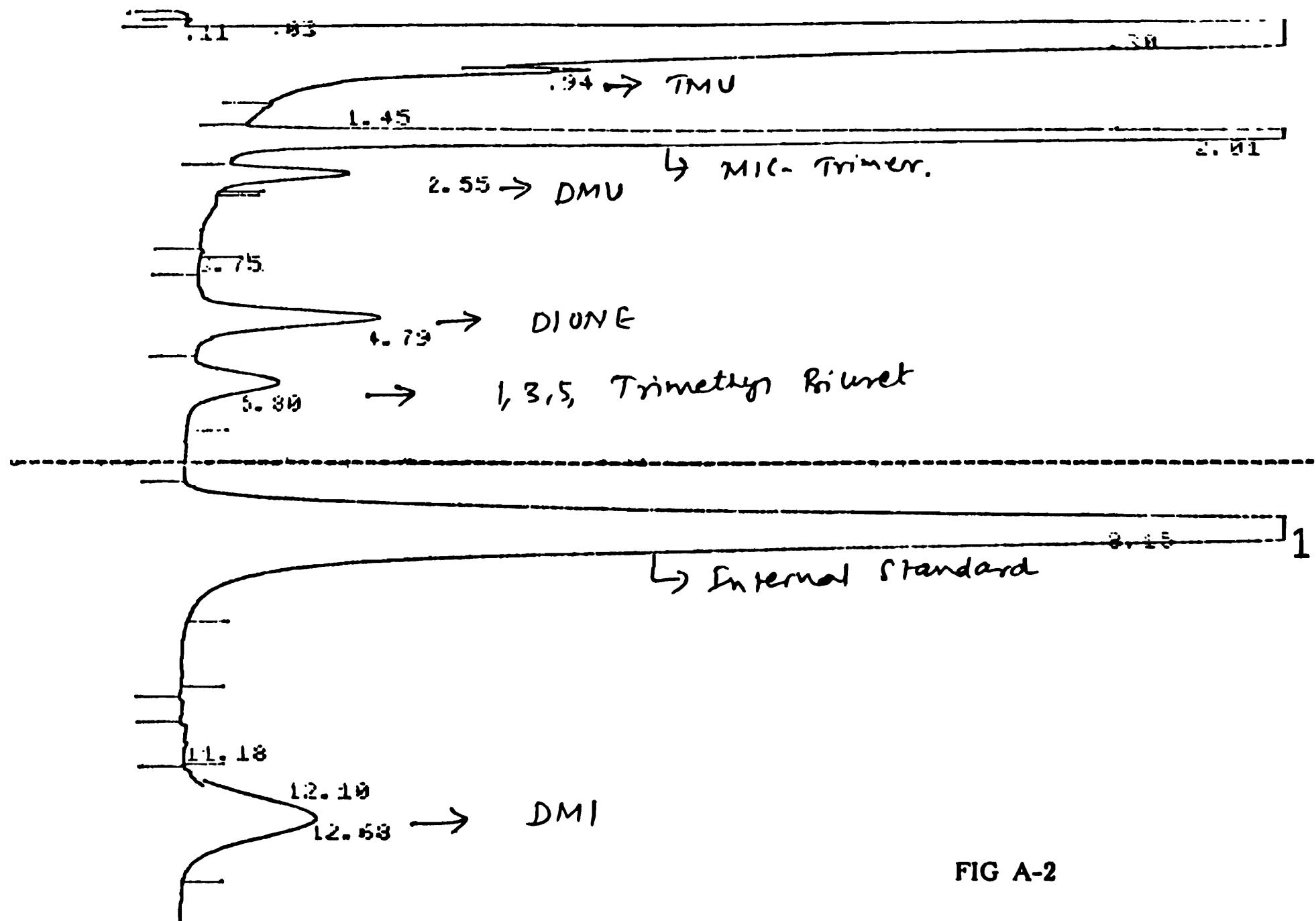
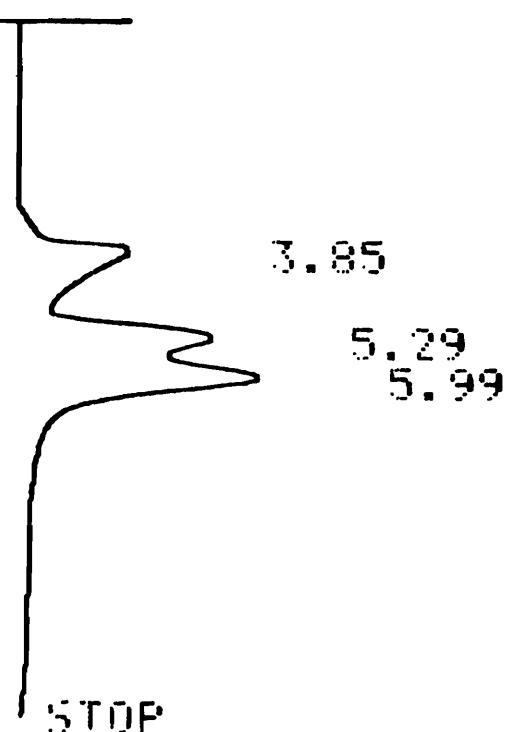


FIG A-2

FIG A-3

START 11.06.12.40.



Instrument and chromatographic conditions

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

GLC conditions

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

Detector - Flame Ionisation Detector(FID)

Carrier gas - nitrogen (50 ml/min)

Column oven temperature - 85°C

Injection port temperature - 150°C

Detector temperature - 225°C

Total analysis time - 15 min

Quantitation method - Absolute calibration curve method 44

Determination of Chlorides by Potentiometric Titration

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

Reagents and Apparatus

A R Grade reagents were used for all the work.

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

A magnetic stirrer was used for stirring the solutions during titrations. The end point of the titration was determined by plotting mV against volume of standard AgNO_3 added. The end point potential was set at + 300 mV.

Procedure

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

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

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

Preparation of Standard Compounds

Trimethyl Urea

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

1,3,5 Trimethyl Biuret

MIC and sym-dimethyl urea (dry) were heated at 100°C in s.s. bomb for 2 hr. The reaction mixture was felt at room temperature overnight. The following day the reactor was opened and the excess MIC was evaporated by keeping the

reactor in a hot water bath. The residue was crystallised from hot benzene.

1,1,3,5 - Tetramethylbiuret

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

Dione

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

MIC Trimer

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

20 g of the residue from tank 610 was extracted with chloroform. The chloroform

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

Dimethyl Isocyanuric Acid

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

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

Amine Hydrochlorides

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

3.0 CHEMISTRY OF FORMATION OF COMPOUNDS IN TANK 610

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

3.1 Experiments:

Since simulation of the exact conditions of the total event that occurred in tank 610 was not possible, experiments were carried out by taking small quantities of MIC and subjecting them to different reaction conditions. The MIC used for these experiments was from material collected from tank 611 from the Bhopal plant. Its composition is given in Table 2.2. It contained CHCl_3 and hydrolysable chlorides.

Two sets of experiments were carried out:

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

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

3.2 Observations:

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

- i. MIC reacts with small quantities of water slowly at room temperature, with a half life of 3 to 4 hours.
- ii. Addition of a trace of ferric chloride to the above reaction mixture at room temperature results in a vigorous reaction after an induction period.
- iii. DMU and TMB are readily formed by reaction of MIC with water.
- iv. MICT is formed readily from MIC. (Presence of MICT has also been noted in various parts of the plant). It can also be formed from TMB by heating. It is very stable product and is not easily transformed into other products.
- v. The formation of DMI is not noticed below 200°C . TMB alone on heating to temperatures above 200°C also gives DMI.
- vi. Dione formation was noticed only above 220°C and the quantity increase as the temperature is raised.
- vii. Presence of chloroform is considered necessary for the formation of Dione.
- viii. It appears that part of the chloride present has come from chloroform present in MIC when the reaction temperatures exceed 200°C .

- ix. The reaction of MIC with small quantities of water and chloroform at 250°C gives all the products formed in tank 610 with the exception of tetramethyl biuret. Formation of amines and amine hydrochlorides was also noticed.

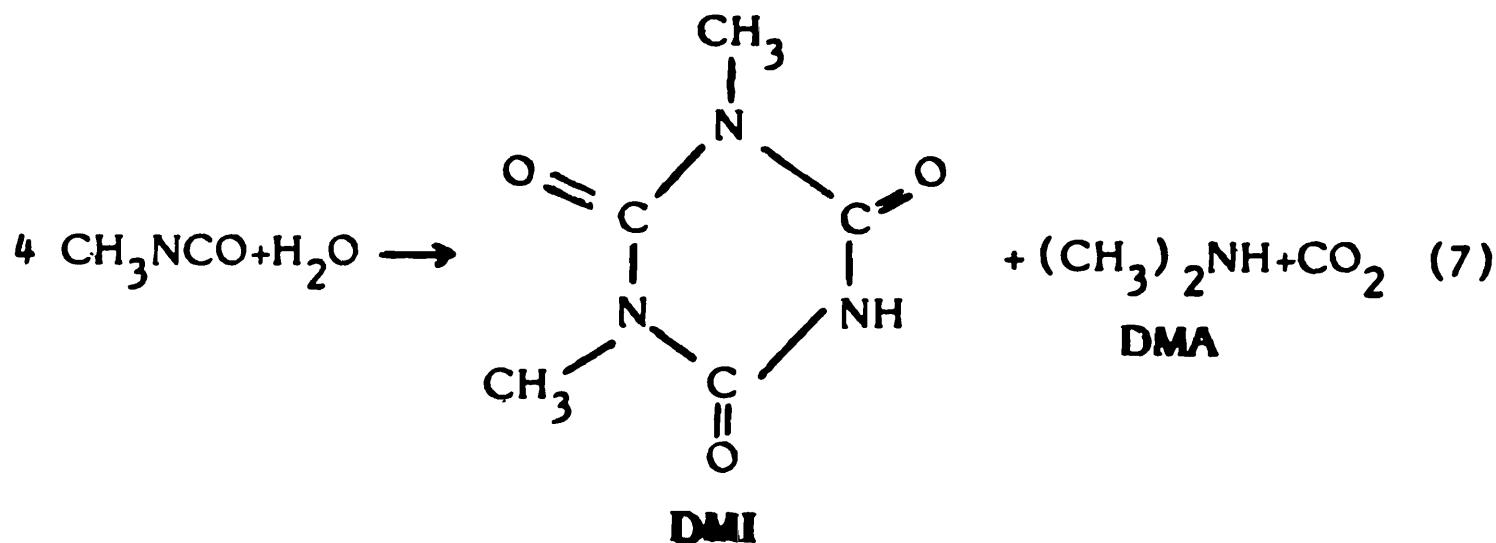
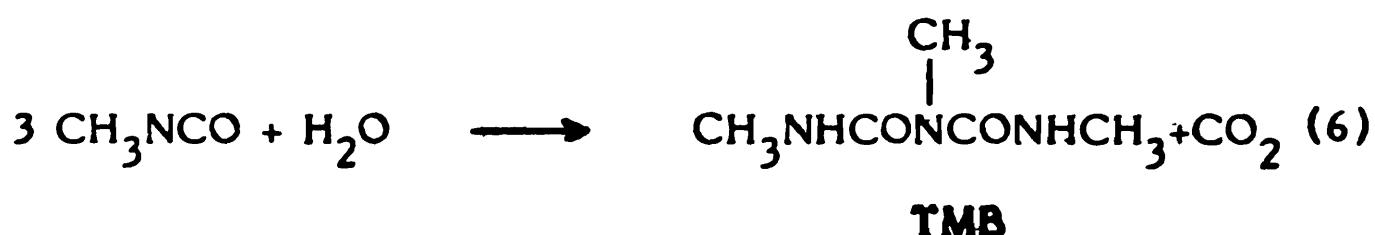
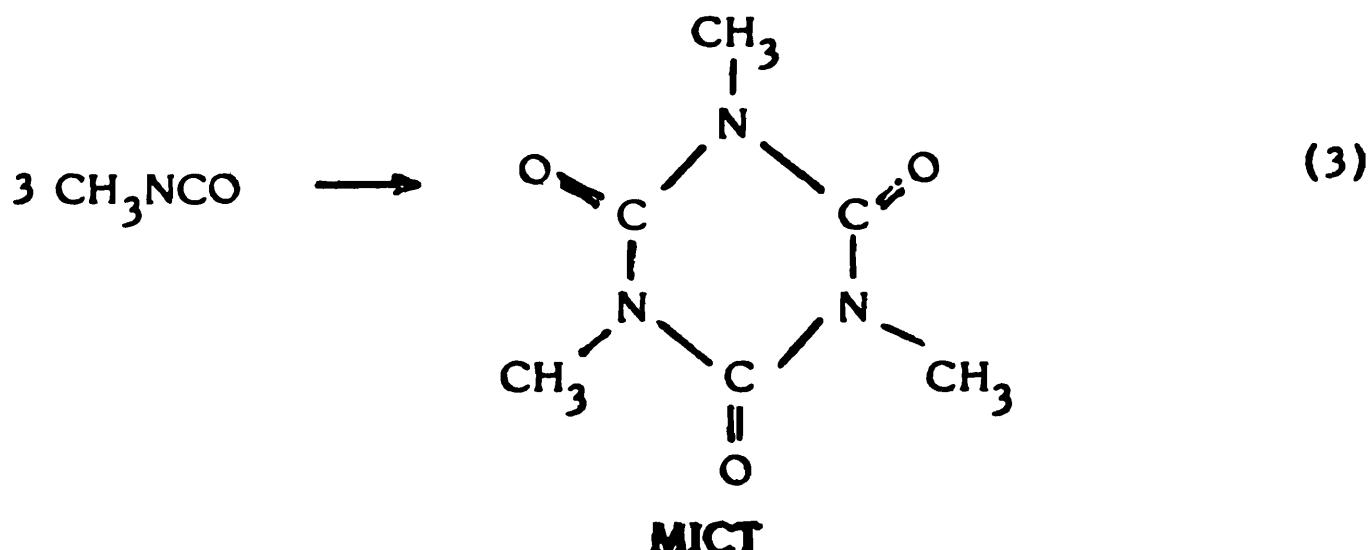
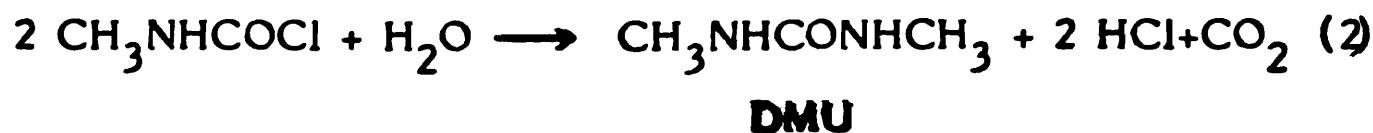
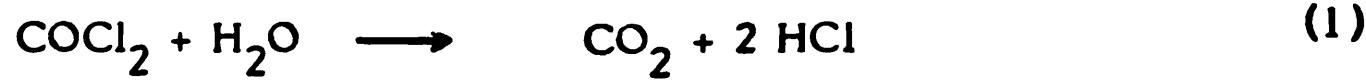
3.3 Discussion:

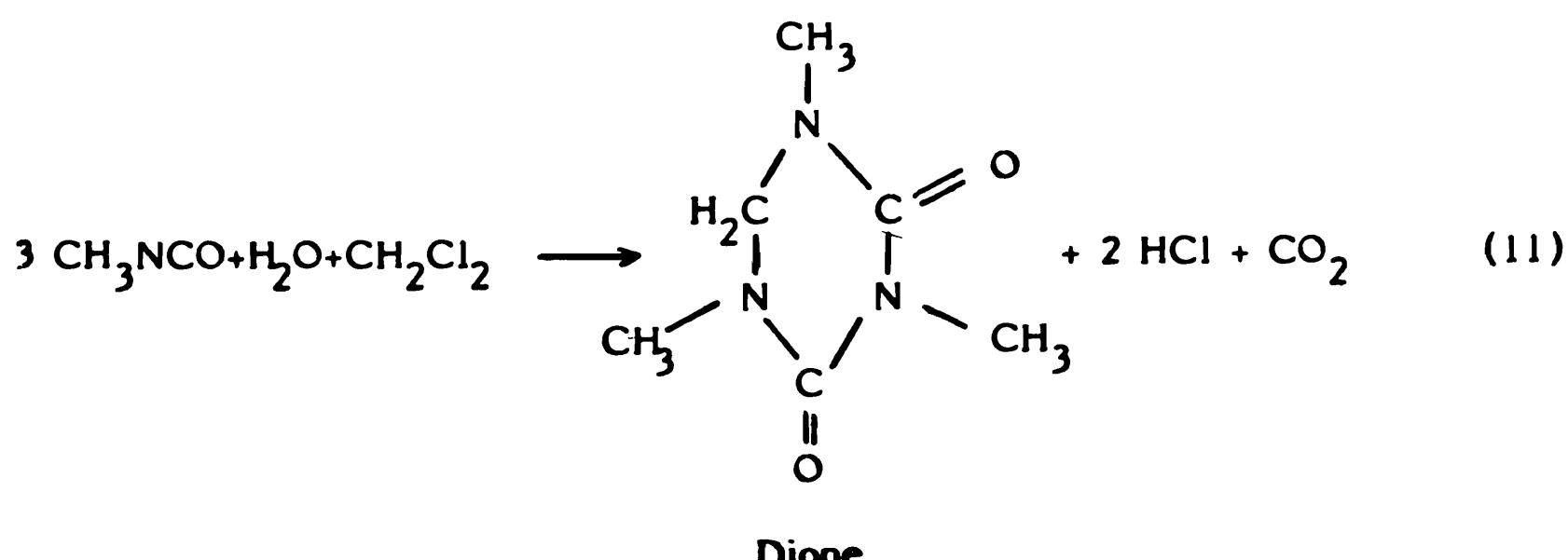
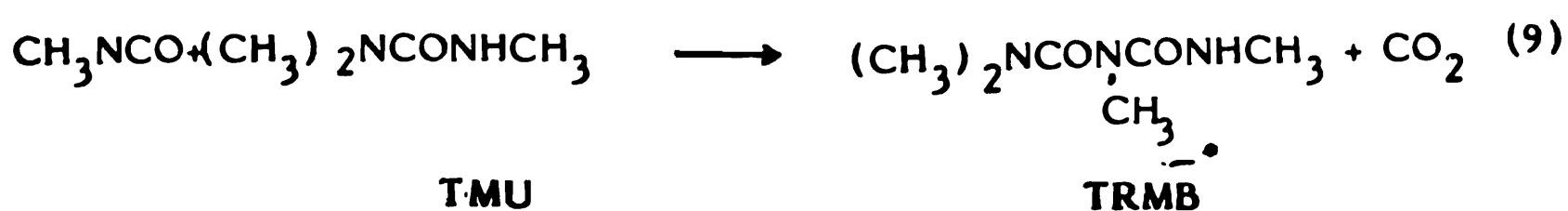
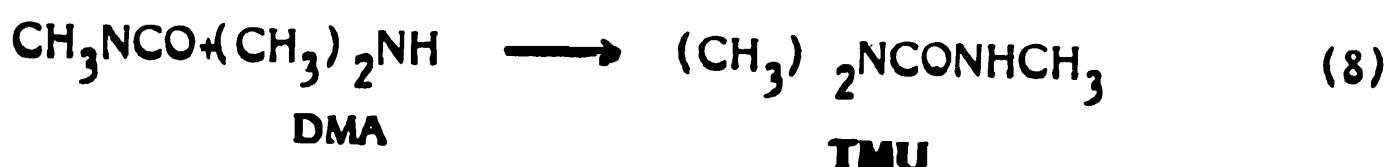
Based on the above observations and on the composition of the residue given in Table 2.7,

the following statements can be made:

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

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





Assumptions

- i. The above reactions represent initial reactants and final products without specifying possible intermediates.
- ii. Chloroform present could enter into reactions only above 200°C. at which stage, all the water present would have been consumed by reaction with MIC. Chloroform or its thermal decomposition products could be available to react with DMU or TMB to produce the Dione.
- iii. The formation of DMI takes place at high temperatures. It is assumed that N-alkylureas are converted to DMI with the simultaneous formation of alkylamines.
- iv. The gaseous products emitted are assumed to be mainly MIC, carbon dioxide, methylchloride (CH_3Cl), methylene dichloride (CH_2Cl_2) and carbon tetrachloride (CCl_4). Some alkylamines may have been present in very small amounts.
- v. Phosgene (COCl_2) and MCC (CH_3NHCOCl) present in very small amounts are readily hydrolysed with water to give hydrogen chloride.
- vi. A part of the chlorine of chloroform is converted to hydrogen chloride. The hydrogen chloride produced is present in part as hydrochloride of amines and as metal chlorides.

3.3.1 Material Balance

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

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

3.4 Comments

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

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

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

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

3.5 Gaseous Products of Reaction of MIC

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

In preliminary experiments, MIC, water and ferric chloride were placed in a stainless steel tube as described under Annexure 3.1. The tube was closed with cap to which was attached a pressure valve and a thin pipe. The valve was closed and the tube heated to 300°C and maintained at the temperature for half an hour. The tube was then cooled to -5°C and the end of the pipe was placed in a known quantity of dilute aqueous alkali. The valve was opened and the tube and contents were warmed up to 80°C to volatilise gases and low boiling materials. The gaseous products were thus trapped in the dilute aqueous alkali. The aqueous alkali was examined for the presence of cyanide by standard APHA methods. Cyanide was not

detected.

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

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

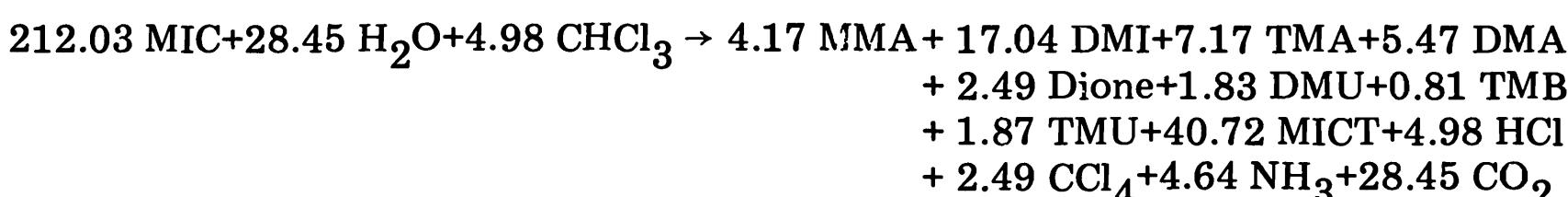
TABLE 3.1
Representative Laboratory Experiments with MIC & Derivatives

Sl. No.	Reactants	Reaction Temp. °C	Time (Minutes)	GLC of Acetone Extract (Approx. %)
1.	MIC + H ₂ O + trace HCl	Rose 23 to 28	6	Not analysed. Temp. rose from 23° to 28°, remained at 28° for 15 minutes and started decreasing.
2.	MIC + H ₂ O + trace HCl + trace FeCl ₃	1. Rose 23 to 29 2. Rose 29 to 31 3. Rose 31 to 45	3-5 60 in a few minutes boiled off	Residue was a solid mass which analysed for DMU, TMB and MICT qualitatively.
3.	MIC + CHCl ₃ + H ₂ O	100	40	DMU (7), MICT (5), TMB (84)
4.	MIC + CHCl ₃ + H ₂ O	190	40	DMU (3), MICT (60), TMB (36), Dione (Trace)
5.	MIC + CHCl ₃ + H ₂ O	200	15	DMU (1), TMB (54), MICT (45), Dione (0.5)
6.	MIC + CHCl ₃ + H ₂ O	250	45	TMU (2), DMU (14), MICT (41), TMB (2.5), DMI (6), Dione (3)
7.	TMB + MIC + CHCl ₃	240	40	TMU (1), DMU (4.5), MICT (80), TMB (3), DMI (6), Dione (5)
8.	TMB + CHCl ₃	245	45	TMU (2.5), DMU (40), MICT (6), TMB (4), DMI (9), Dione (2)
9.	TMB	250	45	DMI (4), Dione (nil), TMB (1), MICT (29), DMU (61), TMU (trace)
10.	DMU	280	45	DMU (100)
11.	DMU + MIC + CHCl ₃	250	45	TMU (3), DMU (13), MICT (52), TMB (8), DMI (4), Dione (2)
12.	TMU + MIC + CHCl ₃	251	45	TMU (10), DMU (1.5), MIC (47), TMB (3.5), TRMB (2), DMI (12), Dione (2)
13.	MICT + CHCl ₃	280	45	MICT (100)
14.	MICT + CH ₃ NH ₃ Cl	300	45	MICT (100)

TABLE 3.2
Material Balance

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

Overall reactions



ANNEXUTE 3.1

EXPERIMENTAL PROCEDURE:

- a) The reactions at atmospheric pressure and room temperature were carried out either in a pyrex or stainless steel tube with a loosely fitting cork through which a thermometer was fixed to observe the temperature of the reaction. The rise in temperature due to the exothermic reaction was noted. In the reaction, wherein a trace of iron catalyst was added (Expt. No. 17 of Table A-3.1), after an induction period of about 1 hr a vigorous trimerization reaction set in. The temperature rapidly rose to 4045°C, and MIC boiled off through the loosely fitting cork.
- b) The reactions were carried out in closed stainless steel bombs at specified temper-

tures and predetermined times as given in Table A-3.1. The bombs were cooled to 0°C or less and the product extracted, first with acetone and then with water. The residue from the acetone extract was subjected to direct GLC analysis. Both an OV-210 plus OV-17 on a chromosorb column, which shows tetramethylbiuret (TRMB) as a clear separate peak and FFAP on a chromosorb column, were used for analysis. Details of analytical instrumental conditions and methods of standardisation and peak matching are in Annexure 2.

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

TABLE A-3.1
LABORATORY EXPERIMENTS WITH MIC & DERIVATIVES

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm		GLC analysis of acetone extract (% w/w)	Wt in gms Cl Ions in water extract
				Acetone extract	Water extract		
1.	MICT (2.00g), CHCl_3 (9.09g)	200	120	-	-	MICT (100)	-
2.	MICT (1.30g), CHCl_3 (3.00g)	200	120	-	-	MICT (100)	-
3.	MICT (0.41g), $\text{CH}_3\text{NH}_3\text{Cl}$ (0.14g)	200	120	-	-	MICT (100)	-
4.	MICT (0.43g), $\text{CH}_3\text{NH}_3\text{Cl}$ (0.29g) DMU (0.48g)	200	120	-	-	MICT + DMU(qualitative)	-
5.	MICT (0.52g), NH_4Cl (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) in solvent CH_2Cl_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_2Cl_2	27	30	-	-	MICT, DMU, TMB (qualitative)	-
10.	MICT (4.7g), CHCl_3 (0.22g), H_2O (0.1g), HCl 20% (0.05g)	200	120	-	-	MICT (100)	-
11.	MIC (3.0g), CHCl_3 (0.150g), H_2O (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	-

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract	
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 - nil, 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		
		<u>Rise in temp</u>	<u>Time</u>				
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 (3.5g), 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)	

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product In gm Acetone extract Water extract	GLC analysis of acetone extract (% w/w)	Wt In gms Cl Ions In water extract
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)	-
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(103), TMB(2) DMI(3.2), Dione (0.8)	0.05
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(nll) 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),MICT (44.4), TMB(3.7), DMI(13.0), Dione (5)	0.04
33.	DMU (3.00g)	280	45	3.033 -	DMU(100)	-
34.	MIC(4.2g) + CHCl 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

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product In gm Acetone extract Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions In Water extract
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) Dlone (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) Dlone(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), Dlone (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), Dlone (1) NII
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) Dlone(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), Dlone (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), Dlone(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), Dlone(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
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) Dlone(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), DMI(5.13), MICT(60), TMB(15), DMI(6), Dlone(1.22) 0.005

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
47.	TMU(3.43g) + CHCl ₃ (0.3g)	220	40	2.50	-	TMU(64), DMU(13), TetMU (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
55.	TMB(0.820g) + CH ₂ Cl ₂ (0.45g)	250	60	0.68	-	TMU(0.92), MICT(12.9), DMU(39.4), Dione(4.4), TMB(30), DMI(1.5)	-

4.0 ANALYSIS OF DESIGN AND ENGINEERING FEATURES

4.1 MIC and its Characteristics:

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

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

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

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

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

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

The brochure further states that the cooling medium in the heat exchanger should not be one

that reacts with MIC or catalyses the reactions. While chloroform is an example of a safe coolant, use of water does create a hazard.

4.2 Storage Tank

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

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

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

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

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

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

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

4.3 Nitrogen:

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

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

4.4 Instrumentation and Control System:

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

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

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

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

4.5 Refrigeration

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

4.6 Vent Gas Scrubber

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

The accumulator volume of 80m³ (21000 gal) if filled with the recommended 10% caustic solution can neutralise a maximum of about 13 tonnes of MIC. Also, operation of VGS at temperatures above 70°C for extended periods is not recommended since absorption will be poorer and the heat of neutralization is not

completely removed by the cooler in the VGS system.

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

5.0 AN ANALYSIS OF THE EVENT

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

- MIC readily undergoes chemical reactions with explosive violence, which produce a large amount of heat, and allow a large portion of stored liquid MIC to vapourise. This is inherent to the nature of the material. Neither the precise conditions under which such run-away reactions could be initiated in MIC nor its manner of prevention are well known.
- A large quantity of MIC was stored in underground tanks which have many inlets and outlets that can permit entry of contaminants which can trigger off explosive reactions.
- The studies described earlier indicate that a reaction was initiated and the temperature rose rapidly. There was no 'rate of rise in temperature' alarm to indicate the rising temperature which would have alerted the operator to an early detection of a run-away reaction.
- Any emergency dumping of liquid MIC into the VGS would not have been feasible because the alkali available in the accumulator is grossly insufficient. Further more, this would also lead to an abnormal temperature rise in the VGS.
- It is conceivable that gaseous MIC would be emitted due to a rapid reaction inside the tank. This gas is expected to be neutralised by circulating alkali solution in the packed section of VGS. This system is also grossly inadequate to handle quantities of vapourised MIC as large as were emitted during the event. Calculations show that even if the normal design load for VGS is taken into consideration, the VGS is inadequate to neutralise a discharge of 28 tonnes of vapourised MIC in about 2 hours.
- Therefore, neither the liquid nor the gaseous disposal system was capable of handling the event which occurred on the night of December 2, 1984.
- The relief valve design could not permit free flow of large quantities of gases, certainly at the level at which they were generated during the event. Thus, the tank contents were subjected to pressures much higher than 40 psig and correspondingly high temperature.
- From the examination of the tank residue and from the conditions of formation of the residue, it is surmised that the temperature reached in the bulk storage tank may have been around 250°C. The total energy balance on the tank also indicate that the probable temperatures would be in the range of 200 to 250°C. Information from the mechanical examination of the tank indicate that the pressure may have reached 11 to 13 kg/cm²g with the corresponding temperatures in the range of 200 to 350°C.
- The chemical analysis of the tank residue clearly shows the evidence of entry of approximately 500 kg. (1100 lb) of water. The fact that the tank 610 was not under pressure of nitrogen for approximately two months prior to the accident also indicates that conditions existed for entry of contaminants such as metallic impurities through the high pressure nitrogen line. As emphasised earlier, many such impurities have a catalytic effect on the possible reactions MIC can undergo.

- The hydrolysis of MIC with about 500 kg. (1100 lb) of water by itself and in the absence of other contaminants is not expected to lead to thermal run-away conditions. The presence of this quantity of water would have possibly resulted in reaction with about three to four tonnes of MIC, generation of carbon dioxide, breaking of the rupture disc and release of CO₂. The temperature of the tank content would have gradually risen to about 60-70°C, below the boiling point of MIC at that pressure. It is surmised that no more than 50 to 100 kg/hr (110-220 lb/hr) of CO₂ along with small quantities of MIC, Ca 100-150 kg/hr (220 - 330 lb/hr) would have been released. Such emissions will cease once the water has been consumed.
- 500 kg (1100 lb) of water could have entered the tank 610 either from the MRS condenser (through condenser tube leaks) or through RVVH/PVH lines. The fact that about 50-90 ppm of sodium was found in the tank residues is also significant. The observed sodium levels are substantially higher than what would have normally been present due to the entry of 500 Kg (1100 lb) of water (below 0.5 ppm).
- Entry of water from the MRS condenser appears less likely as the MRS make line from MRS condenser to tank 610 was flushed with nitrogen, evacuated and blinds were inserted in the line between 23 to 25 October, 1984. Water could have entered from the MRS prior to 23 October but it would have probably reacted much earlier than 2 December, 1984.
- The presence of trace amount of metallic contaminants derived from the material of the tank or its attachments or from extraneous sources, may not necessarily initiate a violent reaction under dry conditions. Small amounts of local trimerisation may take place, as noticed throughout the pipelines and plant. However, the ingress of water, would provide for active species of initiator to be generated and distributed in the liquid.
- A detailed analysis indicates that water entry through RVVH/PVH lines is quite likely. It has been reported that around 9.30 P.M. on 2 December, 1984, an operator was clearing a possible choke of the RVVH lines downstream of phosgene stripping still filters by water flushing. Presumably the 6" isolation valve on the RVVH was closed but a slip blind had not been inserted. Under these conditions when the filter lines are choked, water could enter into the RVVH, if the 6" isolation valve had not been tightly shut or passing.
- This implies that conditions which were ripe for the initiation of a run-away trimerisation reaction already existed in tank 610 on the day of the event, and that entry of water would generate active initiators and the hydrolysis of MIC would provide the necessary heat also for the trimerisation reaction to take off with explosive violence. The carbondioxide evolved upon hydrolysis would provide the necessary mixing leading to even more rapid chemical reactions. The storage tank thus equalled the conditions of a well mixed tank reactor, supplied with heat.
- Furthermore, it is likely that alkaline water could have backed up from the VGS accumulator into the RVVH and PVH under certain conditions. Indeed, several litres of alkaline water was drained from the RVVH/PVH lines in the MIC structure in May 1985, lending credence to such a possibility.
- Once initiated, the trimerisation reaction rapidly led to a temperature increase leading to levels as high as 250°C with autocatalytic and auto-thermal features. At these high temperatures, secondary chemical transformation occurred leading to the complex mixture of products actually found in the tank 610 residue.
- Furthermore, RVVH/PVH lines are made of carbon steel. Back up water or alkali through these lines increase the possibility of metal contaminants entering the tank, especially in the absence of positive nitrogen pressure.
- The water that entered RVVH at the time of water flushing along with baked up alkali solution from the VGS already present could find its way into the tank 610

- through the RVVH/PVH lines via the blow down DMV or through the SRV and RD. To account for say 60 ppm of sodium in the residue, quantity equivalent to 25 litres (about 6.5 gal) of 5% sodium hydroxide would have been sufficient. Such an eventuality would have required that the blow down DMV was malfunctioning or the SRV was not tightly shut and rupture disc had been damaged.
- It was entirely unnecessary to provide facilities for storage of such large amount of MIC in tanks. The quantities stored were quite disproportionate to the capacity of further conversion of MIC in downstream unit. This permitted MIC to be stored for months together without appreciation of potential hazards.
 - The absence of practically any nitrogen pressure on tank 610 for over a month and the observation that MIC was leaking out of a branch of RVVH on the downstream side of Regeneration Gas Cooler Pressure Safety Valve at 23.30 hours on the night of 2 December, 1984 indicated the possibility of malfunctioning of blowdown DMV.
 - The rapid rise in temperature and violent reactions that occurred necessitate the onset of metal ion catalysed polymerisation. The presence of chloroform has no influence whatsoever in initiating or accelerating the run-away reactions. The chloroform present was involved in chemical transformations when the temperature had risen above 200°C at which stage all the water would have already been consumed by reactions.
 - The quantum of toxic leakage by violent chemical reaction is not related to the amount of metal and water which initiate the reactions but to the quantity of MIC stored in a single container. If 42 tonnes of MIC had been stored in 210 stainless steel drums of 200 litre capacity each, as alternative to a single tank, there would be no possibility of leakage of more than one fifth of a tonne and effects of even such a leakage could be minimised by spray of water or alkali.
 - It has been reported that a large number leakages of MIC in comparatively small quantities have occurred from storage vessels and tanks in Union Carbide. The causes for such leakages have not been made known. While Union Carbide product brochure refers to chemical properties and reactivity of MIC, including possibilities of violent reaction as well as of possibilities of spillages from drums and tanks during transport, no information is provided on the extraordinarily lethal toxic effects of inhalation. Public preparedness for eventualities arising out of leakage would have been substantially greater if information on these had been generally available. For instance, substantial care is exercised in the storage and transport of explosives

or in handling even weakly radioactive materials or in the use of X-ray equipment, due to the awareness of hazards.

In retrospect, it appears the factors that led to the toxic gas leakage and its heavy toll existed in the unique properties of very high reactivity, volatility and inhalation toxicity of MIC. The needless storage of large quantities of the material in very large size containers for inordinately long periods as well as insufficient caution in design, in choice of materials of construction and in provision of measuring and alarm instruments, together with the inadequate controls on systems of storage and

on quality of stored materials as well as lack of necessary facilities for quick effective disposal of material exhibiting instability, led to the accident. These factors contributed to guidelines and practices in operations and maintenance. Thus the combination of conditions for the accident were inherent and extant. A small input of integrated scientific analysis of the chemistry, design and controls relevant to the manufacture would have had an enormously beneficial influence in altering this combination of conditions, and in avoiding or lessening considerably the extent of damage of December, 1984 at Bhopal.

SUMMARY OF WORK DONE BY CONSTITUENT LABORATORIES OF CSIR (FULL REPORTS APPEAR IN VOLUME II)

NATIONAL CHEMICAL LABORATORY, PUNE

A report on the investigations by National Chemical Laboratory (NCL), Pune, could be found in Volume II. 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.

REGIONAL RESEARCH LABORATORY, HYDERABAD

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 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, examina-

tion 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.

RRL 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.

NATIONAL AERONAUTICAL LABORATORY, BANGALORE

The Report deals with investigations on stainless steel plates from MIC storage tank No. 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.

NATIONAL INSTITUTE OF OCEANOGRAPHY, GOA

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 is provided.

NATIONAL ENVIRONMENTAL ENGINEERING RESEARCH INSTITUTE, NAGPUR

The report of work done by the National Environmental Engineering Research Institute (NEERI), Nagpur at Bhopal after the toxic gas leakage deals with the environmental parameters generated at Bhopal after the accident. 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.

INDIAN TOXICOLOGY RESEARCH CENTRE, LUCKNOW

The Indian Toxicology Research Centre (ITRC), Lucknow 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.

