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REVIEW OF
METHYL ISOCYANATE (MIC) PRODUCTION
AT
THE UNION CARBIDE CORPORATION FACILITY
INSTITUTE, WEST VIRGINIA

APRIL 15, 1985

Federal-State Task Force Report
Review of Methyl Isocyanate (MIC) Production at the Union Carbide Corporation Facility
Institute, West Virginia

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West Virginia

Executive Summary and Conclusions

SUMMARY

On December 3, 1984, more than 2,000 people were killed in Bhopal, India, ~~by~~ by a catastrophic release of methyl isocyanate (MIC). Union Carbide's Institute, W.Va. plant is the only facility in the United States that produces MIC. As a result of the Bhopal accident, production of MIC at Institute was suspended in December. On February 12, 1985, Union Carbide announced its intention to resume production of MIC.

Prior to resumption of MIC production at Institute, West Virginia, various Federal and State regulatory agencies reviewed the facility and associated manufacturing process to insure that production of MIC would not pose an imminent and substantial endangerment to the health ~~and welfare~~ of the residents of the Kanawha Valley.

To accomplish this, a Federal/State task ~~group~~ force was formed in February 1985 to review and evaluate the design and operating practices of the MIC production and storage units at Institute. This report was prepared by EPA staff with review and comments by task force members. The agencies and members of the task group are listed in attachment three.

The task-force based its review primarily on information provided by Union Carbide in the form of documents, interviews and plant inspections. The task-force independently evaluated information using basic princip~~als~~les of engineering, physics and chemistry, standard industrial practices and technical judgement. Although the task-force evaluated the entire manufacturing process, including formulation, storage, handling and transport of MIC, the primary focus of the evaluation concentrated on storage, since this was considered the area of greatest potential for catastrophic releases.

The following information was considered critical for determining if any imminent and substantial endangerment to public health exists:

1. Hazards of MIC;
2. MIC process design and materials used for construction of equipment;
3. Emergency vent gas scrubber and flare control equipment design;
4. Safety systems; malfunction warning systems; and release detection systems;
5. Documented operating procedures and maintenance programs;
6. Emergency contingency planning; and
7. Handling and storage for transportation.

West Virginia

Major safety improvements that are scheduled to be in place at the Institute, W.Va. facility prior to resumption of MIC production are:

1. Replacement of brine coolant with chloroform for the unit storage tanks;
2. Installation of redundant storage tank monitoring instrumentation;
3. Modification of the design of the safety valves and vent lines for the storage tanks;
4. Increased caustic storage capacity for the emergency vent gas scrubber;
5. An additional tank which increases residence time for liquid MIC to be in contact with the caustic in the scrubber during emergency operation;
6. Provision for steam addition to maintain temperature in the emission vent scrubber to achieve better reaction rates;
7. Improved caustic concentration control for the scrubber;
8. Modifications to the flare ignition system to increase its reliability;
9. Installation of an air sampling leak detection system for MIC;
10. Installation of a computerized emission warning system (SAFER®) that would assist emergency response officials in deciding corrective actions that should be taken if a significant release of MIC were to occur;
11. Improved internal emergency contingency plans and early warning notification procedures establishing specific criteria for initiating notification of local emergency response organizations;
12. Additional alarm systems for the storage tank monitoring instruments, are being directly wired to the shift administrator's office.

Records reviews and inspections will be periodically conducted by various regulatory agencies to assure that all critical equipment has been properly maintained, all operating procedures are being followed, and all necessary operator training has been provided.

In addition, Union Carbide Corporation will work with the local emergency response planning authorities to develop coordinated emergency response plans.

has agreed to

CONCLUSIONS:

Major findings of the task-force review of the MIC units at Institute, West Virginia, are:

- Major equipment and mechanical features of the plant are state-of-the-art or equal to the chemical industries accepted practice.

- *Standard operting procedures for inspection and maintenance* of critical equipment are in place and acceptable. Union Carbide maintains an acceptable program for training MIC operating personnel.

- The design capacity of ~~the~~ emergency vent gas scrubber and flare are adequate to nutralize and/or destroy an "extreme case" accidental release of MIC. SP

- Instrumentation, alarms and control devices are adequate to indicate abnormalities in production, storage and handling of MIC.

- Internal and external contingency plans for accident mitigation are in place. These plans are continually being reviewed and improved. Important changes to the local emergency response contingency plans, as recommended by the Regional Response Team, have been addressed in verbal agreements between Union Carbide, Kanawaha County and the State.

Based on these findings, the task ~~group~~ Force concludes that resumption of production of MIC at the Institute facility does not present an imminent and substantial endangerment to public health. ~~or the environment.~~

Introduction

On December 3, 1984, methyl isocyanate (MIC) escaped from a Union Carbide Company (UCC) plant in Bhopal, India, killing 2,000 people and injuring thousands more. As a result of this tragic accident, Union Carbide shut down MIC production facilities at its plant in Institute, in the Kanawha Valley of West Virginia, the only place in the United States where MIC was being produced. Remaining inventory of MIC at Institute was converted to product or destroyed.

On February 12, 1985, Union Carbide ~~announced~~ its intention to resume production of MIC at Institute, W. Va., in April 1985.

Three days later, ~~on~~ February 15, 1985, Stanley Laskowski, Acting EPA Region III Administrator at the time, indicated by letter to Union Carbide that EPA would ~~review the~~ company's start-up procedures, and requested information relevant to that review.

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An intergovernmental task force was formed ~~to~~ carry out the review. There The agencies and members of the task ~~group~~ are listed in attachment ~~two.~~ Task force members interviewed Union Carbide officials and reviewed technical material that the company submitted (see Documents Reviewed by Task Group).

The purpose of the review was to determine if resumption of MIC production in Institute would pose an imminent and substantial endangerment to public health or ~~the environment~~ in the Kanawha Valley, and to determine the potential for a catastrophic release of MIC during its manufacture, handling, or storage. The task force based its review primarily on information provided by Union Carbide in the form of documents, interviews and plant inspections. The task force independently evaluated information using basic princip~~als~~ les of engineering, physics and chemistry, standard industrial practices and technical judgement.

This report presents the findings of the task force.

Chapter One

Manufacturing and Reactivity of MIC

PURPOSE:

To describe the basic chemical and physical characteristics of MIC, the process used in its manufacture, and potential health effects of human exposure to MIC.

DISCUSSION:

MIC is a stable but reactive toxic, volatile, and flammable compound. It is used as a chemical intermediate in the manufacture of agricultural pesticides such as SEVIN® and LARVIN®.

Scrubber

1. Reactivity. Because MIC is particularly reactive with water, acidic materials, alkalies, amines, and their salts, contact with these substances is to be avoided. However, MIC's reactivity with water and alkalies, also allows it to be destroyed rapidly using a caustic scruber system. In the reaction with water, MIC produces carbon dioxide and dimethyl urea. In the presence of catalyzing agents such as iron, MIC may combine with itself to produce its trimer, a larger molecule made up of three MIC molecules.

   Both trimerization and reaction with water are highly exothermic, or heat-producing, yielding respectively 540 and 585 Btu per pound of MIC reacted (see Methyl Isocyanate F-41443A-7/76, Union Carbide). In such a reaction this heat, if not removed, would tend to vaporize liquid MIC which, at ambient conditions, is a colorless liquid with a boiling point of 39°C. If this vapor were to be released by a pressure relief valve it would need to be treated with a scrubber or burned in a flare to prevent a release to the environment. Reactivity is controlled in storage through rigid quality assurance practices and through refrigeration, which keeps the bulk temperature of the MIC at or below 0°C. Equipment is also kept closed and the MIC is blanketed with dry nitrogen to prevent contamination, which could lead to undesirable reactions.

2. Production. MIC is produced by reacting anhydrous monomethylamine (MMA) with phosgene in a high temperature vapor phase reaction. Phosgene is produced by reacting chlorine gas with carbon monoxide. Phosgene and carbon monoxide are produced on-site at the Institute plant; the MMA and chlorine are transported to the plant by rail.

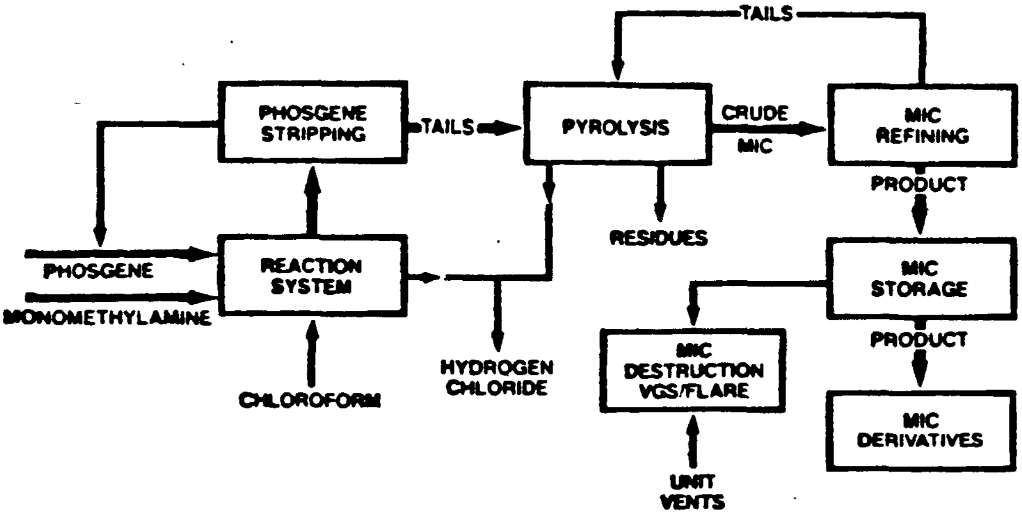
The MIC manufacturing process yields hydrogen chloride (HCl) as a by-product. This is removed from the MIC by subsequent refining processes using conventional distillation techniques. Chloroform is a system solvent. A simplified explanation of the overall chemical reaction can be expressed this way:

$$CH_3NH_2 + COCl_2 \longrightarrow CH_3NCO + 2HCl$$

Monomethylamine + Phosgene yields MIC + Hydrogen Chloride

A simplified block flow diagram of the process looks like this:

MIC PROCESS



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At Institute, MIC is stored and handled in corrosive-resistnat equipment made of stainless steel or containing appropriate linings such as HASTELLOY®, INCONEL®, or TEFLON®.

Once manufacturing and refining are complete, MIC is temporarily stored as a liquid in a refrigerated tank, where it is sampled to assure compliance with product specifications. These specification require the MIC to be essentially free of water, chloroform, hydrogen chloride, and other impurities which might lead to later undesirable reactions. If the MIC meets specifications, it is pumped to larger underground storage tanks; if it does not meet specifications, it is reprocessed or destroyed.

3. Health effects. MIC is considered a hazardous material by any means of contact. Because of its high vapor pressure, the potential for inhalation exists if MIC reaches the environment. Exposure via inhalation can cause chest pains, coughing, choking, asthma-like breathing, and fatal pulmonary edema. Skin contact can cause severe burns. Even at very low concentrations, MIC can irritate or injure the eyes.

   Exposure to phosgene, used to produce MIC, can cause eye irritation, vomiting, coughing, dyspnea, chest pains, cyanosis, skin burns, and dry, burning throat, and can be lethal.

CONCLUSION:

MIC is a reactive, volatile, and toxic material that can be safely handled if appropriate corrosion-resistant material, refrigeration, and dry nitrogen blanketing are used in processing and storage.

Chapter Two

Mechanical Review of MIC Production

PURPOSE:

To assess the design and materials of equipment at the Institute, West Virginia Plant; to contrast them to the industry standard; and to determine their relative safety in MIC production, storage and distribution.

DISCUSSION:

The extremely reactive nature of MIC requires that storage and process equipment receive special design consideration.

1. Reaction equipment. As described in the previous chapter, MIC is made by combining monomethylamine and phosgene. This reaction takes place at high temperature with excess by-products being directed to a a flare for destruction before venting to the atmosphere. Reaction equipment includes several unit operations such as reaction vessels, distillation columns, ancillary reboilers, condensers, and scrubbers to destroy the hydrogen chloride gas generated in the reaction. The process equipment which contacts the HCL gas are of graphite, Hastolloy® and other highly corrosion resistant materials of construction. All storage and transfer material of construction are of corrosion-resistant material such as stainless steel. Piping is welded stainless steel with gaskets of TEFLON®, or better material, to prevent leakage. Such equipment is the accepted norm for corrosive materials. If checked routinely for stress corrosion, it represents acceptable equipment.

2. Storage equipment. The following is a list of the MIC storage, process and relief tanks at Institute:

Quantity	Type of Tank	Maximum Designed Storage Capacity*
3	Process tanks (make tanks)	14,000 gallons each (one always kept empty)
3	Underground storage tanks	30,000 gallons each (one always kept empty)
1	Relief tank for MIC	30,000 gallons ~~each~~

Quantity	Type of Tank	Maximum Designed Storage Capacity*
1	Process tank for LARVIN® production	7,000 gallons
1	Relief tank for LARVIN® production	8,500 gallons
1	Process tank for SEVIN®	7,000 gallons (will no longer be used)
2	Transportation/ Distribution tanks	15,000 gallons each ok (will ok no longer be used; ~~however, may be~~ ok ~~replaced~~ with 3,000-gallons shipping containers) Leave
1	Relief tank for transportation distribution	10,000 gallons ~~each~~ (will no longer be used)

* Standard operating procedures call for total loading not to exceed 85-90 percent of storage capacity. ing

MIC is piped to pressurized process tanks. The contents of each process make tank are pumped through a heat exchanger, which is cooled by a refrigerant. Prior to the Bhopal disaster, Union Carbide used brine as the refrigerant, but has agreed to replace the brine with chloroform before resuming production. Chloroform is inert to MIC at normal operating temperatures. The cooling system is a key to controlling potential runaway reactions of MIC in the tanks since, MIC is less reactive at reduced temperatures. For example, the reaction rate of MIC and water is 3.45 times faster at 25°C when compared to the reaction rate at 0°C.

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Duplicate pumps (one operational and one spare) circulate the MIC through the cooling system. For added safety, one of these pumps is electrically powered; the other steam driven. Back-up electrical substations are provided for each pump to increase the reliability of the power supply. The pumps are internally sealed to prevent low level leakage to the environment. This type of pump is the accepted industry norm for hazardous liquids which cannot be released safely to the environment.

MIC that meets specifications is transferred from the process tanks to 30,000 gallon ~~capacity~~ underground storage tanks with similar safety equipment. The process and ~~storage~~ tanks are now equipped with new pressure relief valves that are set so that venting to the scrubber will occur at 20 pounds per square inch (psi) pressure on the make tanks and 30 psi pressure on the storage tanks. These relief valves were previously set at 50 psi.

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3. Emergency Vent Gas Scrubber. The capacity of the scrubber to neuteralize emergency releases has been increased by the following modifications:

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   a. Caustic storage capcity has been increased by 70,000 gallons

   b. Liquid residence time has been increased at the base of the scrubber to assure for more complete neutralization of liquid MIC.

   c. The ability to maintain the operating temperature of the scrubber has been assured by the use of a steam supply. This assures a rapid rate of reaction with MIC.

   d. An instrumentation system has been installed to control the caustic concentration at 10% during emergency operation.

   e. The feed nozzle configuration into the scrubber has been modified to prevent backflow of caustic into the storage tank.

4. Additional Reaction Equipment. Under normal operations, after MIC leaves the storage tanks, it is fed to process operations where it is used to manufacture SEVIN®. Equipment in these operations is also of corrosion-resistant stainless steel, with vent gas scrubbers and flares similar to those in the storage tanks.

CONCLUSION:

Equipment used in the MIC process at Institute represents, in many cases, the state of the art in the chemical industry and, in all cases, accepted industrial equipment for hazardous materials. The possibility of a catastrophic release due to poor design or materials of construction at Institute is remote.

Chapter Three

Emission Control Systems

PURPOSE:

To review the reaction kinetics of MIC in order to determine the volume of gas discharged under an "extreme case" event; and, by reviewing the design calculations for the flare and scrubber, to assess their adequacy for controlling emissions from a runaway reaction of MIC under "extreme case" conditions.

DISCUSSION:

Union Carbide describes an "extreme case" event as a situation in which 1) the MIC in one of the underground storage tanks is contaminated with water at the limit of solubility at ambient conditions, 2) the refrigeration and back-up refrigeration systems of the tank have failed, and 3) it is not possible for some mechanical reason to transfer the liquid MIC to the scrubber for destruction.

Union Carbide chose as their "extreme case" the contamination of their largest storage tank. This is because, all else being equal, the larger the tank the greater the potential hazard. Within the Institute plant there is a second MIC storage location, a derivative production site, with one (smaller) tank and a smaller emergency scrubber followed by a flare. The same design philosophy was followed at this second scrubber as was followed at the larger scrubber analyzed in detail in this chapter and the conclusions reached in the examined "extreme case" apply to the smaller derivative storage tank and scrubber.

It should be noted that this "extreme case" event, though highly unlikely, is still not the worst case that could occur. For example, it would be possible, although even much more unlikely, that more than one tank could be contaminated at the same time, or that a tank could be contaminated by caustic or other material, which would react faster than water.

A caustic scrubber and a flare are used to control relief valve discharges. The scrubber neutralizes the discharges by breaking them to carbon dioxide and urea compounds and renders them harmless; the flare burns any discharge that might escape neutralization in the scrubber.

Sodium
Ca.bon

The first step in determining whether the scrubber and flare are adequately designed is to calculate the maximum rate at which gas could be discharged from the storage tanks during an "extreme case" event. This calculation is done by computer model developed by Union Carbide which performs a heat balance and calculates the temperature and pressure resulting from simultaneous trimerzation and MIC-water reactions. Two kinetic parameters -- the activation energy and the frequency factor -- and the heats of reaction are required to determine the rate for each of these reactions. Union Carbide has determined the kinetic parameters experimentally.

1. Scrubber design. The answers to four questions help determine the adequacy of the scrubber design:

   a. Will the scrubber flood at the maximum off-gas rate expected? Flooding occurs when the gas flow rate to the scrubber is so high that it prevents the caustic scrubbing solution from flowing down through the packing and reacting with the MIC. The scrubber flood point is calculated from the dimensions and shape of the scrubber packing and the ration of liquid to gas flow rates through the scrubber. It reflects the maximum gas flow at which the liqluid can no longer pass downward against the rising gas. SP

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   b. Is the caustic rate (in pounds per hour) and the amount of caustic available (in pounds) enough to control the peak MIC emission rate and the total MIC emission? This calculation is based on the stoichiometry of the reaction and a material balance.

   c. Can the caustic-MIC reaction take place without an excessive temperature rise which would decrease scrubber efficiency? If the scrubber gets too hot, the scrubbing solution can boil and the chances of flooding are increased. This calculation is based on heats of reaction and dilution and heat balance.

   d. Will the MIC vapor and the caustic solution stay in contact with each other long enough for the neutralization reaction to be completed? This depends on the number of transfer units in the scrubber. (A transfer unit expresses the relative difficulty of absorbing a gas with a given liquid. It is based on measurements of absorption efficiences at varying liquid flow rates and varying inlet gas concentrations with the given scrubber packing. The nunber of transfer units can be related to removal efficiency.) SP The calculation requires experimental data which Union Carbide has developed by testing another scrubber at its plant in Woodbine, Georgia.

An examination of all of the above factors shows that the scrubber is larger than required to control the calculated maximum storage tank off-gas. Estimated control efficiency is calculated at over 99.9 percent.

2. Flare design. Steam assisted flare combustion efficiencies depend primarily on the heat content of the combusted gas and the exit velocity from the flare. In "extreme case" conditions, the maximum off-gas would be controlled by the scrubber, with less than one tenth of one percent going to the flare for final cleanup. In conditions even worse than this, if the scrubber were out of commission, the entire maximum off-gas release could go to the flare.

   Even under the latter conditions, the gas mixture, in the flare conforms to the EPA ~~guidelines~~ for minimum heat content and maximum exit velocity to meet 98 perscent combustion efficiency.

SR

CONCLUSION:

The scrubber and flare are each capable of controlling the described "extreme case" discharge from the storage tanks. The scrubber alone could reduce emissions by 99.9 percent; the flare alone, by more than 98 percent. As a result, the total estimated emissions of MIC with both the flare and scrubber operating, under the "extreme case" is less than 10 pounds per hour. These reductions will be adequate to protect public health and the environment. During normal operation, both devices operate in series, with the flare combusting any gas not neutralized in the scrubber.

SR

99.9
Scrubber

Flare

60,000 #/hr
.001

= 60
.02
1.20

= 1.2/hr

60,000
.02
1200.00

1200 #/hr

Chapter Four

Safety Program

PURPOSE:

To determine if Union Carbide's safety programs are adequately designed to 1) prevent a release of MIC into the atmosphere, and 2) minimize any chance of public harm should such a release occur.

DISCUSSION:

1. Engineering/instrument design. The task force felt that equipment associated with preventing and/or controlling MIC emissions into the atmosphere should: a) provide ample warning of any malfunction or runaway reaction, b) be redundant, i.e., have back-up, and c) initiate corrective actions through alarms or other systems. The following information addresses these criteria for all critical instruments and equipment.

Table 1

Engineering/Instruments Associated with Safety Systems

	Equipment	Purpose of Equipment	Redundancy	Warning System
1.	Temperature sensors for MIC storage tank	One of the first indicators of a reaction which could become a runaway reaction is a temperature rise in the storage tank since water contamination initiates an exothermic reaction.	Yes	Each thermocouple sets off an alarm if the temperature reaches 2°C. If the temperature continues to rise, another alarm is set off at 5°C. The alarms are in the control room.
2.	Computer software to monitor rate of temperature rise in storage tanks	Some temperature fluctuation is normal, however, water contamination would cause a greater rate of change than normal.	Yes	Each thermocouple sets off an alarm if the rate of temperature change is greater than 0.5°C/hour. The alarm is in the control room.
3.	Pressure monitors in storage tanks.	If a reaction which could become a runaway reaction were to begin, another indicator would be a rise in tank pressure due to increased temperature and reaction by-products.	Yes	Both pressure sensors are set to start alarms if the tank pressure reaches 2 psi and 10 psi. The alarm is in the control room.
4.	Liquid Level Monitors for Storage Tanks	The liquid level monitors prevent overfilling the storage tanks.	Yes	The liquid level indicators are connected to alarms and also have an automatic shutdown for the feed and recirculation lines with each tank. The alarm is in the control room.

Table 1

Engineering/Instruments Associated with Safety Systems

	Equipment	Purpose of Equipment	Redundancy	Warning System
5.	Refrigeration System ~~for~~ Storage Tanks	It is important to try to keep stored MIC at low temperatures since the reaction rate of MIC is dependent on temperature. Increased refrigeration is one of the first corrective actions taken if contamination is suspected.	Yes	Not Applicable
6.	Devices to assure that flare is always operating: -dual pilot lights -dual thermocouple flame detectors -automatic pilot relight -manual relight system -temperature interlock with scrubber automatically actuates emergency gas	The flare is one of the critical control devices to minimize MIC losses to the atmosphere if an uncontrolled reaction were to generate large amounts of MIC vapors and gases from the storage tanks. Therefore, it is important that the flare always be in operation and these devices are designed for that purpose.	Yes (for ignition systems and back-up gas supplies)	Alarm systems in control room

Table 1

Engineering/Instruments Associated with Safety Systems

	Equipment	Purpose of Equipment	Redundancy	Warning System
7.	Safety Valves for storage tanks	The safety valves on the storage tank relieve the build-up of pressure by venting the gas to the scrubber ~~and~~ flare that results from an uncontrolled reaction. The safety valves have been redesigned and replaced so that the release of MIC gases would be better controlled by the scrubber and flare. In addition, the valves can be manually operated with an air operated remote control system which can over-ride normal operating conditions in case it is needed. This operation would be performed from the control room. The valves are also equipped with rupture disks to prevent back-flow of caustic to the valves and tanks.	There is only one safety valve per tank. However, manual operation, capability of liquid disposal to scrubber, and frequent inspections add to the reliability of the safety valves.	(1) pressure transducer between safety valve and rupture disk would show increased pressure
8.	Emergency Vent Gas Scrubber	This equipment is designed to neutralize MIC vapors or liquid if they were to be released or pumped from the storage tanks. Certain design changes to increase the capacity for neutralization of MIC have been made. The scrubber is continuously running.	(1) Duplicate circulation pumps for scrubber (2) Additional caustic storage capacity (3) Access to reserve caustic	(1) High caustic temperature activates an alarm in the control room and converts the caustic circulating system to a one-pass mode. Additional caustic is added. (2) Pump motor alarm would indicate malfunction of scrubber caustic circulation system.

Table 1

Engineering/Instruments Associated with Safety Systems

Equipment	Purpose of Equipment	Redundancy	Warning System
9. Utilities: -electric -instrument air -cooling water	To provide power to run the equipment and critical instruments.	All utilities have back-ups. Back-ups include: -steam driven pumps -alternative fuel sources -nitrogen for instrument air -separate electrical substations -stand-by generators	Not Applicable
10. MIC Transfer Lines: -pumps -check valves -low-flow shut-offs -nitrogren purging for clearing and drying lines	The MIC transfer lines are designed with certain safety features to prevent pump overloads, back-flows, low flows. The transfer lines have automatic shut-off valves to prevent backflows to the tanks and to stop continued flow in case of transfer line rupture.	Not Applicable	Pumps have amp meters and alarms for overload or failure.
11. Control valve fail-safe system	All control valves would remain in the most conservative position regarding safety in case of electrical failure	N/A	Valve positions indicated in control room

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2. Management accountability system. Proper equipment is not enough. It must also be operated and maintained properly. This is ultimately a management function. The following presents some highlights of the management accountability system in place at Institute.

- A computerized reliability maintenance (RM) program provides for scheduled inspection and replacement of critical equipment. The system establishes accountability for assuring that the program is followed.

- All storage tank temperatures, pressure, and liquid levels are displayed in the control room and simultaneously logged by a computer system, providing documenttion of read-outs of critical instruments. The operation is periodically field checked.

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- Various management reports are required to document preventive maintenance. All maintenance on instrumentation for the MIC unit has just been completed as an additional safety precaution to ensure the integrity of instrumentation. Critical instruments are checked, at a minimum, every 12 months and critical alarms every 6 months for the storage tanks.

- As part of a preventive maintenance program, all major equipment is inspected on a one to three year cycle, depending on usage. Specific testing and inspection programs for process vessels (storage tanks) and safety relief valves are in place.

3. Documented operating procedures. Documented operating procedures, usually referred to as standard operating procedures (SOP), detail specific instructions for operating personnel. They define corrective actions in case certain instruments indicate the possibility of a reaction which, if unattended, could cause a runaway reaction.

   Standard operating procedures for the storage tanks require certain corrective actions if the temperature or the pressure in the tanks reach a certain level. These actions include additional refrigeration pumping of liquid MIC to the base of the scrubber to neutralize the MIC with caustic, and notification of plant management.

   After use of process equipment and transfer lines, standard operating procedures call for isolating equipment to be cleaned with water and nitorgen purging to remove any water vapor before putting into service. This reduces potential for water contamination.

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Standard Operating Procedures call for strict administrative controls (i.e., plant management approval) for removing the scrubber, flare, or refrigeration system from service for maintenance, either planned or unplanned. In a planned shutdown, no MIC is to be stored. Standard operating procedures also require that, if the flare or scrubber malfunction for more than 30 minutes, MIC production must cease and efforts must be taken to reduce MIC inventory.

4. Training. In the first stage of training, operators must take a two-week (80 hour) training program in hazards of contamination, ways to clean equipment and ways to return equipment to service. They are tested at the completion of the program.

   The next stage of training is a maximum of seven days of on-the-job training under the supervision of an experienced operator working exclusively with the trainee. Additional on-the-job training follows, the length of of time depending on the system involved. Trainees are given several exams during this period, culminating in a system walk-through exam with the trainee supervisor, system supervisor, and training coordinator. Trainees who do not qualify may retrain for half the original period of time. If they still fail to qualify, they are terminated or transferred from the MIC unit.

CONCLUSION:

Equipment maintenance procedures, instrument maintenance procedures, training, documented operating procedures, and management accountability systems are in place. Success of these procedures and systems depends on close company management overview to assure that these procedures are followed and retraining is given as necessary.

Various regulatory agencies will conduct periodic inspections to assure that critical equipment is maintained and that all procedures and systems are followed.

All alarms are located in the control room. The added alarm located in the shift administrator's office provides an additional alert system.

And

Chapter Five

Detection and Notification of Emissions, Spill, an Releases

PURPOSE:

To evaluate the instrumentation and systems in place at the Institute, West Virginia plant to detect leaks of MIC or the presence of a condition which might result in a leak, and ~~for providing~~ to provide notification of such a leak or condition.

DISCUSSION:

1. Detection of potential runaway reactions or malfunctions of control equipment.

   a. Temperature and pressure monitor. The process control and monitoring system on the MIC production and storage units serves as the "first line of defense" for detection of conditions, such as contamination, that could result in possible leakage, spillage, or emission of MIC. A recent modification in the process monitoring system now allows the rate of temperature change to be tracked. In addition, continuous liquid level sensors, each with a preset alarm level, detect unexplained changes in volume in each of the tanks and prevent overfilling.

      A series of redundant temperature and pressure sensors in the system give both visual and computer readouts on conditions within the storage and handling system. If Standard Operating Procedures for the maintenance, calibration, and use of these monitors are followed they will successfully indicate the potential for a major release of MIC. Further, they should give sufficient warning to allow mitigating action to be taken and to allow company notification of Federal, State and local authorities.

   b. Flare Monitoring. Dual thermocouple flame detectors on the MIC flare serve two functions. They are wired into an automatic pilot relight system to assure that if the pilot or flame goes out, immediate steps are taken to relight it. They are also wired into alarm systems to notify the MIC operators and the control room that the flare is out.

   c. Scrubber Monitoring. The continued operation of the scrubber is monitored by instrumentation that indicates the level, the flow, pressure, and the temperature of caustic in the scrubber and whether or not the pumps are operating. In the event of a failure in caustic flow, which would be detected by the caustic flow monitor, MIC will be directed from the scrubber to the flare. If the packed column floods and channeling of vapor occurs, the temperature as detected by the thermocouples, will not rise as much as expected, therefore, this is considered another indication of scrubber malfunction or failure.

2. Detection of MIC releases.

a. Operator Attention. During normal operating conditions, respirators or gas-tight goggles are not required because no MIC is released to the air. The operators' eyes and olfactory systems are, therefore, sensitive indicators of even a trace of MIC release to the air.

If standard operating procedures are followed, then, in the event that MIC is detected, the area is cleared and the foreman is notified. He will notify plant management and initiate mitigating action.

b. Air Monitoring System. After evaluating several air monitors that could serve as back-up release detectors of low levels of MIC, Union Carbide selected a flame ionization detector-process gas chromatograph (GC) capable of analyzing up to 16 sampling points in a sequence. Each analysis of MIC in air at a 0.1 parts per million (ppm) detection limit takes one and one-half minutes. The full sequence at 16 points therefore takes approximately 24 minutes.

Although the system is in the first stages of utilization with many aspects not yet finalized, discussions with Union Carbide have revealed that the system might be modified to add more sample points, or that other detector systems might be used, if necessary.

The system does have shortcomings, the most important of which are that Union Carbide has limited operating experience using it for MIC and there is no assurance, at present, that the system can achieve the claimed detection level of 0.1 ppm. However, even with these limitations, it it should be viewed as an attempt by Union Carbide to advance the state-of-the-art in leak detection.

c. Air Dispersion Modeling System. Union Carbide has recently installed a site specific air plume dispersion modeling system known as SAFER®. The system is a minicomputer-based mathematical model with real time data input of wind direction, wind speed, and other weather data from the plant's meteorological tower. This data is used by the computer to predict concentration and location of a major air release.

An operator enters such data as the location of the leak, size of the leak, and other parameters. The computer calculates the direction of the plume, rate of travel of the plume, and displays the plume location on a map of travel of the plume, and displays the plume location on a map of the area around the site by using a color video display. Critical impacted areas in the community (schools, hospitals, etc.) are highlighted. Notification and response actions can therefore be arranged in advance of the plume impact with ~~these institutions~~.

the community

Other scenarios of major releases, including worst case scenarios, can be simulated and appropriate actions arranged in advance with local authorities.

Union Carbide has not yet finalized standard operating procedures for use of the system during an emergency, nor, aside from some small smoke bomb observations, has it performed calibration of the air dispersion model, but these will be completed by May. Based on EPA experience with air dispersion models, several other actions should be taken as soon as practical including: model verification to assure that predictions are within the desired accuracy range; training of response personnel to assure that they understand the limits of the model's prediction; ~~development~~ of an integrated contingency plan to assure that predictions triggered proper response actions; and a community information effort to proper response actions; and a community information effort to assure that the public understands the system. Even before these actions are completed the SAFER® System will still be useful in determining worst case scenarios that can be used to aid in response decisions.

M.x

3. Notification.

a. Notification of Local Authorities. If standard operating procedures are followed, the foreman would be informed of any abnormal conditions in the process and storage areas, and an in-plant toxic gas alarm would be sounded if there is a possibility, no matter how uncertain, that a leak has occurred. At that alarm, the shift administrator is informed, and decides whether the incident is serious enough to warrant notification of off-site authorities. In addition, Union Carbide has agreed to initiate the following off-site notification procedures:

- Within a period of two (2) hours, when and if all available refrigeration to MIC storage tanks is inoperable (but only if MIC is in storage);
- Immediately, when and if the temperature of MIC in a storage tank reaches 5°C and temperature cannot be reduced by 1°C within a period of fifteen (15) minutes;
- Anytime the scrubber and flare are concurrently out of service for more than thirty (30) minutes.

Union Carbide plans to continue to meet with state, county, and Kanawha Valley Emergency Planning personnel to revise and update applicable contingency plans.

is released

b. Notification of the Federal Government. If a reportable quantity of a hazardous substance leaves the plant site, Union Carbide must notify either the National Response Center or the EPA Regional Office.

CONCLUSION:

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Instrumentation, detailed standard opeating procedures, and well-trained operators and supervisors make it unlikely that any but a minute release of MIC could occur without being detected. Improvements made in notification procedures will save valuable time and help eliminate confusion in the event of an MIC release.

Chapter Six
Contingency Plans

PURPOSE:

To determine if contingency plans that exist or are being developed provide for an adequate response by local, county, state, and federal communities to an MIC release in Institute, West Virginia.

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DISCUSSION:

EPA involvement in reviewing existing contingency plans was initiated through agency chairmanship of the Regional Response Team (RRT). Attachment two presents the results of the review.

To implement the recommendations of the RRT, EPA met with officials of the Federal Emergency Management Agency, the West Virginia Office of Emergency Services, and the West Virginia Department of Natural Resources. Participants agreed that:

- ° The County emergency management agency should receive first notice of a release and should assume initial command of a response.

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- ° The responsible party should notify, in additon to the Federal Government, the County emergency management agency as soon as it knows of the release into the environment of a hazardous substance in an amount equal to or greater than the reportable quantity defined by federal regulation.
- ° These two recommendations are being implemented expeditiously.

These issues and others have been discussed and agreed to by Union Carbide officials during recent task force meetings.

A number of events are now taking place which will serve to improve the Kanawha Valley's preparedness in the event of a hazardous substance incident. Some of these are mentioned in the preceding chapter. Other significant events include:

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- ° Meetings between state and county officials to resolve problems in the areas of notification and responsibility. Existing State code requirements are being evaluated to determine if modifications are necessary to further clarify these issues.
- ° Incorporation of additions to the West Virginia Hazardous Materials Emergency Response Plan to address RRT comments, particularly in the areas of county responsibility/authority and state/EPA coordination regarding Superfund.

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cap

- Agreement between the West Virginia Office of Emergency Services and the Kanawha Valley Emergency Planning Council that notification will be to the county, which will be responsible for public messages and evacuation decisions. Discussion of appropriate stages of notificatio by industrial managers is planned for future meetings. sp

- Revision of the Kanawha Valley Emergency Planning Council's contingency plan to insure that it is compatible with local, county, and state requirements. cap

- Installation by Union Carbide of a more effective warning siren to alert surrounding communities that an announcement is being made by county officials on the emergency broadcast system.

CONCLUSION:

As the RRT has indicated, contingency planning is necessarily a dynamic process requiring continuous revision and updating. The RRT comments are being actively considered, and significant progress is being made in preparing changes to all relevant contingency plans. The major immediate issues needing resolution have been adequately addressed in verbal agreements between the State, County and industry. Other issues raised by the RRT are being addressed in a draft update to the West Virginia Hazardous Materials Emergency Response Plan currently under review by the State. Changes to local government and industry contingency plans are scheduled to follow.

Chapter Seven
Handling and Storage for Transportation

PURPOSE:

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To determine if steps are being taken to reduce the danger of a MIC release during transport.

DISCUSSION:

Prior to the Bhopal incident, Union Carbide shipped MIC to customers in rail tank cars, portable tanks, and drums. The MIC was transferred from one container to another via stainless steel hoses. All operators working with MIC were required to wear self-contained breathing apparatus and to avoid all contact with MIC vapor and liquid. Specsific loading and handling instructions are detailed in their SOP. sp

Since the Bhopal incident, Union Carbide says it has no intentions of shipping MIC in any form at the present time, but that it may do so in the future if required to contractually. Should that be the case, the company says it will ship MIC only in portable tanks which can be hauled on a flatbed truck and that it will no longer ship MIC in rail tank cars nor store MIC in tanks at transportation/distribution points. Thus a major storage area which held much of the plant inventory of MIC before the Bhopal incident is now eliminated. As a safety procedure, the tanks are sampled before filling and kept on site for 24 hours to assure that no adverse reactions are occuring. portable

Since Bhopal, the U.S. Department of Transportation (DOT) has issued stricter regulations for the shipment of compounds which exhibit high acute air toxicity such as MIC.

CONCLUSION:

The U.S. DOT will be further reviewing the shipping and handling procedures submitted to the task force by Union Carbide Corporation.

Documents Reviewed by the Task ~~Group~~ Force

1. Methyl Isocyanate: Institute Plant Start-up Review (UCC 1)
2. MIC Safety Valve Design Considerations, March 18, 1985 (UCC 2)
3. Reaction and Refining System, Safety Valves (UCC 3)
4. MIC Vent Scrubber Design Considerations, March 18, 1985 (UCC 4)
5. MIC II Emergency Vent Scrubber Calculations, March 19, 1985 (UCC 5)
6. Flare for MIC II Unit (UCC 6)
7. Flare (UCC 7)
8. MIC Storage Tank Process Dynamics (UCC 8)
9. MIC Storage Tank Instrumentation (UCC 9)
10. Prevention of Backflow from Emergency Vent Scrubber to Emergency Vent Header (UCC 10)
11. Back-up Utilities (UCC 11)
12. MIC Air Monitor (UCC 12)
13. Additional Questions (UCC 13)
14. Governmental Agency Questions, March 14, 1985 (UCC 14)
15. Results of Methyl Isocyanate Scrubber Performance Tests Performed on March 16, 1978 and April 12, 1978 at the Woodbine Carbamoylation Unit (UCC 15)
16. Bhopal Methyl Isocyanate Incident Investigation Team Report, March 1985 (UCC 16)
17. In-Plant Methyl Isocyanate Network (UCC 17)
18. Letter from H.J. Karawan to Greene Jones, March 25, 1985
19. Letter from H. J. Karawan to Greene Jones, March 26, 1985

20. Testing and Inspection of Instruments, SOP

21. Testing and Inspection of Process Vessels, SOP

22. Pressure Testing of Process Equipment, SOP

23. Safety Relief Device Procedure, SOP

24. MIC Operator Training, SOP

25. RM Program, SOP

26. Administrative Controls, SOP

27. Local Toxic Gas Alarm Procedure, SOP

28. MIC No. 2 Unit Safety, Reactive Chemical Data, SOP

SP

29. MIC Distrubution Procedures, September, 1984

30. Letter from Robert Oldford, President, U.C. Agricultural Products, Co., Inc. to Greene Jones, EPA dated April 10, 1985

31. MIC Storage at Methomyl/LARVIN® Unit

ATTACHMENT ONE

BHOPAL METHYL ISOCYANATE INCIDENT

INVESTIGATION TEAM

REPORT

MARCH, 1985

UNION CARBIDE CORPORATION
DANBURY, CONNECTICUT

TABLE OF CONTENTS

SUMMARY

The Bhopal Methyl Isocyanate Incident Investigation Team included seven engineers and scientists who were charged with assisting in the safe disposal of the remaining methyl isocyanate (MIC) at the Bhopal Plant, investigating the incident and determining its probable cause. The team spent 24 days in India and continued its work for a period of more than two months thereafter.

The team was able to inspect many relevant written documents in India, but was restricted by the Indian Central Bureau of Investigation from interviewing the Union Carbide India Limited (UCIL) employees directly involved. Interviews were held with the Works Manager and the MIC Production Manager and informal discussions were held with a few witnesses to the event.

The team was able to obtain core samples of the residue in Tank 610, the MIC storage tank involved in the incident, as well as samples of the methyl isocyanate (MIC) in some other tanks and associated lines. These samples were analyzed by UCIL and Union Carbide Corporation (UCC) research groups. Although the team was not permitted to conduct a detailed examination of Tank 610 and associated piping, through extensive experimentation, the UCC research groups succeeded in replicating reactions which yielded residues with the same major components found in residue from Tank 610. The team examined many possibilities, including those deemed remote or unlikely, and arrived at a hypothesis for the event in which it has a high degree of confidence.

Early on December 3, 1984, the safety valve on Tank 610 opened as a result of a chemical reaction in the tank. At the time, the tank contained approximately 90,000 pounds of stored MIC. The team believes that the safety valve remained open for approximately two hours before it reseated and during that period in excess of 50,000 pounds of MIC in vapor and liquid form was discharged through the safety valve.

This incident was the result of a unique combination of unusual events. The team's hypothesis is that the reaction in the tank occurred when a substantial amount of water was introduced into Tank 610. Through an extensive amount of experimentation, it appears that the substances found in the Tank 610 residue were produced by the reaction of MIC with large amounts of water, higher than normal amounts of chloroform and an iron catalyst at a high reaction temperature. It was concluded that the reaction which occurred in Tank 610 had to involve all of these factors. The exothermic reaction between the water and the MIC raised the temperature in the tank. Since the MIC in the storage tank was at ambient temperature, the rates of reaction and temperature rise were rapid. A concurrent exothermic trimerization of MIC was catalyzed by iron resulting from corrosion of the tank walls due to the high temperatures produced by the reacting mixture. The laboratory work indicates that 1,000 to 2,000 pounds (120 to 240 gallons) of water would have been required to account for the chemistry of the residue. The source of the water is unknown, but the report discusses possible means by which water could have entered the tank.

1.0 INTRODUCTION

This report provides the knowledge and understanding that the investigation team has at this time of the Bhopal Methyl Isocyanate (MIC) incident that occurred on December 3, 1984. The report is organized into five sections following this introduction.

Section 2.0, "Background," presents how the investigation team was organized, the investigative process it used, the types of information it gathered and the restrictions it encountered in doing its work.

Section 3.0, "The MIC Process," provides the reader with an overview of the process and details of items of equipment relevant to the incident.

Section 4.0, "The Event," describes the incident, tank residue sampling and quantity, and disposal of the MIC remaining after the incident.

Section 5.0, "Chemistry of the Event," presents the composition of the tank residue, the chemistry by which the residue components could be formed, the experiments used to replicate the chemistry and the probable sources of the components which caused the chemical reactions.

Section 6.0, "A Hypothesis for the Event," describes the team's hypothesis for the event.

2.0 BACKGROUND

The Bhopal Methyl Isocyanate (MIC) Incident Investigation Team convened in India at 10:30 AM on Thursday, December 6, 1984, for its first meeting. The team included seven engineering and scientific specialists who worked directly on the task. In addition, the team was assisted by many other UCIL and UCC technical personnel. The team had access to the UCIL Bhopal plant starting at 3:30 PM on December 7, 1984. The team worked in India 24 days and then continued its work in the United States from January 2, 1985, until the completion of this report.

The objectives of the team were to:

- Assist in the safe disposal of the remaining MIC.

- Investigate the incident and determine its probable cause.

The first objective required 15 days and was completed on December 22, 1984. The team then concentrated on investigating the incident which took more than two months thereafter.

The team was organized into two subteams:

(1) The Process Information Subteam had accountability for tracking down and reviewing written records, inspecting equipment and gathering information from interviews. The team was permitted to inspect many of the relevant documents.

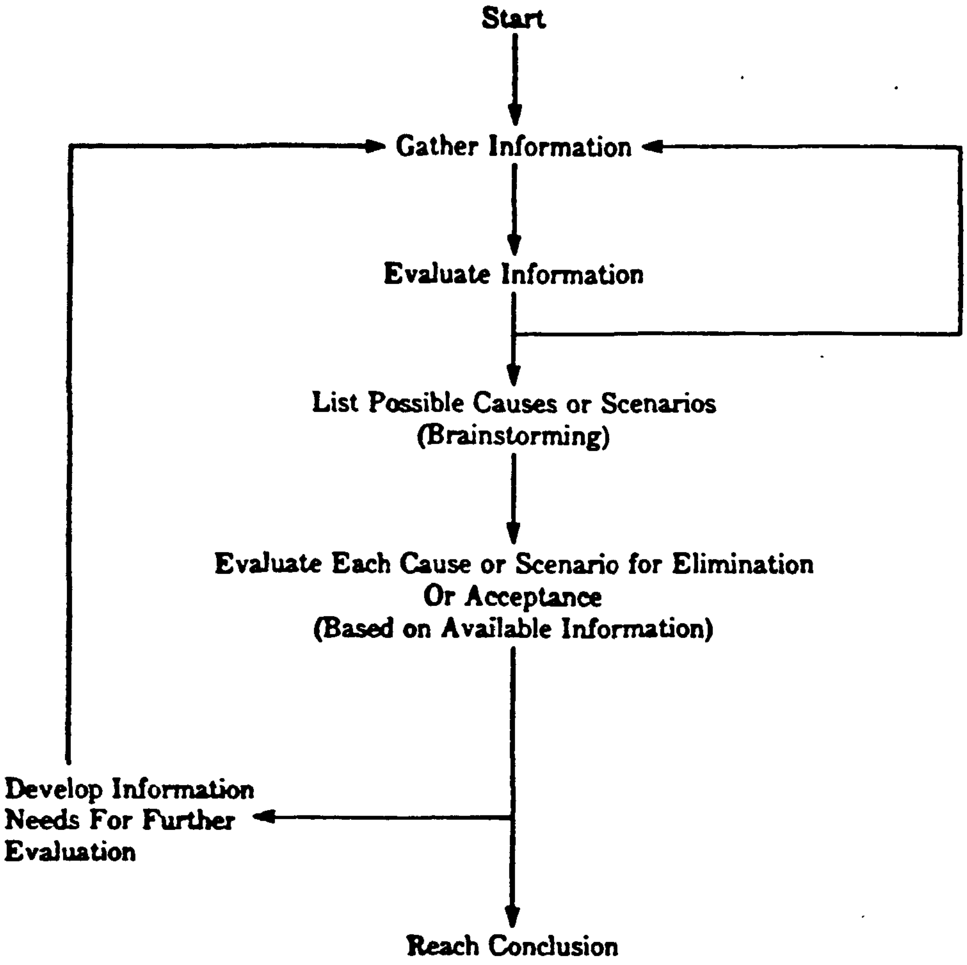
To date, the team has not been permitted to interview the UCIL employees directly involved in the incident. This restriction has been established by the Government of India Central Bureau of Investigation which is also investigating the incident. Consequently, the description of the event in this report is constructed from interviews with the Works Manager and the MIC Production Manager. They arrived at the plant after the event and developed their information from informal discussions with personnel directly involved. Various team members also had informal discussions with a few first-hand witnesses as they worked together during the processing of the MIC remaining in the plant after the event. Information gathered from these informal discussions is also included in the description of the event.

(2) The Chemical/Physical Information Subteam had the task of defining the physical and chemical nature of the event. This was done by analyzing samples of the process streams and residues to determine their composition. This subteam inspected relevant plant quality assurance laboratory records and while in India worked with the UCIL research group. The team was permitted to obtain core samples of the residue in Tank 610, the tank involved in the incident. Since returning to the United States, they have been working with UCC research groups to replicate the reaction/event to give a residue with the same major components as that obtained from Tank 610. The team also sampled and analyzed the MIC in Tanks 611 and 619, in the MIC refining still product line, in the transfer line to the Derivatives Unit, in the charge tank at the Derivatives Unit and in drums. However, various restrictions by Indian government authorities and courts have resulted in the team not being able to:

- Open and inspect Tank 610 and its piping.
- Do further sampling and analysis on the contents of the tank, other equipment and piping.

The investigation methodology used by the team was a carefully disciplined, "no-stones-unturned," approach. During the initial phase, the team gathered available information that might be relevant to the incident. Because of the need to identify all factors, every effort was made to avoid premature dismissal of any possible explanation or contributor. This general approach is illustrated in the following diagram:

Problem Solving Approach



A key element of problem solving was to identify many possibilities, including those deemed remote or unlikely. Each possibility or scenario was examined in the light of information available to the team. Some of the possibilities were ruled out at that point, but in other cases additional information was required. The required information was defined and appropriate assignments were made to obtain it. This led to an iterative process of examining, gathering information and re-examining that was repeated many times. Consequently, each possibility or scenario was rigorously studied, and eliminated only after exhaustive checking against a slowly growing number of accepted facts. In addition, the team periodically stopped its deductive process to explore any new possibilities that may have evolved.

3.0 THE MIC PROCESS

This section contains an overview of the MIC process and a description of four items of equipment associated with this event: the MIC refining still (MRS), the MIC storage system, the vent gas scrubber (VGS) and the flare tower.

3.1 Overview

This overview contains three parts: (1) the two basic chemical equations used in producing MIC, (2) a simplified block diagram of the MIC process, and (3) a word description of the MIC process.

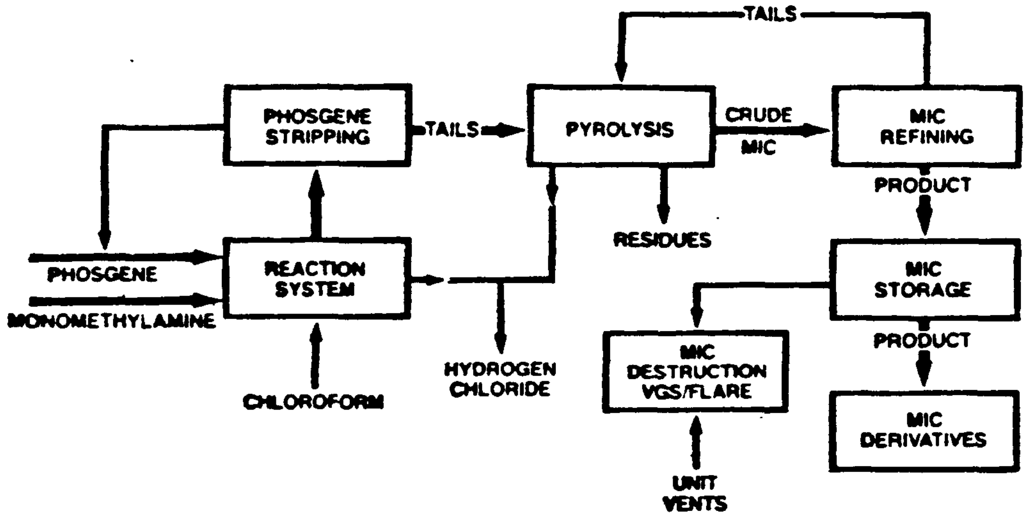
Chemical equations for MIC production are given below:

$$(1)\quad \underset{\text{Phosgene}}{COCl_2} + \underset{\substack{\text{Monomethylamine}\\ \text{(MMA)}}}{CH_3NH_2} \longrightarrow \underset{\substack{\text{Methylcarbamoyl}\\ \text{Chloride}\\ \text{(MCC)}}}{CH_3NHCOCl} + \underset{\substack{\text{Hydrogen}\\ \text{Chloride}}}{HCl} + \text{Heat}$$

$$(2)\quad \underset{\text{(MCC)}}{CH_3NHCOCl} \xrightarrow{\text{Heat}} \underset{\substack{\text{Methyl Isocyanate}\\ \text{(MIC)}}}{CH_3NCO} + HCl$$

Simplified block diagram is shown below:

MIC PROCESS



Description of the MIC process follows:

The raw materials used to make MIC are monomethylamine (MMA) and phosgene. Phosgene is produced on-site by reacting chlorine and carbon monoxide (CO). CO is produced by an adjacent production facility within the plant. The MMA and chlorine are brought in by tank truck from other parts of India, stored in tanks, and used as needed. Chloroform is used as a solvent throughout the process.

A vapor phase reaction system converts the phosgene and MMA to methylcarbamoyl chloride (MCC) and hydrogen chloride (HCl). An additional amount of phosgene is used to assure conversion of all the MMA fed.

The reaction products are then quenched with chloroform and fed to the phosgene stripping still (PSS) where the unreacted phosgene is removed and recycled. The tails or bottoms from the PSS are then fed to the pyrolyzer to achieve separation of the MIC from the HCl.

The MIC refining still is fed from the pyrolyzer condenser. This feed stream contains mostly MIC, MCC, chloroform and small amounts of residues. MIC is separated from the chloroform in the upper part of the still. MCC, chloroform, residues and some MIC go out the bottom of the still and are recycled back to the process. This distillation operation is discussed in more detail in Section 3.2. The refined MIC is taken from the overhead of the still to the mounded, type 304 stainless steel storage tanks. MIC is transferred from these tanks to the MIC derivatives units as needed.

The materials of construction throughout the process are chosen to resist corrosion. These include materials such as Hastelloy [*], nickel, Inconel [*], stainless steel, glass, Teflon [*], Karbate [*] and Haveg [*].

3.2 Equipment Description

This section details four items of equipment: the MRS, MIC storage system, VGS and flare tower.

MIC Refining Still (MRS)

The MRS is a 45-tray column used in the final step of the production of MIC. The purpose of the MRS is to purify MIC by separating it from chloroform, MCC and residues. The key operating conditions that control the purity of the MIC are temperature, pressure, reflux ratio and heat input. Instrumentation is provided to properly control the column operating conditions.

Maintaining the temperature and pressure is critical to the quality of the material produced. An increase in temperature above normal operating limits can lead to an increase in impurities beyond specification limits.

A high reflux ratio of approximately 20 to 1 is required for this separation. Low reflux ratio and high product rate can result in impure material being produced.

Excess heat input causes an overload or flooding condition in the still which allows impurities from the lower sections of the column to be driven overhead and possibly enter the storage tanks.

MIC Storage System

Refined MIC can be stored in two of three horizontal, mounded, 15,000 gallon tanks. The third tank is used for emergency storage of MIC and for temporarily holding off-specification MIC prior to reprocessing. The contents of tanks are circulated through heat exchangers cooled by a 30-ton refrigeration system to maintain the MIC at a temperature of about 0°C. Refined MIC is then transferred to Derivatives Units as needed.

MIC that does not meet specification can be returned to one of two locations in the system for reprocessing. If necessary, the MIC can be transferred to the VGS and destroyed.

Instrumentation of the MIC storage tanks includes the following:

- A temperature indicator/alarm that is activated by high temperature.

- A pressure indicator/controller which regulates the pressure in the tank by adding nitrogen or venting vapors to the VGS and/or the flare.

- A liquid level indicator/alarm with high and low level alarm set points.

All the above instruments have indicators at the tank and in the control room. Alarms are audible and have indicating lights in the control room when activated.

The tanks were designed as storage vessels with the following specifications:

- Nominal capacity - 15,000 gallons
- Diameter - 8 feet
- Length - 40 feet
- Material of construction - type 304 stainless steel
- Design pressure - full vacuum to 40 psig at 121°C
- Hydrostatic test pressure - 60 psig
- Cathodic protection to prevent external corrosion
- Mounding of the tanks for puncture protection from outside sources, protection from external fire and as insulation
- Construction in accordance with the ASME code for lethal service vessels
- Additional bolting strength for leak protection provided by using 300 psig rated flanges on process lines and equipment. Screwed piping connections were minimized.

A diagram of the MIC storage tank is shown on the following page.

The MIC storage system includes provisions, procedures and programs for (1) the prevention of contamination, (2) early detection when contamination occurs, and (3) the handling of contaminated material. The provisions, procedures and programs are as follows:

(1) Prevention of Contamination

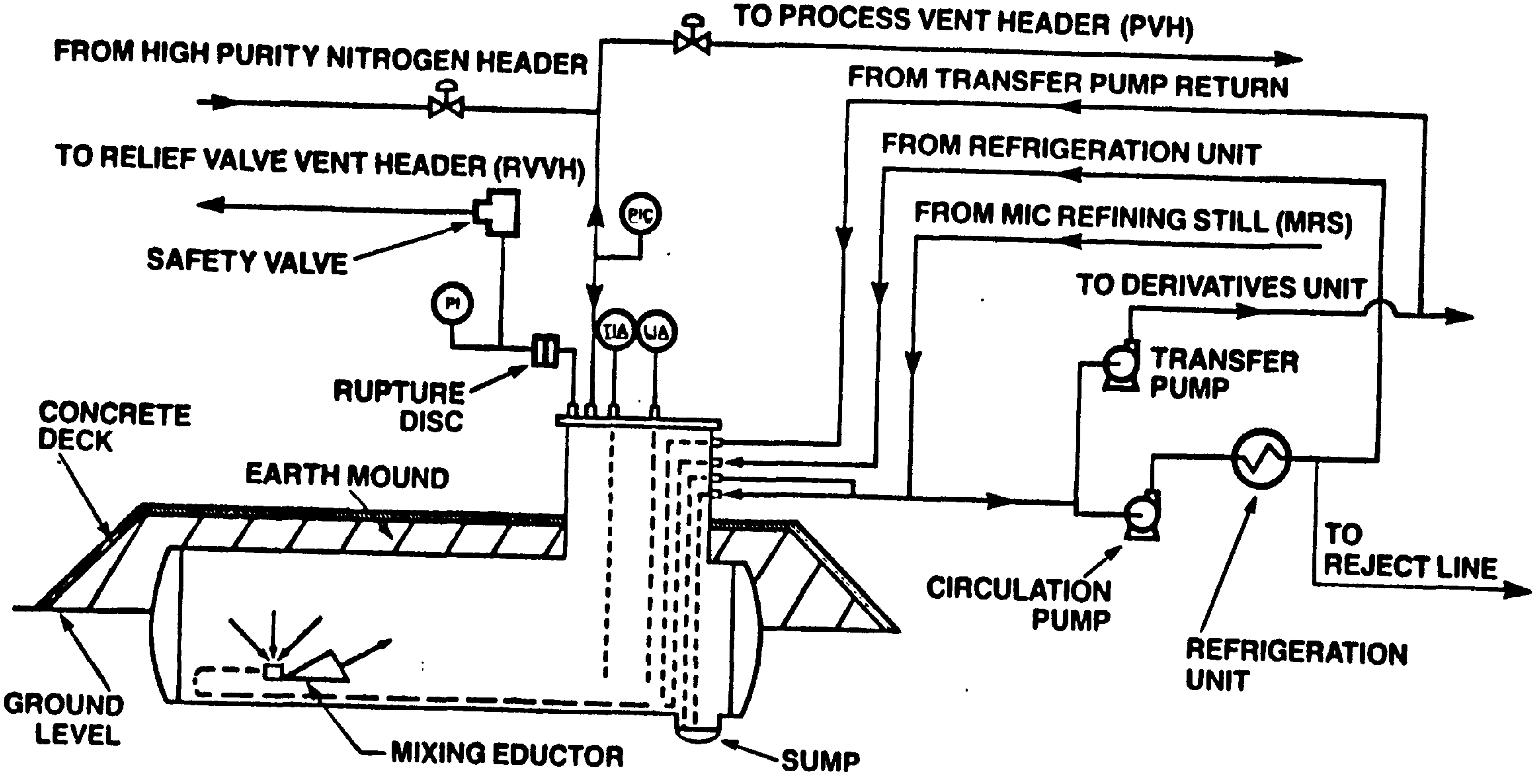
- Storage tanks and associated process lines are dedicated to MIC service and no other materials are permitted in this equipment.

- The material of construction of the tanks and related process piping is type 304 stainless steel, which resists corrosion in this service.

- Each tank has a rupture disc installed to provide a positive seal between the safety valve and the tank. This prevents any materials from backing into the tank from the relief valve vent header. A pressure gauge between the rupture disc and safety valve is used to determine that the disc is intact.

- Nitrogen used for tank instruments, pressure control and purging is dry, high-purity nitrogen. The nitrogen supply is protected with a bank of 450

MIC STORAGE TANK



PI — PRESSURE INDICATOR
PIC — PRESSURE INDICATOR/CONTROLLER

TIA — TEMPERATURE INDICATOR/ALARM
LIA — LEVEL INDICATOR/ALARM

- A storage tank temperature alarm is activated when the temperature is higher than the set point.

(3) Handling Contaminated Material

- A refrigeration system is provided to maintain the stored material at low temperatures which retard reaction rates and allows time for reprocessing or destruction in the case of contamination.

- A reject line is provided so that contaminated material can either be returned to the system at one of two locations for reprocessing, or be destroyed in the VGS.

- An emergency tank is provided to receive off-specification or contaminated material for recycle or disposal, to receive material from faulty equipment, and to provide additional vapor space and cooling capacity in the event of a reaction.

- Versatile arrangements of piping and valves, as well as spare pumps, are provided to transfer contaminated material.

- A safety relief system protects each tank by relieving pressure above 40 psig to the relief valve vent header.

Vent Gas Scrubber (VGS)

The vent gas scrubber (VGS) is a 5'6" diameter packed tower in which all gases entering are contacted with circulating caustic soda solution. The MIC facility has two vent headers which go into the VGS. These are the process vent header (PVH) through which MIC system vents are routed and the relief valve vent header (RVVH) which collects discharges from the MIC facility safety valves. The PVH and the RVVH are connected to the VGS and the flare line with an option to be routed either way. The vent from the VGS can either go to the atmospheric vent or to the flare line.

The VGS system has several functions. First, it handles process vents from the PVH. Second, it has the ability to destroy contaminated MIC in a controlled manner in liquid or vapor form. The VGS is also one element of an integrated system for handling contaminated MIC. Contaminated material can be sent to the MIC process, VGS, flare or moved to the spare storage tank to permit additional expansion and cooling capacity or reprocessing.

Instrumentation for the VGS includes:
- Caustic flow indicator and alarm in the control room. This system will automatically start the spare circulating pump in the case of low flow.
- Remote and local switches to manually start the caustic circulating pumps.
- A pressure indicator in the control room.
- A high pressure alarm audible in the control room.
- Local temperature indicator at the VGS base.
- Local liquid level indicator at the VGS base.

Operating procedures for the VGS include:

- Log and continually maintain the circulating flow of caustic.
- Analyze the caustic strength daily.
- Maintain the caustic strength by the addition of 50 percent caustic from the caustic storage tanks.
- Monitor the VGS accumulator temperature for an indication of a reaction in the VGS.
- Log the VGS pressure every 2 hours and verify correct operation.

Flare Tower

The primary purpose of the flare tower is to burn vent gases from the carbon monoxide unit and the MMA vaporizor safety valve. The flare also burns normal vent gases from the MIC storage tanks, the MRS and the VGS. Vents from the MIC storage tanks can be routed to the VGS or directly to the flare. The flare tower is equipped with a flame-front generator for ease of lighting in the event the flame goes out. A wind shield is in place to ensure the pilot flame is protected from high winds. At the base a seal tank is installed to prevent backfiring in the vent lines.

4.0 THE EVENT

4.1 Description

The following description of the event begins on Sunday, December 2, 1984, at 10:20 PM near the end of the second shift. The description extends through the disposal of MIC inventory at Bhopal on December 22, 1984. It is developed primarily from interviews with the Works Manager and the MIC Production Manager and informal discussions with others, as indicated. Since both the Works Manager and the MIC Production Manager arrived at the plant after the release had stopped, their accounts of the event are based upon their discussions with operating personnel on duty during the event.

Prior to the event, MIC Storage Tank 610 was reported to contain 41 metric tons as determined from plant inventory records. This amount equates to 90,400 pounds or 11,290 gallons. The liquid level in Tank 610 was near 70 percent of capacity, which is below the maximum operating level. This level results in a headspace of 2 feet, 9 inches in the eight-foot diameter tank. It was reported that all valves to and from the tank were closed except for the relief valve line containing the rupture disc and safety valve. The pressure in Tank 610 was later reported by the operator via the Works Manager to be 2 psig on Sunday, December 2, at 10:20 PM. Earlier readings had been recorded to be 2 psig since the second shift on December 1.

Shift change took place at 10:45 PM. At 11:00 PM the control room operator noticed the pressure in Tank 610 was at 10 psig. This pressure was not thought to be unusual because the tank was normally operated at a pressure between 2 and 25 psig. It is not known whether the 2 psig pressure reading observed 40 minutes earlier by the operator on the previous shift had been communicated to the new operator. Corresponding tank temperatures were not available since no tank temperatures were logged.

At 11:00 PM the field operator reported a MIC leak in the structure near the VGS and process filters, but the source of the MIC was not discovered by the operating personnel.

At 12:15 AM on Monday, December 3, the field operator reported a MIC release in the MIC process area. The control room operator looked at the tank pressure again. The reading was 30 psig and rapidly rising. Within moments the pressure was beyond 55 psig (top of scale). He called his supervisor and ran outside to the tank. He heard rumbling sounds from Tank 610, a screeching noise from the safety valve, and felt heat radiating. As he ran back to the control room, he heard the cracking of the concrete over the tank. As soon as he returned to the control room, he turned the switch to activate the VGS. The VGS had been removed from an operating mode to a standby mode on October 23, 1984, after the MIC unit was shut down with a total MIC inventory of 183,000 pounds in Tanks 610 and 611. The return to an operating mode was dependent upon the operator being alerted to a problem and taking prompt action to activate the circulating pump. The flow meter did not indicate that caustic circulation had been started. The operator did not go into the unit to check the pump and verify a flow. Prior to the incident, the flare had been removed from service for maintenance work and was not operating at the time of the incident.

At 12:20 AM, the MIC Production Supervisor notified the Plant Superintendent of the release. The Plant Superintendent, who was in the formulations area, arrived in the MIC Unit around 12:25 AM and found much MIC in the atmosphere.

The timing of the following events are the best recollections of various people during a very active period. At 12:45 AM, the Supervisors Log records that Derivatives Unit operations were suspended because of the high concentration of MIC in the area. About 1:00 AM, a Derivatives Unit operator turned on the Toxic Gas Alarm. Also at about this time, the Plant Superintendent and the MIC operator verified that MIC from Tank 610 was being emitted from the VGS stack to the atmosphere. They turned on the fixed firewater monitors and directed them to the stack and the MIC process area to knock down the MIC vapor as much as possible. In a test subsequent to the event with two monitors in service, water reached beyond the top of the stack. Water streams were also directed on the MIC tank mound and on the relief valve line to the VGS for cooling. Steam came from the cracks in the concrete indicating the MIC tank was hot.

Sometime between 1:30 AM and 2:30 AM, the safety valve reseated, indicating a tank pressure below the 40 psig safety valve setting, and the emission of MIC stopped. The MIC tank and associated piping remained intact throughout the event. This is confirmed by the sub-atmospheric pressure that developed in the tank prior to noon on December 3 as the tank cooled. Nitrogen was later used to raise the pressure in the tank to 7 psig.

The MIC Production Manager reported that Tank 610 was hot to the touch (45-60°C) around 5:30 AM on December 3. The MIC Production Superintendent reported that the thermometer on the VGS caustic accumulator read 60°C about 6:00 AM on December 3, indicating that a MIC reaction had taken place. This would indicate that caustic circulation had occurred during the event. The caustic concentration at the start of the event was not known since no analysis had been made since October 23. Subsequent to the event, the caustic circulating pump remote start capability was tested and found to be working properly. According to verbal reports, the flow indicator was cleaned after the event and thereafter functioned properly.

4.2 Tank 610 Residue

On December 20, six core samples of solids in Tank 610 were taken through the 1 1/2-inch thermowell nozzle using a section of one-inch stainless steel pipe. The pipe was 14 feet, 8 inches long and sharpened at one end to allow it to be driven through the solids to the bottom of the tank. The core of solids collected inside the pipe was extracted using a close-fitting pusher rod. From measurements taken during the core sampling operation, Tank 610 appears to have about ten inches of solids lying in the bottom, with some evidence of a crust four inches above the solids with a void in between. A uniform 10-inch bed of solids would represent 10,000 pounds of material at the measured bulk density of 1.5 grams per cubic centimeter.

It is quite possible that either more or less solids are in the tank. For instance, more solids may be in the tank if what appears to be a crust with a 4-inch void above the 10-inch bed of solids were really a 14-inch bed of solids throughout most of the tank. In this case there would be 21,000 pounds of solids in the tank. In addition, it is reasonable to expect crystals attached to all of the interior surfaces of the tank since the thermowell removed from the tank had a thin coating of crystals.

Alternatively, the tank may contain less than 10,000 pounds of solids. The core sample was taken near the tank sump. Even prior to the event, this end of the tank was slightly lower to achieve complete draining. From the appearance of the crack in the concrete above the tank, the far end of the tank may have been raised even more as a result of the event. In this case, the solids may be at a maximum depth where the core sample was taken with less solids at the far end.

4.3 MIC Inventory Disposal

The disposal of Bhopal MIC inventory remaining after the incident was completed without difficulty on December 22. The MIC was processed in the normal fashion to carbaryl insecticide after a safety review of the facilities and operating procedures. The Bhopal Operating Staff, the Indian Government Officials and the UCC Team participated in the safety review.

The 45,000 pounds of MIC in Tank 611 (remaining after use of 47,600 pounds for derivatives production since November 24, 1984) and the 3,300 pounds in drums met product specifications. The 2,400 pounds in Tank 619 was out of specification, but this is not unexpected since one purpose of this tank is to collect off-specification material prior to reprocessing or disposal. Under the circumstances prevailing at the plant at the time, conversion of the off-specification MIC to carbaryl was judged to be the safest approach. The safety of this approach was verified by a laboratory test prior to conversion in the plant.

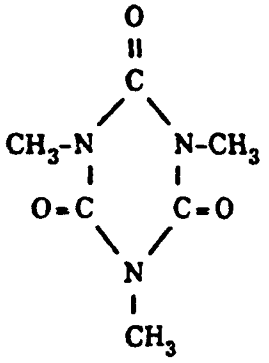
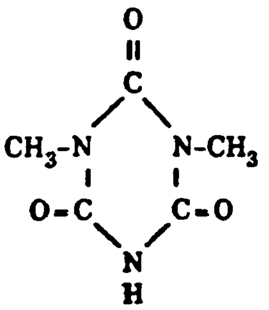
5.0. CHEMISTRY OF THE EVENT

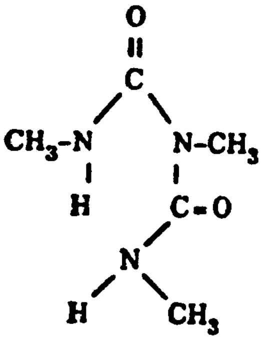
5.1 Residue Samples from Tank 610

Two of the six core samples obtained on December 20, 1984, as described in Section 4.2, were given to the team for analysis. These are the only samples of Tank 610 contents the authorities have permitted the team to examine, and the compositions presented are based on these samples. The plant retained one sample, and three were taken by Indian Government authorities.

5.2 Composition of the Samples

The two core samples were divided into three portions each - top, middle and bottom - for analysis. The six portions were similar but distinctly heterogeneous and represent only a small fraction of the residue in the tank. The significant components and their levels were:

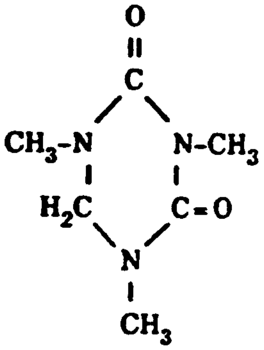
	40 - 55%	MIC trimer = 1,3,5-Trimethylisocyanurate = 1,3,5-Trimethyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (Trimer)
	13 - 20%	1,3-Dimethylisocyanurate = 1,3-Dimethyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (DMI)
$(CH_3)_3N.HCl$	3 - 4%	Trimethylamine hydrochloride (TMA.HCl)
$(CH_3)_2NH.HCl$	2 - 2.5%	Dimethylamine hydrochloride (DMA.HCl)
$CH_3NH_2.HCl$	1 - 1.5%	Monomethylamine hydrochloride (MMA.HCl)
Cl^-	2 - 3%	Additional hydrolyzable chloride



4 - 8%

1,3,5-Trimethylbiuret

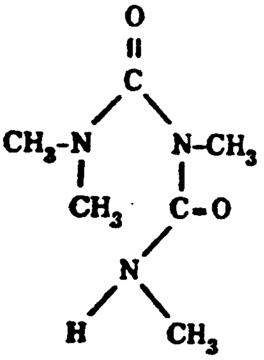
(TMB)



5 - 7%

Dihydro-1,3,5-trimethyl-
1,3,5-triazine-2,4(1H,3H)-dione

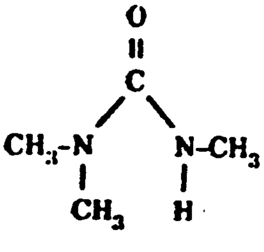
(Dione)



3 - 6%

1,1,3,5-Tetramethylbiuret

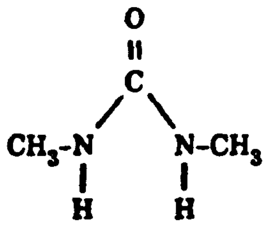
(TRMB)



2 - 4%

1,1,3-Trimethylurea

(TMU)

	1 - 2%	1,3-Dimethylurea (DMU)
Fe, Cr, Ni	0.18 - 0.26%	Iron, chromium and nickel salts
CH_3NCO	0.2 - 1.0%	Methyl isocyanate
$CHCl_3$	0.4 - 1.5%	Chloroform
H_2O	Up to 2%	Water

The water analysis may not reflect actual water content in the residue immediately following the event, because of the tendency of the water sample to absorb water from the atmosphere (hygroscopic).

The foregoing analyses were made using several analytical methods. The team has a high degree of confidence in the accuracy of the results, which have been reviewed by other scientists within Union Carbide Corporation.

The team faced the task of:

- proposing the chemistry which could lead to these components
- experimentally replicating the reactions to form the identified components
- discovering the route by which the initiating substances entered Tank 610.

5.3 Chemistry by Which the Components Could be Formed

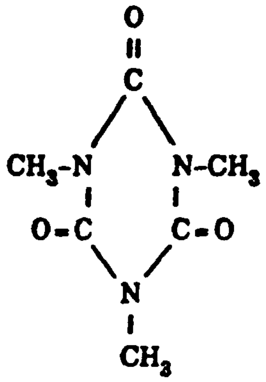
Three significant findings about the residue were:

- The presence of a relatively large proportion of chloride, approximately 5 percent, requires that a chlorine-containing compound was in the tank, and that before and/or during the event it was converted to hydrolyzable chloride. About 87 percent of the total chloride present in the tank residue samples was hydrolyzable chloride.
- Iron, chromium and nickel were present in approximately their ratio in type 304 stainless steel, suggesting that their origin was from the corrosion of stainless steel. Under certain conditions, chlorides are known to corrode stainless steel, particularly in the presence of water. The amount of residue in the tank has been estimated to be 10,000 pounds, on which basis the metal content in the residue would have been about 20 pounds.

- The mixture of organic components found in the residue requires complex chemistry to explain.

If iron-catalyzed trimerization of MIC had been the sole reaction, the only significant product expected would have been MIC trimer. Though trimer was the most abundant component, it comprised only about half the product. Trimerization certainly occurred, but there were other reactions also.

(3) $3CH_3NCO \xrightarrow{\text{iron catalyst}}$



MIC Trimer

Linear polymerization of MIC is a known reaction. However, no linear polymer was found in the residue.

If hydrolysis of MIC by water had been the sole reaction, the only significant products expected would have been a mixture of 1,3-dimethylurea and 1,3,5-trimethylbiuret. Although both were found, they comprised only a small percentage of the total residue.

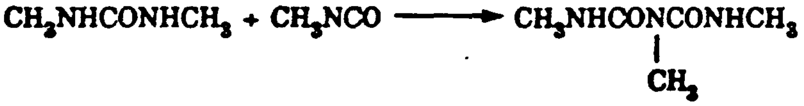
(4) $CH_3NCO + H_2O \longrightarrow CH_3NH_2 + CO_2$

MIC Monomethylamine

(5) $CH_3NH_2 + CH_3NCO \longrightarrow CH_3NHCONHCH_3$

1,3-Dimethylurea (DMU)

(6)



$$CH_3NHCONHCH_3 + CH_3NCO \longrightarrow CH_3NHCO\underset{\displaystyle CH_3}{\underset{|}{N}}CONHCH_3$$

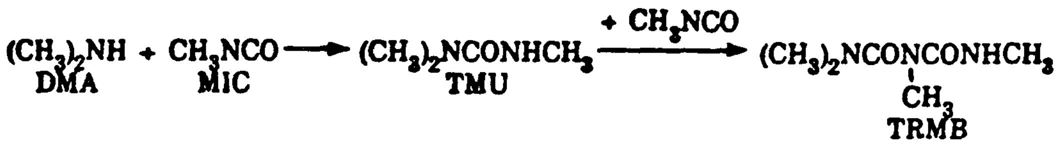
1,3,5-Trimethylbiuret (TMB)

Sodium hydroxide (caustic soda), the solution in the vent gas scrubber, accelerates a water/MIC reaction; but the fact that the residue contained less than 0.001 percent sodium indicates that sodium hydroxide did not play a role.

It is known from the literature (*J. Phys. Chem.* 69 791 (1965)) that liquid monomethylamine hydrochloride disproportionates at high temperatures to an equilibrium mixture of ammonium chloride and other more highly methyl-substituted amine hydrochlorides, as illustrated in the following equation. The equilibrium mixture is temperature dependent.

(7) $CH_3NH_2.HCl \rightleftharpoons NH_4Cl + (CH_3)_2NH.HCl + (CH_3)_3N.HCl + (CH_3)_4NCl$

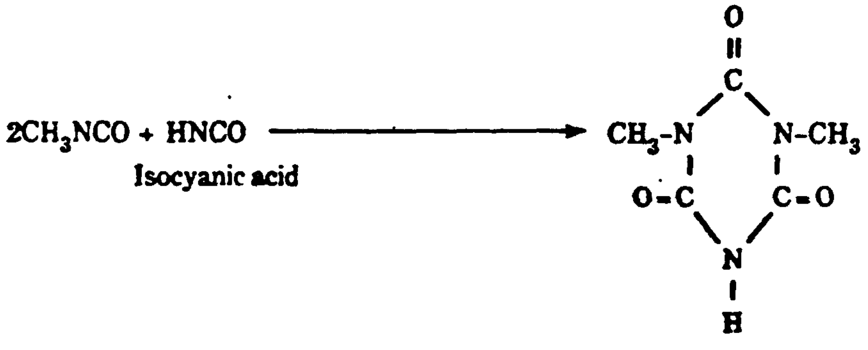
Such disproportionation could explain the presence of DMA.HCl and TMA.HCl. Subsequently the reaction of DMA with MIC could form TMU and TRMB.

(8) 

$$\underset{DMA}{(CH_3)_2NH} + \underset{MIC}{CH_3NCO} \longrightarrow \underset{TMU}{(CH_3)_2NCONHCH_3} \xrightarrow{+\ CH_3NCO} \underset{TRMB}{(CH_3)_2NCO\underset{CH_3}{N}CONHCH_3}$$

It is also known from the literature that methylated ureas will undergo exchange of amine groups at elevated temperatures (US Patent 3,633,614 (1972) and Japanese Patent 72 07004 (1972)). And in the process for preparing DMU from MMA and carbon dioxide, monomethylurea and TMU are also formed (Japanese Patent 79 30116 (1979)). These references suggest possible routes to TMU and TRMB under conditions in the tank during the event.

The second most abundant compound in the core sample of the residue was DMI. This compound is readily formed by the reaction of MIC with isocyanic acid or its salts (*J. Org. Chem.* 35 (7) 2253 (1970) and 44 (22) 3769 (1979)). DMI and other derivatives of isocyanic acid have occasionally been isolated as a residue from process streams in the MIC unit, notably in the phosgene stripping still, which operates above 100°C.

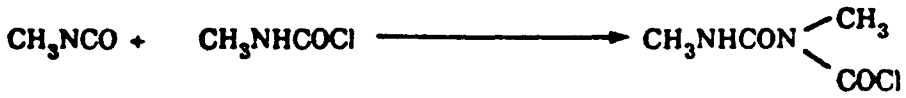
(9) 

DMI

In the MIC process the HNCO can be produced from reaction of phosgene with ammonia formed from dissociation of ammonium chloride produced in equation 7, or with the small amount of ammonia contained in the methylamine.

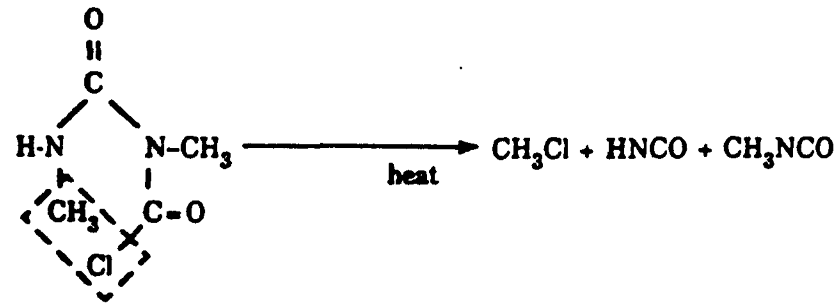
(10) $COCl_2 + NH_3 \longrightarrow HCl + H_2NCOCl \longrightarrow HNCO + HCl$

Isocyanic acid can also be produced by thermal decomposition of dimethylallophanyl chloride (DMAC) in chloroform (UCC unpublished results). DMAC can be formed from MIC and methylcarbamoyl chloride (MCC). In equation 12 the DMAC configuration shows how methyl chloride might be formed, leaving the remainder of the molecule to become HNCO and MIC.

(11) 

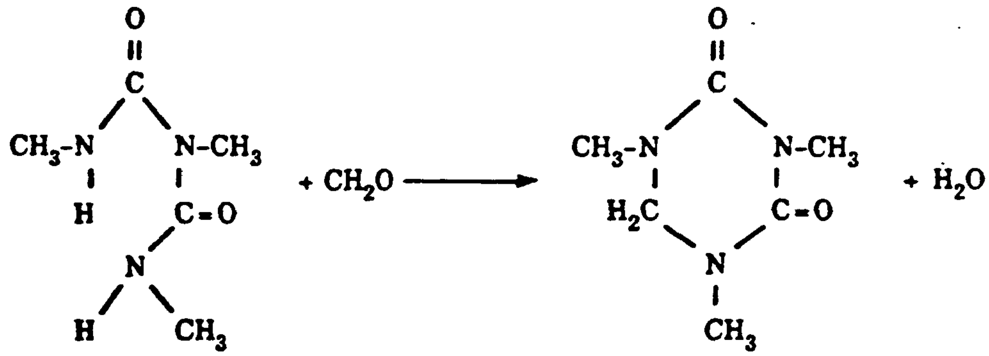
$$CH_3NCO + CH_3NHCOCl \longrightarrow CH_3NHCON(CH_3)COCl$$

MCC DMAC

(12) 

DMAC

The dione can be readily formed by reaction of TMB with formaldehyde or its acetal (*Bull. Soc. Chim. Fr.*, 5-6 Pt. 2, 1419 (1975)).

(13) 

TMB Dione

Whether formaldehyde could have been formed during the event is uncertain, but it is known that chloroform and water do react under certain conditions to produce formic acid and hydrochloric acid (*J. Chem. Soc.* 398 (1959) and *J. Research Inst. Catalysis Hokkaido Univ.* 3 147 (1955)). Also, it is likely that dichloromethane (CH_2Cl_2) was formed during the event, and served as an intermediate to produce formaldehyde. Chloroform can be reduced to dichloromethane under a variety of conditions (METU *J. Pure Appl. Sci.* 6 (3) 255 (1973), *Izv. Akad. Nauk SSSR, Ser. Khim.* (2) 354 (1982) and *Ind. Eng. Chem. Prod. Res. Rev.* 17 (3) 236 (1978)). The hydrolysis of dichloromethane to formaldehyde is also well documented (*J. Chem. Soc.* 1326 (1958); U. S. Patents 1,616,533 (1927) and 1,679,673 (1927), Japanese Patent 72 02608 (1972)).

In summary, all of the significant components of the residue could have resulted from recognized, albeit complex, chemical reactions.

5.4 Replication of the Chemistry

The team decided that in order to substantiate the chemistry, it would have to establish reaction conditions which would produce the major components in the residue. Elevated reaction temperatures, 120-275°C, were used for two reasons: to avoid waiting through an induction period which might be days long, and to achieve temperatures in the range likely reached during the event. The surface to volume ratio was much greater in the laboratory experiments than in Tank 610, so external heat had to be supplied to replace heat losses through the walls. Reactions were conducted in closed systems, whereas during the reaction in the tank, MIC vapor escaped through the safety valve. Accordingly, reactants were mixed in proportions likely to react to complete conversion to give the residue components found in the tank.

The presence of so much chloride in the residue, the fact that chloroform is the process solvent, and the conclusion that an excessive amount of chloroform probably was in the tank as discussed in Section 5.5, led the team to include chloroform in the reaction simulations. Experiments in which MIC and chloroform were the only reactants did not yield the products observed in the residue. However, when water was present, at high temperature the chloroform was consumed, chloride ion was formed, and the major components found in the tank residue were produced. Water was included in the experiments because of the presence of ureas and biurets in the core samples. These materials are produced when MIC reacts with water.

Because of the high level of metals in the residues, direct addition of iron chloride as a reaction catalyst was included in some reactions. This produced about the same product mix as exposure of the hot reaction to types 304 and 316 stainless steel experimental reactors. Stainless steel was also found to corrode under these hot reaction conditions. At temperatures in excess of 200°C, the reaction mixture is sufficiently corrosive to type 304 stainless steel so as to account for the metals found in the tank residue.

Also investigated were various levels of hydrogen chloride in the form of MCC, DMAC, phosgene and hydrochloric acid. Experimentation most recently concluded indicates that their presence had a less significant effect on the residue composition than water, chloroform and iron. Other reactive chemicals added to MIC in the experiments to determine their effect on residue composition included materials which were available within the plant, e.g., monomethylamine, chlorine, trimethylamine, carbon tetrachloride, dichloromethane, and process residues. None of these additions was as effective in replicating the desired residue composition as a combination of water, chloroform and iron.

Through the above experimentation, involving over 500 experiments, it was demonstrated that the major components found in Tank 610 residue can be produced by materials and conditions whose presence in the tank can be accounted for: MIC, chloroform, water, iron and high temperatures. In general, it appears that reaction temperatures in excess of 200°C are needed to produce the mixture of products, especially to form large amounts of DMI and significant quantities of TMU. In particular, there was a strong positive correlation between the amount of chloroform added and the amount of DMI produced. Chloroform also influenced the formation of Dione and of the amine hydrochlorides, probably through its conversion to dichloromethane, which reacted with some of the DMU and TMB already formed.

The one material found in significant proportions in the tank but not in the experiments is TRMB. Its absence can be explained by rapid depletion of the MIC during the experiments, so that none was left to react with TMU after that compound was formed. In Tank 610 there must have been MIC present during the cooling period which followed reseating of the safety valve, so that DMU and TMU would have reacted with it to form TMB and TRMB, respectively. Both reactions have been demonstrated in the laboratory.

Considering the product distribution in the tank, the experimental results, and the probability that solids and liquids were vented with the gas during the incident (Section 6.0), the amounts of water and chloroform originally present in Tank 610 are estimated to have been 1,000 to 2,000 pounds of water and 1,500 to 3,000 pounds of chloroform.

5.5 Sources of Reaction Components

Given the technical data and information available to date, it seems likely that the reaction was caused by the entry of a large quantity of water into Tank 610, which contained MIC with an abnormally high level of chloroform. The presence of chloroform alone in MIC would not have caused the incident.

Water

The exact source of the water is not known, but laboratory work demonstrated that 1,000 to 2,000 pounds of water would have accounted for the chemistry of the residue. Water could have been introduced inadvertently or deliberately directly into the tank through the process vent line, nitrogen line or other piping. Records indicate that the safety valve discharge piping to the RVVH from four MIC process filters was being washed shortly before the incident. Oral discussions indicate that a slip blind was not used to isolate the piping being washed. However, entry of water into Tank 610 from this washing in the MIC unit would have required simultaneous leaks through several reportedly closed valves, which is highly improbable.

Tank 610 could not be pressurized on November 30 and December 1, although nitrogen was reported to be flowing into the tank (per records and discussions). It is possible that a vent valve was leaking and/or the rupture disc was not intact and the safety valve was leaking. Oral discussions indicate that the rupture disc was tested and found to be intact on November 30. If nitrogen was indeed escaping, the escape route could also have provided a route of entry for water.

Chloroform

Records for the operation of the MIC refining still for the period October 18-22, 1984, indicate that the column was being operated during part of that time at higher than normal temperatures. Computer simulation of the distillation column indicates that under those conditions, a higher than normal amount of chloroform would have distilled along with the MIC.

Also, there is no record of analyses of MIC in Tank 610 after October 19. However, MIC Unit logs show that in preparation for shut down, MIC containing a high concentration of chloroform was sent to Tank 610 instead of to the empty Tank 619. The chloroform content of the MIC left in the MRS product line was between 12 and 16 percent, as reflected in samples taken and analyzed on December 16. This indicates that the last product from the MRS to Tank 610 contained well over the specification maximum of 0.5 percent chloroform. This would in turn have raised the chloroform content of Tank 610.

In addition, material sampled on December 5 and 9 from the MIC transfer line from the storage tanks to the Derivatives Unit contained 2.5 and 1.9 percent chloroform, respectively. Two MIC samples from the Derivatives Unit charge tank on December 7 contained 1.5 and 0.8 percent chloroform. All these results were higher than normal. Samples from the other possible sources, Tanks 611 and 619, showed lower amounts of chloroform, i.e., less than 0.3 percent chloroform in Tank 611; and less than 0.6 percent in Tank 619. Therefore, it appears that the high-chloroform MIC transferred to the charge tank came from Tank 610.

Iron

As discussed in Section 5.4, high corrosion rates of stainless steel at high temperatures would be required to generate the metals found in the tank residue. These kinds of corrosion rates have been demonstrated in laboratory experiments. The corrosion rates were found to be 10 to 20 mils per year at 100°C and 1,700 to 3,500 mils per year at 200°C using MIC containing 18 percent chloroform and 2 to 7 percent water. (One mil equals one-thousandth of one inch.)

The rates, dependent on chloroform level, are far lower at room temperature. Corrosion rate tests showed the rates to be 0.18 mils per year with refined MIC containing 16 percent chloroform, compared with 0.04 mils per year with MIC containing 2.5 percent chloroform. These rates were measured over a 15-day exposure period. The corrosion rate with MIC containing a normal amount of chloroform (0.5 percent maximum) is negligible (nil) at room temperature.

6.0 A HYPOTHESIS FOR THE EVENT

Based on the information gathered by the team, several hypotheses and scenarios were proposed and examined for compatibility with known facts. They were tested experimentally where necessary for compatibility with pertinent analytical and chemical data. The investigative process outlined in Section 2.0 was used to choose the most probable scenarios. A single scenario to fit the event could not be proposed with complete certainty, since sufficient critical information was missing in each case due to restrictions placed on the team. However, a high probability can be given to the following scenario.

One to two thousand pounds of water entered the tank. Although entry from vent headers (RVVH, PVH) cannot be ruled out at this time, direct introduction of water through the vent or other piping has a higher probability for occurrence because it does not require the simultaneous leakage through a series of reportedly closed valves. The chemistry, described in Section 5.0, indicates that the large amount of water and higher-than-normal levels of chloroform were necessary to obtain the particular mix of significant residue components found in the core samples. The large amount of water was necessary to generate the heat needed to initiate and accelerate the subsequent reactions. The temperature of MIC in Tank 610 before the incident was at 15 to 20°C as compared to the requirement of about 0°C. The lower temperature would have retarded the reaction rates and considerably extended the time available for corrective action. The refrigeration system provided to cool the MIC in the storage tanks had been made non-operational in June, 1984.

The reaction of water with MIC led to an increase in pressure due to evolution of carbon dioxide as well as an increase in temperature due to the exothermicity. The higher pressure, 10 psig, noticed at 11:00 PM on December 2 is believed to be due to this phenomenon. The increase in temperature was not signaled by the tank high-temperature alarm since it had not been reset to a temperature above the storage temperature. The nitrogen escape route discussed in Section 5.5 would have allowed carbon dioxide and MIC vapor to flow to the VGS. Since the VGS was not in service prior to the incident, this would explain the untraceable MIC leak reported in the MIC unit at 11:00 PM. Although the pressure in the tank could not be increased by nitrogen addition in earlier attempts, it increased at this time due to the far higher rates of carbon dioxide evolution.

A transfer of 2,300 pounds of MIC was made to the Derivatives Unit charge tank at about 11 PM as shown in transfer logs. As discussed in Section 5.5, this probably was from Tank 610. Since it may have come from Tank 610 after the introduction of water, this material would be expected to contain water. This water would have eventually been consumed by reacting with MIC. Alternatively, there is the possibility that the transferred material may not have contained water because the transfer point is the tank bottom sump. The last MIC to enter the tank through the make line to the sump on October 22 contained between 12 and 16 percent chloroform, and would have had higher density than water. Therefore, the water introduced at the top of the tank may not have reached the lower portion of the tank. The tank contents were not mixed after October 19.

As the temperature in Tank 610 increased due to the exothermic reaction of MIC with water, the corrosion rate increased markedly because of the presence of an abnormally high level of chloroform. The iron thus produced catalyzed a concurrent exothermic trimerization of MIC. Both reactions accelerated as temperature increased and the mixing of water and iron with the bulk of the MIC further increased the violence of the reaction. As temperature and pressure increased rapidly, the rupture disc in the line to the safety valve burst (if not already broken) and the safety valve opened at 40 psig. The chemistry of the residue shows that 1,000 to 2,000 pounds of water and 1,500 to 3,000 pounds of chloroform were required. Calculations have shown that the presence of 2,000 or more pounds of water would have caused the incident without chloroform being present.

The amount of material forced out of the tank cannot be determined exactly. However, based on the heats of reaction, about 40 percent of the MIC reacting would release enough heat to raise the temperature of the tank and vaporize the remaining 60 percent of the MIC. From this calculation, 36,000 pounds of solids would be expected in the tank instead of the estimated 10,000 pounds. One explanation for the lower amount of solids is the loss through the safety valve of some liquid and solids along with the vapor, due to foaming of the reaction mass during the most active period of reaction.

An initial discharge rate of 10,000 pounds per hour of MIC vapor would occur when the pressure in the tank reached 40 psig, the rupture disc burst and the safety valve opened. The exact time period the safety valve remained open is not known, but a two-hour period is reasonable based upon the available information. In order to discharge most of the contents of the tank within two hours, the pressure had to average 180 psig. At these conditions, material would be discharged at a rate of 40,000 pounds per hour: 29,000 pounds per hour of vapor and 11,000 pounds per hour of solids/liquid mixture. Approximately 54,000 pounds of unreacted MIC left Tank 610 together with approximately 26,000 pounds of reaction products. As discussed in Section 5.4, the maximum temperature reached was probably greater than 200°C.

A better estimate of the maximum pressure and temperature reached in the tank can be made when it is inspected and measurements are made to determine whether the metal started to yield. The start of permanent head deformation of Tank 610 would occur at about 100 psig. The stainless steel would start to yield above 200 psig. The tank would not be expected to rupture until the pressure exceeded 300 psig. The tank did remain intact.

The sequence of reactions required to duplicate the composition of the core sample cannot be determined exactly. These are discussed in Section 5.0. However, recognizing the limitations imposed upon the investigation team, the overwhelming experimental data indicates that a large amount of water must have entered the tank containing MIC with an abnormally high amount of chloroform, and initiated the chemical reactions.

ATTACHMENT TWO

SUMMARY OF REGIONAL RESPONSE TEAM COMMENTS
REGARDING WEST VIRGINIA CONTINGENCY PLANS

As provided for in Subpart D of the National Contingency Plan, the Regional Response Team (RRT) has met several times since the incident in Bhopal for the purpose of reviewing existing contingency plans relating to the Union Carbide plant in Institute, West Virginia. Member agencies and their representatives participating in this review included the following:

1. EPA	Tom Voltaggio (Co-Chair)
2. USCG	Captain Pete Lauridsen (Co-Chair)
3. FEMA	Karen Larsen
4. HHS	Frank Piecuch
5. DOJ	Dave Buente
6. OSHA	Ken Gerecke
7. DOD	Jack Dempsey
8. WVDNR	Ron Shipley
9. WVOES	Manny Griffith
10. EPA (HQ)	Jim Makris
11. EPA (ERT)	Dr. Joe Lafornara
12. CDC	Kent Gray
13. DOI	Anita Miller
14. NOAA	Frank Rossi
15. USDA	Bob Adams

Our review sought to determine what improvements can be made to Contingency Plans relevant to Union Carbide's Institute Plant. We believe the need for detailed pre-planning and contingency plan development is crucial in order to provide for efficient, coordinated and effective response to a release of hazardous substances, thus minimizing the potential impact on human health, welfare and the environment.

The various Plans that were reviewed include the following:

1. W.V. Hazardous Materials Emergency Response Plant (draft, dated 12/84) prepared by Office of Emergency Services (final version anticipated in March 85).

2. Kanawha County and local jurisdictions - Emergency Response Operations Plan (updated 1982; in print now; may be subject to change based on current events).

3. West Virginia Emergency/Disaster Plan (dated 12/83; prepared by OES).

4. Kanawha Valley Industrial Emergency Planning Council Manual (revised 5/81)

5. Union Carbide Institute Plant Emergency Procedures Manual (updated 12/84).

We realize that some of these plans are in draft stage, and that because of all the concern presently focused on Union Carbide's Institute facility, there are events underway which may result in supplemental plans or significant changes to existing ones. Given this dynamic situation, our comments are generally broad in scope, attempting to identify major issues of concern, and as such should not be construed as delineating in detail each specific item which requires attention.

Based on our review, we believe that some of the plans, as presently organized, need to be improved to effectively deal with the wide range of hazardous situations that can occur. In particular, the County Plan appears to need significant improvements to fulfill the need for a comprehensive operations plan that could be employed in a variety of emergency/ disaster situations.

Our comments have been organized into six major categories, as presented in the following paragraphs. These categories are somewhat interrelated, and should be read in that context.

1. Responsibility

A. Assignment of the responsibility and authority for overall direction and control during an accident needs to be established in a single location at each governmental level and within each plan. The clear and specific designation of a lead Agency/ individual for response organizations is needed to help avoid disputes between Agencies at a critical time in the response operation.

B. The assignment of authority to order an evacuation of the general public is vital, but appears inconsistent throughout the plans. References are made to "senior law enforcement official," "senior elected official," "first responder," "field CP group," etc. Clarification may be needed with regard to KVIEPC's ability to initiate protective actions by the general public via activation of the Emergency Broadcast System.

C. While it is quite logical that KVIEPC and its constituent companies have a major coordinating role in response to incidents within their plants, it is unclear how and when the local, County and State authorities will assume control regarding offsite effects of an incident occurring. This does not reflect the preeminent authority and responsibility of local government to protect the health and safety of its citizens.

2. Coordination

A. Coordination between the plans needs to be strenghtened. Questions such as who has authority, what are its limits (both legal and geographical), when does transition of authority take place, etc., need to be clarified. Formal, written agreements between the various response organizations should be considered. Such agreements could identify availability of resources, methods of gaining access to them during an emergency, uniform protective action guides, and provide a mechanism to limit liability for assisting personnel. They would help to provide a synchronized response while avoiding duplicated effort.

B. Air modelling and meteorological projections from the National Weather Service Forecast office to ascertain the area of impact, and more attention to the location and characteristics of the population at risk should be incorporated into the plans. Response patterns should be predicatated on such information and be predictable. Without a map of prevailing wind patterns, it is difficult to determine the potential people and resources at risk. In the case of an air release there is a possibility that areas that seem remote could be affected. If this were the case, response personnel and residents in remote areas must receive adequate notification of a need to evacuate or take other protective action.

C. Relationships with medical authorities should be clarified regarding health effects consultation, including decisions to evacuate (who makes the decision, based on what information, etc.) and personal protection equipment to be worn. Based on the types and numbers of injuries that could be expected for various possible hazardous materials incidents, the capabilities of available medical facilities should be evaluated. Where helpful, agreements should be established between local governments, industry and hospitals; hospital plans for dealing with foreseeable emergencies should be incorporated or referenced in the plan. Joint government/hospital drills or exercises should test response plans for casualties resulting from the most probable occurrences.

3. Operations

A. An overall "concept of operations" is needed, particularly in terms of determining 1) the severity of an incident and the type of response actions necessary; 2) the adequacy of cleanup or response by the responsible party; 3) compliance with all applicable local, State and Federal requirements.

B. The various plans need to be focused more directly towards hazardous material incidents, and to incorporate appropriate private, State, and Federal resources and capabilities available to respond to such incidents. In other words, who will do what, when, and at whose direction?

C. Criteria should be considered for relinquishing controlled access to an area which has been cleaned up and is able to be returned to unrestricted use.

D. A mechanism for funding and performing necessary cleaning operations in the absence of the spiller voluntarily undertaking this responsibility should be developed.

E. Procedures for conducting monitoring of air, water, or food-chain that may have been contaminated during a release, and continued monitoring after the release to determine "how clean is clean" must be addressed.

4. Notification

A. Clarification is needed regarding the notification system to be followed between industry, local, County, and State agencies, as well as the procedure to alert surrounding communities of an incident. There must be mutually agreed upon bases for notification and exchange of information between the various governments and the chemical industries in the area. For this purpose, telephone listings should be incorporated into all the plans, and periodic updating of notification lists should be required.

B. It is not immediately apparent how and when the community awareness alarm becomes activated, who's decision it is to sound it, or what the consequences of an alarm are. In discussions with the community, more information regarding this process should be made available. Tests of the alarm systems and other notification procedures should be regularly scheduled and conducted, and the effectiveness of the systems in reaching the desired areas should be determined. (Guidance for the evaluation of off-site warning systems is available through FEMA).

C. Contact mechanisms with the Federal response commuity need to be identified and emphasized. Through the National Response Center (NRC) (800-424-8802) there is a well established system in place to notify Federal agencies of potential or actual emergency incidents. A list of Federal contacts should be presented in a single section of all plans, as well as notification/action sequences to be followed in the event of a hazardous material incident.

5. Public Information

A. The degree to which the Public has been involved in the planning process and its awareness of the existence and significance of the various notification systems, alarms, etc. is unclear. An ongoing community relations program should be established to inform residents of the community awareness alarm and its significance. Protective action guides, potential limits, and types of recommended protective actions for the general public should be pre-established and clearly understood by the local population.

B. Methods to coordinate public information activities so as to clearly and effectively communicate specific information and thereby avoid confusion and rumors should be strengthened. Public information releases during an emergency response should be prepared by a central coordinating source. A system should be considered for releasing information contained in the initial and follow-up messages received for the accident site, including verification procedures. Standard news release formats may be developed which only require the application of site-specific information. Concise messages that are easily understood by persons unfamiliar with the technical aspects of an accident should be stressed.

6. Regional Inventory Needs

A. A comprehensive data base including the types, quantities, and locations of hazardous materials, as well as toxicological information related to these materials is needed. This should be provided to the appropriate response personnel on an ongoing basis. The companies could provide periodic briefings to local response staff, identifying specific chemical hazards that may be encountered in any sort of response effort. Due to the rapid nature of a toxic release, the role of the companies cannot be underestimated. While they are aware of the substance at their facilities and the associated toxicology, it must be assumed that the majority of the standing response team will have to acquire and assimilate the information before action be taken.

B. Availability and locations of personal protective equipment and other equipment suitable for response needs should be identified. This equipment should be tested, and training for first responders in its use should be provided. Types of equipment needed for specific response activities may vary with the type of emergency. Guidance on the proper selection of the available personal protective equipment should be made available. OSHA and NIOSH both have recommended programs for users of personal protective equipment. These include:

1) material identification
2) environmental surveillance
3) medical surveillance
4) selection of equipment
5) training in and fitting of equipment
6) decontamination and cleaning
7) inspection, maintenance and storage
8) written program
9) program review and evaluation
10) operational use

Our review of the various plans reveals that the documents, by themselves, do not indicate the establishment of an effective personal protective equipment program useful in the control of hazardous material incidents. The elements which are lacking may be adequately addressed in other documents, however.

C. Training for first responders and others in the response team is needed regarding regulations pertaining to personal protective equipment. The deployment of individuals to the site without proper training or equipment can result in casualties. Periodic briefings for employees and response personnel should be provided. Simulations of releases of hazardous substances should be held to test response systems. Joint government/hospital drills or exercises should test response plans for casualties resulting from the most probable occurrences. Training and plan update should, of course, be part of an ongoing process. The need for training of governmental services personnel should be based to some extent on the agreements spelled out between government and industry regarding responsibility for various parts of the emergency response.

D. Medical support capabilities (location of hospitals, critical care facilities, etc.) and special evacuation considerations (schools, nursing homes, etc.) should be addressed. Based on the types and numbers of injuries that could be expected for various possible hazardous material incidents, the capabilities of available medical facilities should be established between local governments, industry and hospitals; hospital plans for dealing with foreseeable emergencies should be incorporated or referenced within the plan. Evacuation plans including special consideration such as schools, nursing homes, etc. should be formulated with the involvement of these institutions. This should be followed by drills supervised by response team members.

We note that Congressman Bob Wise, in his 1/11/85 memorandum (copy enclosed) has identified a number of specific proposals relating to emergency response in the Kanawha Valley. These suggestions are well thought-out and compatible with our comments, although in general they go beyond the limits of the RRT's purview.

In summary, the member agencies of the RRT were requested to review, based on their particular areas of expertise, each of the available Contingency Plans, and provide relevant comments. There has not been an attempt to develop totally new plans, or to substantially rewrite the existing ones, but rather to point out areas which should be strengthened. Our review was conducted with the understanding that it is impossible, by definition, to totally prevent accidents and emergencies from occurring. By insuring that contingency planning procedures are thorough and properly implemented, the impact of such events can be minimized. The concept of accident prevention, either through Regulatory procedures or voluntary changes enacted by Union Carbide, was outside the scope of the RRT review.

Furthermore, we did not intend to determine the degree of risk to the local population, or to quantify/qualify it in any way. We did not believe it appropriate, at this time, to evaluate methods of providing for, or implementing, mass evacuations from the surrounding communities. We believe that Congressman Wise is certainly correct in his assessment of a need for additional development and public communication regarding this procedure.

By transmitting our comments to the WVDNR and (through FEMA) to OES, we hope these Agencies will cooperatively insure that our comments are implemented at the appropriate levels in the planning process. We suggest that a task force consisting of representatives from FEMA, EPA, WVDNR and WVOES be formed to oversee the implementation of these recommendations for improvement. The RRT will be available as an advisory body if needed by the task force.

The RRT members are commended for their valuable contributions to this crucial review process. A great deal of time and thoughtful consideration has been provided, frequently under extremely tight schedules. These efforts will undoubtedly enhance the level of preparedness in the Kanawha Valley, and may lead to an increased awareness nationally of the importance of contingency planning and prevention methods.

ATTACHMENT THREE

Attachment Three

Membership of Federal-State Task ~~Group~~ Force on the review of the Resumption of MIC Production by Union Carbide Corporation, Institute, West Virginia.

U.S. Environmental Protection Agency (lead agency)

Greene Jones, Chairman - B.S. Civil Eng.
Robert Kramer - B.S. Env. Sci.
Rick Horner - B.S. Chem. Eng. - M.B.A. Bus. Adm.
Joseph Lafornara - Ph.D. Organic Chem. Inorganic
Peter Schaul - M.S. Chem. Eng.
Les Evans - B.S. Chem. - M.S. Bus. Adm.
Michael Zickler - M.S. Env. Sci.
Robert Borgwardt - B.S. Chem. Eng.

Occupational Safety and Health Administration

Doug Ray - B.S. Biology
Rich Jeffrey - M.S. Safety and Health Management

Federal Emergency Management Administration

Provide technical assistance on emergency response planning.

James Asher - 35 years experience in Emergency Response
Karen Larson - B.A. Soc. and Dev. Phy.

West Virginia Department of Natural Resources

Ron Shipley - B.S. Chem. Eng. - MPA, J.D.
Sanja Kanth - B.S., M.S. Chem. Eng.

West Virginia Air Pollution Control Commission

Carl Beard - B.S. Chem.
Dave Fewell - B.S. Chem. Eng.
Steve Pierce - B.S. Chem. Eng.