Comments/suggestions received on the NEERI, NGRI and IICT reports related to Bhopal Gas Leak Disaster

Indian National Academy of Engineering

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Ref : INAE/120

July 22, 2010

Dear Shri Jairam Ramesh,

I am thankful to you for your D.O. letter No.7(161)/2004-HSMD(Part-II) dated July 13, 2010.

As desired, I am enclosing the comments of Indian National Academy of Engineering (INAE) on the Reports related to decontamination and remediation of the Union Carbide plant site in Bhopal.

With warm regards,

Yours sincerely,

(PS Goel)

Encl: As above.

Shri Jairam Ramesh
Minister of State (Independent Charge)
Environment & Forests
Paryavaran Bhavan
CGO Complex, Lodhi Road
Govt. of India
New Delhi-110 003

DP (SR)

Cc : Dr. KV Raghavan, INAE Distinguished Professor, Reaction Engineering Lab., Indian Institute of Chemical Technology (IICT), Hyderabad

Cc : Dr. Purnendu Ghosh, Executive Director, Birla Institute of Scientific Research, Jaipur

Comments on Report on UCIL, Bhopal

1. There is need to clear the entire area of UCIL campus of contaiminated equipments / structures and bushes before undertaking proposed field studies. All the equipments / structure need to be decontaminated and dismantled employing scientific methods. It will not serve very useful purpose, if areas covered by the equipments / structure and bushes are not cleared by the identified agency prior to undertaking remediation measure at the site.

2. As contaminants from the dumps are prone to dispersion by surface runoff in directions controlled by surface slope characters, contaminating the top soils away from the dump and SEP sites, it is necessary to have a detailed high resolution ground slope map to track such possible surface pathways of contaminants.

3. The extent and intensity of surface dispersion of contaminants from the dump and SEP sites would depend on the ground slope and surface runoff parameters. Geophysical study (HERT) might have located the dumps but such studies may not delineate low to medium level contaminated soil zones (contamination halos).

4. The boundary wall of the entire UCIL site to be fully secured and well protected to prevent entry of unauthorized intruders. The contaminated bore wells to be adequately sealed to prevent water usage by the population.

5. The incinerable wastes can be disposed off in a well designed incinerator facility provided the waste gases from incineration safely recovered, treated and disposed off after decontamination.

6. Phytoremediation which is a vegetation based remediation technique, may be very useful for accumulating, immobilizing and transforming low level of persistent contaminants in the rest of UCIL site. It is well suited for very large field sites where other methods of remediation are not cost effective. R&D inputs may be required from Indian institutions keeping UCIL site specific conditions in view. It may also provide an environmentally congenial option for long term maintenance of UCIL site.

7. The study suggests that the main aquifer is confined and hence the chances of groundwater contamination are minimal. However, several wells indicate contaminated groundwater at different groundwater levels which means that the aquifer system of the area has hydraulic connectivity with the surface water and the main aquifer may be leaky. Therefore, the suggested immediate remedial measure of pumping and treating the contaminated wells may in fact disturb the aquifer dynamics and the new flow regime may contaminate other parts of the aquifer.

8. As an immediate remedial measure excavation and in situ relocation of the dumps has been suggested. Such an activity may disturb the stable soil system and the "critical zone". This zone at present is not a major groundwater recharge zone in the area, but under disturbed condition the surface water-groundwater interaction may change and the aquifer may get

contaminated in the future. This aspect need to be studied before taking up dump relocation remedial measure.

9. The proposal to shift contaminated soil from identified sites by NEERI and NGRI into a secured landfill looks to be the one of the better options to provide near term solution to the soil contamination problem. However, it is only an interim solution since the land filled contamination remains on the site, requiring monitoring and maintenance of the isolation barriers on a long term basis with all the associated costs and potential public liability.

One of the options to be seriously examined is to implement a viable **insitu bio remediation at the landfill site** at a later date. There is accordingly a need to develop appropriate landfill design strategy and technology that favour an insitu bioremediation at a later date. It is particularly important to keep depth limitation of insitu bioremediation.

The proposed disposal of non incinerable wastes 'ex situ' in a secured landfill facility is quite challenging because of its very large size and magnitude of the job (2m thickness and 16 hectares area). Under this, following options to be examined further to remediate the collected soil at the landfill facility:

a) Insitu bioremediation option and its technical feasibility have to be examined at the landfill rate at UCIL campus either together or separately since they contain following major contaminants in varying proportions:

1. Sevin /Carbaryl ($C_{12}H_{11}NO_2$),a carbamate insecticide
2. Aldicarb ($C_7H_{14}N_2O_2S$)
3. Hexachloro Cyclohexane (HCH) isomers which are generally obtained from Lindane manufacture
4. α – Naphthol, a polycyclic aromatic hydrocarbon
5. Mercury.

A brief literature review shows that following bioremediation options were tried earlier for the specific components. They are merely indicative and more thorough literature search by experts may be necessary.

a) Carbaryl : Microbial degradation was reported by two novel bacterial strains (Arthobacter species) by Japanese investigators (J.Forest Research 4 (4), 275-280, 1999 (Nov)). They reported high degradation capability to the bacterial strain.

b) Aldicarb : Methylosinus bacteria isolated from soil contaminated with aldicarb was tried by Turkish investigators (Enzyme and Microbial

Technology 24 (5-6), 291-296 (1999)) in a packed bed contactor after immobilization. The degradation was reported to be partial.

c) HCH Isomers : CFTRI (Mysore) reported in 2002 (Chemosphere 56(8), 803-811 (2004)) bioremediation of HCH-contaminated soils within 120 hours.

d) α – Naphthol : It has been reported (Polish J. Enviro Studies 12(1), 15-25 (2003) that microbial degradation of polycyclic aromatic hydrocarbons including α – Naphthol is an attractive technology for restoration of polluted sites.

e) Mercury : It is non biodegradable. However, treatment methods have been reported to transform mercury through sorption, methylation, complexation and change in valence state. Their feasibility has to be seen as far as UCIL site is concerned. However, the use of microorganisms like Alcaligenes and pseudomonas which can affect the reactivity and mobility of metals like mercury can be employed for their detoxication in soils.

It is also reported that Entomology Group of CSIRO, Australia has developed (2001-04) enzyme based technology that can remove residues in drainage water of organo phosphorous, carbamate and pyrethroid insecticides. Their expertise may be relevant to well water remediation at UCIL site. An international Patent (WO/1996/033821) describes a method of remediating soil contaminated with organochloro pesticides employing methanotropic bacteria (if it is not already present in the soil) and denitrifying bacteria. NEERI has reported the use of biostimulation and bioaugmentation strategies followed by evaluation using a molecular method for bioremediation of organochloro pesticide contaminated soils. This expertise may be useful for adoption at UCIL site after adequate development and scale up.

Dr. Dilip B. Boralkar
M.Sc., Ph.D. (Mumbai)
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Former Assistant Secretary, Central Pollution Control Board

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Date: 16th July, 2010

To

Shri Jairam Ramesh
Hon.'ble Union Minister of State (Independent Charge)
Ministry of Environment & Forests, Government of India,
Paryavaran Bhavan, C.G.O. Complex, Lodhi Road,
New Delhi - 110 003.

Subject: NEERI's Report, on Assessment and Remediation of HW Contaminated Areas in & around M/s UCIL, Bhopal: Comments of Dr. Dilip B. Boralkar.

Reference: Hon.'ble Minister's letter No. D.O. No.-7(161)/2004-HSMD (Part-II) dated 13.7.2010

Dear Sir,

Many thanks for your kind letter under reference. I am really pleased to see model scientific approach and efforts of the Ministry to deal with the decontamination and remediation of the site(s) at the UCIL, Bhopal. I see this as a beginning of Indian regime for industrial contaminated lands reformation. Congratulations. I would be gladly willing anytime if I could be of any use or help in your endeavors.

As desired, please find enclosed my comments on NEERI's Report for your consideration.

With kind Regards,

Yours sincerely,

DBBoralkar

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Encl: as above.

MOS (I/C) E & F
Dy. No. 2976/MEF
Date 23/07/10

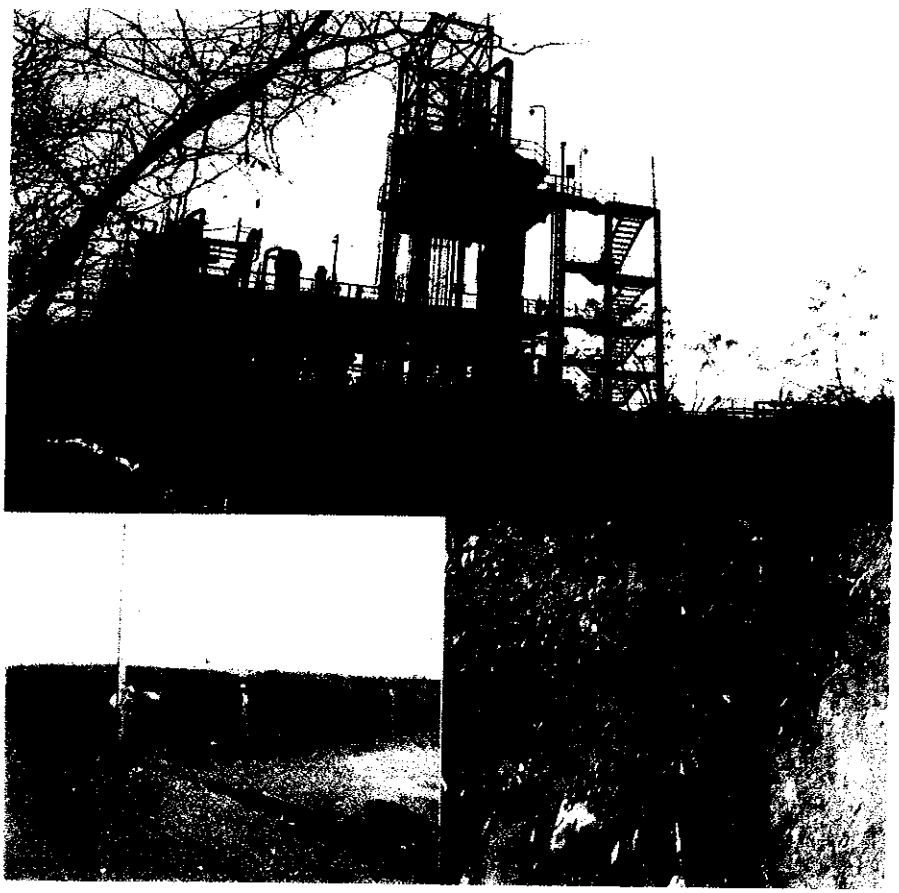
Pl See me 24/07

DD (SR)

COMMENTS OF
DR. DILIP B. BORALKAR

ON

NEERI'S REPORT, JUNE, 2010, REGARDING ASSESSMENT AND REMEDIATION OF HW CONTAMINATED AREAS IN & AROUND UCIL, BHOPAL.



Submitted to

Shri Jairam Ramesh
Honorable Union Minister of State (I/c)
for Environment & Forests, New Delhi.

16th July, 2010

COMMENTS OF DR. DILIP B. BORALKAR ON NEERI'S REPORT, REGARDING ASSESSMENT AND REMEDIATION OF HAZARDOUS WASTES CONTAMINATED AREAS IN & AROUND M/s UCIL, BHOPAL.

1. Background:

The Group of Ministers on Bhopal Gas Tragedy under the Chairmanship of Shri P. Chidambaram, Hon.'ble Union Home Minister, considered the reports submitted by NEERI, NGRI and IICT on decontamination and remediation of the UCIL site at Bhopal and recommended to a peer review of these reports. Shri Jairam Ramesh, Hon.ble Union Minister of State (I/c) for Environment & Forests vide his letter dated 13th July, 2010 sought comments on these reports, particularly the NEERI's report. Accordingly these comments are submitted to the Ministry for consideration.

2. NEERI's Report:

Based on the directives of the Task Force constituted by the Hon'ble High Court of Madhya Pradesh, the Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTRRD), Govt. of Madhya Pradesh, assigned National Environmental Engineering Research Institute (NEERI), Nagpur and National Geophysical Research Institute (NGRI), Hyderabad to undertake a study on fresh assessment of the extent of contamination and delineate suitable strategies for the remediation of contaminated areas in and around the UCIL site. The study was awarded by BGTRRD in March 2009. The NEERI submitted its report in June 2010 on Assessment and Remediation of HW Contaminated Areas in & around M/s UCIL, Bhopal.

3. Comments:

(i) It is clarified in the report that the contamination of soil and groundwater in and around UCIL premises is solely due to dumping of hazardous wastes and other wastes during 1969 to 1984. The MIC gas tragedy has no relevance to it.

(ii) While data on production during 1969 to 1976 (7 years) is not available, it is stated that during the year 1977 to 1984, M/s UCIL manufactured 11,447 MT of pesticide carbarly (known as Sevin) and 2709 MT of Methylisocyanate (MIC). During the manufacturing of various intermediates and products at UCIL, Bhopal from 1969 to 1984

various solid, semi-solid and liquid wastes were generated. These include:

(a) Treated waste water from various process units.
(b) Tarry residues from distillation units of Sevin and napthol units.
(c) Off specifications products.
(d) Burnt and un-burnt residues from past fire accident.

(iii) It would be useful to know, if any estimate is made, regarding the quantity of the hazardous waste generated and disposed till 1984. If we consider 30% waste generation (solid +liquid) per ton of product, then waste generated till 1984 would be about 4250 MT. Besides, there could be leftover products/raw materials which are of hazardous nature and dilapidated plant and machinery being contaminated with hazardous substances.

(iv) GTZ in its study referred in the report stated that quantity of the hazardous waste would be about 25,000 MT at UCIL.

(v) The Madhya Pradesh Pollution Control Board recovered and stored 359 MT of hazardous waste in the year 2005. This includes contaminated soil 165 MT, Sevin residue 11 MT, semi-processed pesticides 143 MT and Lime sludge 40 MT.

(vi) The hazardous wastes are found dumped mainly at two places. These are designated as Disposal Area I (DA I) and Disposal Area II (DA II). The NEERI in its study in 1996 found that soil in the DA I and DA II were highly contaminated mainly due to sevin and temik pesticides/residues. In the remaining area smaller values of tamik were recorded at two locations.

(vii) However, the NEERI its report in 2010 (i.e. after 16 years) found that the concentrations of the contamination have gone down substantially. This is mainly due to surface runoff and leaching into the ground and also some natural decomposition.

(viii) Levels of soil contamination as of now will have to be taken into consideration to assess techno-economic feasibility, technology requirements and applicable standards of treatment and disposal so as to meet regulatory requirements.

(ix) Extent of ground water contamination was reported by NEERI in the 1996. This was according to the risk based quality criteria for soil and ground water delineated by US EPA. It was concluded that the entire

Disposal Area I (0.3 ha to a depth of 60 cm) and a few identified contaminated zone in Disposal Area II (0.32 ha to a depth of 30 cm) and at two sites in rest of area (0.08 ha to a depth of 30 cm) were contaminated and required remediation.

(x) The analysis of the ground water samples collected by MPPCB around the M/s Union Carbide premises reveled that some of the wells investigated had pesticide (BHC, Aldrin, Endosulfan I, & II, diendrien, methoxichloro and endrin) in µg/L levels. The water samples also contained heavy metals such as chromium, zinc, nickel and Iron. Other chlorinated organics such as dichloro and trichloro benzene could not be detected. The emergence of these pesticides and heavy metals is highly varying and are subjected to seasonal variations.

(xi) The geophysical investigations carried out by NGRI indicated possibility of contamination at three sites (Site I, Site III and Site V) out of nine sites. The depth of contamination at these sites was limited to about 2 m, except at one dump (Site III) that could be deeper (4-8m). These dumps were isolated from each other.

(xii) The hydro-geological studies and well inventory carried out by NGRI in the year 2008 generated information regarding soil regime and ground water conditions. The data will be useful in formulation of detailed proposal for site remediation.

(xiii) Entire area of UCIL premises is occupied by a thick layer of black silty clay and yellow silty clay up to a depth of about 22 to 25 m below ground level. The groundwater occurs in sandy alluvium with pebbles at a depth of around 25 m below ground surface under confined condition. The groundwater flow direction, in and around the UCIL premises, was in south-east direction which could change with time. It was also reported by NGRI that there existed a subsurface elevation or mound near the central part of the UCIL premises, which diverted the subsurface water flow in north-east or south-east directions depending on the approach of the flow.

(xiv) Monitoring of soil and ground water done during April 2009 and May 2010 by adopting standard protocols for sampling and analysis. Parameters selected for monitoring are relevant. The analytical results are therefore reliable and can be used to draw conclusions and useful in preparation of action plan for remediation.

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(xv) Contamination of soil due to pesticides and/or intermediates is well established. About 16 ha of area in and around UCIL is contaminated and would be subject to remediation.

(xvi) Groundwater samples within UCIL premises did not show any contamination. However, samples around UCIL indicated presence low concentrations of pesticide residues. Thick layer of clay overlain on the aquifer could prevent leaching of contaminants from waste dumps and migration of aquifer.

(xvii) Contamination of well water can be attributed to surface runoff from the dumps. However, the quantum of contaminated ground water is not estimated due to isolated nature of contamination but such information will be required for project formulation for remediation.

(xviii) Since the plants, buildings, tanks and other equipment were not decontaminated and decommissioned prior to the commencement of study by NGRI and NEERI, the open areas around such structures could not be monitored by NGRI and NEERI during the present study. During decontamination and decommissioning the area in and around these structures is likely to be contaminated. The quantum of this area is about 9 hectares.

(xix) The Solar Evaporation Ponds (SEPs) and the secured landfill located outside UCIL premises cover an area of about 14 hectares. This area also needs to be remediated.

(xx) Total quantity of soil subject to remediation has been estimated at @ 11, 00,000 MT (i.e. 1.1 million tons).

4. Strategy for Remediation:

Disposal of solid, semi solid and liquid wastes without proper treatment and without environmentally sound management practices during the years 1969 – 1984 at UCIL, Bhopal, has caused contamination of soil and ground water. Total quantity of soil contaminated as estimated at 1.1 million tons, where as quantity of ground water contamination could not be established by the NEERI/NGRI due to various reasons given in the report. Comments on suggested strategies by NEERI are as under:

(i) Construction and repairing of the compound wall of UCIL premises and proper fencing of solar evaporation ponds and abandoned secured

landfill area should be completed as soon as possible so to cordon off the area and prevent trespassing.

(ii) Contaminated wells (5 Nos.) should be immediately sealed to prevent their use by people.

(iii) Plant and machinery should be dismantled immediately and proper segregation of material be done in terms of hazardous and non hazardous.

(iv) Hazardous wastes lying in and around UCIL plant (other than contaminated soil and ground water) should be subjected to the thermal treatment of high degree so as to achieve complete destruction of toxic persistent organic pollutants, halogens etc. if any present in the waste.

(v) For remediation of ground water, NEERI has not suggested any specific technology approach or policy options. In my opinion *in situ* treatment and ground water re-charge could be preferred option. We need to work on various options and their techno-economic feasibility.

(vi) As for the soil decontamination, NEERI has suggested *on site* construction of secured landfill (SLF) for treatment and disposal of 1.1. Million tons of contaminated soil in and around UCIL.

(vii) Secured Landfill will occupy huge space. Require post-monitoring for 30 years, involving regulatory surveillance, insurance, liability cover etc. Such an elaborate treatment may not be required for *high volume – Low Toxic* waste i.e. 1.1 million tons of contaminated soil.

(viii) If landfill is created, it will also require several tons of soil or other material to backfill the gap created due to excavation of contaminated soil. More over we will also loose large quantity of soil (1.1 million tons) forever which otherwise could be reused after proper treatment rather than burying it in SLF forever.

(ix) Considering the huge volume of the soil and low levels of contamination, thermal treatment of the soil and desorption of contaminants is preferred. This will be environmentally defensible.

(x) Portable rotary kiln or plasma reactor can be installed *on site* for treatment & decontamination of 1.1 million tons of soil. After treatment, soil can be revitalized using microbial solutions and organic manure and reused for gardening, creating lawns for public use.

(xi) Decommissioned and dismantled plant & machinery should also be resorted to the thermal treatment of high degree. Treated metallic waste (slag) would be inert and can be used for ground leveling, road repairing/construction etc.

(xii) Entire area of the UCIL and its surrounding (say about 16 hectares) should be leveled and garden with memorial of victims can be created there.

5. Way Forward:

NEERI has suggested engaging competent and professionally skilled contractors for detailed engineering and execution of remedial measures. It is expected that reports submitted by NEERI, NGRI and IICT on decontamination and remediation would be finalized in the Technical Workshop proposed by the MoEF sometime in August 2010 at Bhopal. Final reports as accepted in the Technical Workshop would form the basis of undertaking detailed engineering, preparation of DPR and execution. In order to fulfill these complex tasks systematically over a period of time, High Level Technical Committee of Experts may be appointed (by MoEF or MP State Govt.) for steering the implementation of action plan through a Nodal Department of the State Government. The Nodal Department will be benefitted by the advice of the Technical Committee during the process of programme implementation. Tasks of the Technical Committee, among other things, are envisaged as under:

(a) Overall coordination and technical support to the Nodal Department of the State for project implementation.

(b) Procurement of Consultant for preparation of Detailed Project Report. (DPR).

(c) Monitoring & Coordination with Consultant and recommendation regarding approval of DPR to the Nodal Department.

(d) Procurement of Consultant for Preparation of RFQ, RFP, Invitation of Bids, Scrutiny of Bids and forwarding recommendation of selection of most competent bidder by the Nodal Department for awarding the contract.

(e) Procurement of Project Management Consultant to supervise and oversee the project implementation in a time bound manner.

(f) Technical Committee will report to Bhopal Environmental Remediation Oversight Committee under the Chairmanship of Union Minister of State (I/c) for Environment & Forests.

(g) Financial, Secretarial and logistic support to the Technical Committee may come from the State Nodal Department.

(h) The Tenure of the Technical Committee will be co-terminus with the Oversight Committee or as may be decided.

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To,

Mr.Jairam Ramesh,
Hon'ble Minister for Environment & Forests.
Ministry of Environment & Forests,
Paryavaran Bhavan (4th Floor),
CGO Complex, Lodhi Road
New Delhi - 110 003

Dated: the 2nd August, 2010

Sub: Bhopal Gas Tragedy – Relevant Reports – Comments regd.

Ref: D.O. No: 7(161)/2004-HSMD (Part- II)

Dear Sir,

I have received your letter dated 13th July. 2010 wherein you desired my comments on the following reports relevant to site remediation in and around UCIL, Bhopal:

1. Detoxification, Decommissioning and Dismantling of Union Carbide Plants.
2. Geophysical Investigation to assess Industrial Waste dumped at UCIL, Bhopal.
3. Assessment & remediation of hazardous Wastes contaminated area in and around Union Carbide India Ltd. Bhopal.

As I was on international travel and arrived very recently after a long vacation, I received your communication in late. However, I looked into these reports and brought out the salient observations on each report along with my comments and enclosed for your kind perusal.

Looking forward to work with you in future.

With regards,

Yours sincerely,

(Dr.M. Sengupta)
Former Adviser,
MoEF

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COMMENTS ON BHOPAL GAS TRAGEDY: RELEVANT DOCUMENTS

Dr. M. Sengupta
Former Adviser
Ministry of Environment & Forest, GOI
New Delhi

August 2010

420 15

BHOPAL GAS TRAGEDY: RELEVANT DOCUMENTS (WWW.MOEF.NIC.IN) Comments

The Website of MoEF was visited and the following reports related to **"Bhopal Gas Tragedy: Relevant Documents"** were found:

1) Detoxification, decommissioning and dismantling of Union Carbide Plants.
2) Geophysical investigation to assess industrial waste dumped at UCIL, Bhopal.
3) Assessment & remediation of hazardous Wastes contaminated area in and around Union carbide India Ltd. Bhopal.

IICT, Pune prepared the first report. Second and third reports were prepared by NGRI, Hyderabad and NEERI, Nagpur after extensive survey & field visit. The third report is a combined report of NGRI & NEERI submitted by NEERI in June 2010. **All these reports were looked into and the salient features of each report were highlighted followed by comments where necessary. The notes on each report are enclosed in the attached sheets.**

While going through the report, following general observations made, are of concern and need to be addressed:

1) Site preparation/clearance prior to initiating site assessment study

It has been stated by NEERI (para 2.3,page 16-17 of its report) that "as per the terms of reference (TOR) for the present study, the decontamination and safe disposal of plant, machinery, buildings and materials from the abandoned manufacturing units as well as clearing of dense bushes from the UCIL premises were to be completed by BGTRRD prior to the initiation of study by NGRI and NEERI. However, these tasks were not completed prior to the commencement of field studies. Hence the areas, which were not clear of structure and bushes, could not be included by NGRI-NEERI in the present study."

This could turn out to be one of the important limitations of the present studies as a lot of uncertainty still prevails about the relevant information pertaining to these un-cleared areas such as possible existence of underground structures, storages, pipelines and the materials there in. Moreover, geophycical investigations would have limited applicability due to presence of concrete structures. In case of unforeseen findings, the quantum of contaminated soil and remediation strategy delineated by NEERI may require suitable alterations.

2) Site security

As stated by NEERI, the boundary wall of the UCIL premises is broken at many places which provided an easy access to the people living around the premises for various activities. It was also reported by NEERI that all the bore wells constructed by NGRI were found to be broken, tampered and filled with unknown materials. This is a serious issue as such activities can alter site conditions and may lead to misleading conclusions.

3) Remediation standards for soil and groundwater

As revealed by NEERI report, the national standards for remediation of contaminated soil and groundwater do not exist. Therefore the report refers to the remediation standards delineated by USEPA. However, it is felt that there is a need for site and contaminant specific risk based remediation standards for Indian scenario as mentioned in detail under report specific comments.

4) Establishment of Clean-up Fund for Contaminated Site

A Contaminated Site Remediation Fund is necessary to assist and clean up uncontrolled or abandoned hazardous waste dump sites as well as accidents, spills and other emergency releases of pollutants and contaminants in the environment. The fund could only be utilized when the company or people responsible for site contamination cannot be found or cannot perform or pay for clean up work. Funding criteria could be developed for selection of sites to be considered under this funding programme.

5) Public Awareness and Confidence Building

Movement of the huge quantum of contaminated soil load to long distance to Pithampur is a sensitive proposition. Public may raise objection about the transfer. The remediation programme should include an awareness programme to bring the common people in confidence.

TECHNICAL AND TENDER DOCUMENT FOR DE-TOXIFICATION, DE-COMMISSIONING AND DISMANTLING OF THE UCIL PLANT, BHOPAL--IICT REPORT

The report contains two volumes (Vol. I & II), Volume I contains technical details for de-toxification, de-commissioning and dismantling (Part 1) procedures for UCIL Plant. Part 2 (Sections I to V) is the proposed draft for Tender Document which is based on the standard procedures followed by the various government departments/public sector companies. Section V (Part 2) of the report explains the scope of the work (technical part) in the Tender Document. The Volume II of the report contains Drawings for detoxification, decommissioning and dismantling of the units. The technical specification and scope of the work have also been described in the bid documents as is mentioned in the technical document. Details of the plant including the chemicals handled in past, brief production process for chemicals (e.g. Carbaryl, MIC, Phosgene etc.) have been incorporated in the report for understanding of the bidder about the nature of the toxic chemicals to be handled and to accomplish the task of detoxifying the chemicals residues present in the equipments and pipelines till the detoxification criteria are met. This section has also described the MIC plant structural detail, its layout, SEVIN plant equipment layout, chilling plant area, chlorine compressor areas and various storage areas flare stack and surrounding areas, pipe rack structures etc. (Page 150 of Sec 5, Vol I)

Salient Features:

The basic objective of this technical and tender document is to detoxify, decommission and dismantle the dilapidated manufacturing units in the premises of UCIL, Bhopal.

Scope of the work:

The scope of the work is enumerated based on the assumption that there may be some residual amount of unconverted toxic chemicals and related products remaining in the equipments and pipelines which must be detoxified, de-commissioned and dismantled, according to the international guidelines and procedures. The focused scope is therefore includes:

1. To detoxify the equipments, pipelines and structures as per suggested methods or as per any internationally accepted methods ,
2. To de-contaminate all the above residual chemicals,
3. To dismantle the de-contaminated equipment, pipelines and structures, and
4. Hazardous waste disposal resulting from the above operations

Plant Areas:

Various plant areas visited by IICT team covered in the document (page 7, Part 1 Vol I) are MIC and SEVIN plant, SEVIN packaging area, tank farm storage areas, chilling plant, flare stack and surrounding areas and pipe racks and it's structure.

Identified toxic chemicals:

The chemicals handled in this plant are MIC, MMA, Phosgene, Hydrochloric Acid, Carbaryl (SEVIN), chlorophorm, alpha-napthol, carbon monoxide and chlorine.

Sample collection and analysis (Ref: DE-DDD-165-DOC-02-02) and (DE-DDD-165-DOC-02-03)

Residual samples were collected from various equipments and pipelines, pre treated, identified the functional group of the chemicals and characterized. The instruments used are most modern equipments such as NMR and HPLC for analysis of the chemicals. Accordingly, detoxification methods are proposed.

Detoxification (Ref: Annexure and process flow sheet Vol. I)

- IICT has suggested the technology for detoxification which is used worldwide. This procedures are:
    - Hot air purging: Hot air is passed through the units followed by alkaline scrubbing of the air before release to the atmosphere.
    - Steam purging: It is purged through the units and followed by alkaline scrubbing for the uncondensed steam and later decontamination of the condensate.
    - Alternate washings of the equipments and the pipelines with alkali (5-10% caustic soda) & dilute acid (5-10% hydrochloric acid).
    - Water wash before dismantling and alkaline soak after dismantling of the equipment and the pipelines.
- The detoxification procedures for individual pipeline are placed in annexure A to Z

Details of detoxification of various toxic chemicals are included in the document (DE-DDD-165-DOC-02-001). The analytical methods are incorporated in document no. DE-DDD-165-DOC-02-002. Samples collected for MIC and SEVIN plant have been analyzed and presented in document no DE-DDD-165-DOC-02-003. General information collected by

IICT team after repeated visit to the site is given in the specification data sheet attached with the Vol. I of the document.

Dismantling:

The detailed procedure and sequence for dismantling of the pipelines and structure suggested in Vol I in the report are quiet logical and appropriate. The dismantling should be done after ensuring that all the equipments and pipelines are properly detoxified.

Decommissioning:

The decommissioning of the plant as suggested is the procedure to deform the detoxified equipments, pipeline mechanically to make it unfit for reuse. The fragmented pieces of metals have been suggested for disposal. Simple gas cutting or other mechanical cutting procedures have been suggested. Workers safety measures have also been suggested during decommissioning.

Safety in the work place:

Though it has been mentioned that safety at the work place is the responsibility of the contractor to be engaged but there is a need for detailing the safety procedure under the existing regulation under Factories Act. In this context, the safety norms set under Gujarat State Maritime Board Act adopted for the Alang Ship Breaking Industry at Gujarat Coast for dismantling of scrapped ship may be used as a guidance document.

Comments:

Brief comments on the above document are as under:

- The IICT Pune is a premier CSIR laboratory has competence in pesticide technology. The institute is in forefront of process development, process design, mechanical design and commissioning of pesticide plants and has experience in process safety. IICT team has visited plants and collected the required background information and samples. The data presented in the technical data sheets of the document appears comprehensive. .
- IICT has followed the sophisticated analytical procedure for sample analysis particularly in functional group detection and characterization of the toxic chemical residues through NMR, GC-MS, HPLC which are comparable with any world class chemical identification techniques (presented in the data sheet).

- The technologies suggested for detoxification of pesticide unit in the report are at par with the conventional technology used worldwide. Moreover, it is believed to be the low cost technology. While implementing this technology for detoxification, continuous monitoring of the program must be conducted under the supervision of the IICT expert.
- Hazardous waste generated from the detoxification, decommissioning and dismantling of the plant (mainly chemical waste and wastes from mechanical activities) are required to be disposed so as to comply with the provisions of the Hazardous Waste(Management Handling and Trans-boundary Movements) Rules,2008 under EPA. Detailed procedures need to be formulated and incorporated in the document. Similarly, waste water expected to be generated during detoxification of plant needs to be treated to comply with the regulatory standards.
- Document no. DE-DDD-165-DOC-02-002 has mentioned about the qualitative identification of the presence of toxic chemicals (as in one instance MIC and SEVIN) in the reactors, storage tank and pipelines. However, there is no mention about the quantum of the residual toxic chemicals remaining in the various units of the plants. Not only MIC and SEVIN, other identified chemicals as presented above are required to be estimated before detoxification. It will help in estimating the optimum use of detoxicant for removing the chemicals and ultimately it will generate less waste material during the time of detoxification.
- While detoxification will start in various units, fugitive emission will be generated inside the units containing toxic chemicals at the work place. This needs to be handled carefully in an environmentally safe manner.
- Document no. DE-DDD-165-DOC-02-001 has mentioned various alternative chemical pathways for chemical detoxification. However, it has not been mentioned who will decide and which method would be site specific and more effective. It is therefore, important that there should be detailed technical briefing by IICT experts to the professional contractor having highly specialized chemical clean up team. Overall, the work should be supervised by the IICT team.
- In absence of any criteria set for level of detoxification to be achieved, efforts should be to achieve 100% decontamination through the procedure applied for decontamination. Continuous monitoring and analysis should be followed after each set of purging and alternate washings till the area is completely decontaminated.
- It is important to check also the presence of PCBs or related compounds and asbestos in the manufacturing units. Presence of PCBs in engine oil, transformers and capacitors may not be ruled out. Similarly presence of asbestos used for insulation in the industrial piping system should also be checked and reported.

- No cost calculation has been done for detoxification, decommissioning and dismantling works involved in this phase of clean-up programme. Attempt may be made to estimate the cost.
- Highly skilled contractors having experience in decontamination of contaminated sites with all up to date safety equipments should be engaged during implementation of the work.
- Proposed Tender document is generally a standard document followed in various government departments. There is a set of procedures which should be followed. A committee may be constituted inducting administrative, legal and technical experts to examine the format to make it project specific. However, technical part of the tender document needs to be examined from the above point of view. All the activities involved in implementing the "scope of work" mentioned earlier need to be properly identified for detailing the extent of works involved. This will help in understanding the works thoroughly by the professional contractors.

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GEOPHYSICAL INVESTIGATION TO ASSESS INDUSTRIAL WASTE DISPOSAL AT UCIL, BHOPAL- NGRI REPORT (PART-I)

The objective of the geophysical investigation is to assess the location and dimension of the waste dump site which sometimes are not visible through inspection prior to adopt any remedial measure. This cost effective and modern technique was used to identify the buried dump site.

Salient Features:

- **Waste Characteristics:** NEERI during its investigation identified the waste materials mainly as solid waste (off specification products from manufacturing of pesticides), tarry waste from distillation unit, burnt and combustion process and dry residues from Solar Evaporation Ponds (SEPs).
- In 1994, NGRI first carried out geophysical investigation for delineating subsurface formations (using resistivity sounding) and identifying possible dump sites (using resistivity profiling).
- In the present study (2010), the NGRI has used the latest technology of resistivity imaging and its application for detecting dump sites by multi electrode, geo-electrical investigation. The High Resolution Electrical Resistivity Tomography (HERT) technology was used to obtain 2D and 3D distribution of resistivity of subsurface strata. The latest equipment used is SAS4000 from ABEM, Sweden, (www.abem.sc) and the data has been interpreted using RES2DINV software.
- The limitation faced for HERT application is due to coverage of various places in UCIL premises with concrete structures, sheds, roads, dense bushes, etc.
- The geophysical profiling was done at 9 sites at different directions (location presented in main Report). The result obtained based on the differences in resistivity has been recorded during geophysical profiling. The possible dumps were demarcated as under:

  Site I: North of Formulation plant

  Site III: South of Storage tank and police post

  Site V: Between Neutralization tank and Solar Evaporation Pond (SEP) including Tarry waste dump in Northern part

- Most of these dumps are limited to 2m depth except one that may be deeper 4 – 8 m. These dumps are limited to few Spots.

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HYDROGEOLOGICAL AND SIMULATION STUDIES OF AQUIFER, UCIL, BHOPAL

- NGRI REPORT (PART-II)

The NGRI has assessed the groundwater regime in and around UCIL premises and reported in Part-II of its report. The assessment was done through various hydro-geological investigations namely, drilling test bores, aquifer characterization, monitoring of water level, reduction of water level to mean sea level and simulation of ground water regime. This study was conducted in 2008-09, financed by MP State Govt. (BGTR & RD).

Salient Observations:

- The geological profile across the study area indicates basaltic formation overlained by Vindhyans, characterized by thin, shallow and poor in ground water potentials.

- The ground elevation of the study area around UCIL shows general slope towards southeast direction. Well inventory of the study area was conducted selecting existing one dug well (shallow) and 7 bore wells to know the groundwater regime in and around the premises. The study of the water levels shows shallow in south western part and deep in eastern part. The water level variation ranges from 3.4 meter to 23.37 meter due to monsoon (2008-09). The electrical conductivity (EC) values, an indicator of salinity is higher at the south eastern part in the vicinity of populated and industrial area.

- Five sites (Site I-V) were selected for drilling bore wells for exploration of aquifer zone and to get lithological information in the area. A Fence Diagram was also drawn on the basis of litho logical information. The result indicates as follows:

    - The weather basalt is overlained by black silt clay of 10-17 meter below ground level; its thickness varies from 2.7 meter to 6 meter in western part.
    - The basalt is further underlained by Yellow silt clay (22-25 meter). The underneath formation is sandy alluvium with pebbles saturated with water forming aquifer of thickness 0.7 meter to 4.6 meter and is thickest in the eastern part.
    - Water is found at about 22- 25 meter below ground surface and risen up to 8.5-14 meter indicating the aquifer is confined in nature.

- Aquifer characterization was done through slug test using digital data loggers. The information was used in deriving aquifer transmissivity using software Aquifer Test

Pro (2007). The transmissivity value obtained during the study used to calculate aquifer permeability which varies from 5-7 meter/day. The aquifer permeability slightly higher in south western part and minimum in the north eastern part of the area.

- Available hydro geological data and geophysical data were used to conceptualize the aquifer system in the area. The model MODFLOW was used to simulate the aquifer system which was calibrated against the water level observed using observed data. The model was used for the following purpose:

1. To map the ground water velocity of the area in Feb, 2010;
2. To predict particle track in the study area and to compute time required to reach the abstraction well; and
3. To predict well head capture zone considering 4 locations in different parts of the area. These results clearly define the zones likely to be affecting the water supply wells in case any pollutant infiltrates the aquifer.

Comments on NGRI Reports (Part-I & Part- II):

Overall comments on Part-I & II reports are summarized in the following paragraphs:

- The Electromagnetic survey is the most common geophysical technique used in various countries. The same has been used here along with conductivity anomalies caused by some contaminants to investigate the waste dump in around the suspect site (UCIL). After review of the past data (1994), NGRI has applied the advanced technology of resistivity imaging and its application for detecting dump sites by multi electrode, geo-electrical investigation. The High Resolution Electrical Resistivity Tomography (HERT) technology was used to obtain 2D and 3D distribution of resistivity of subsurface strata. The latest equipment used is SAS4000 from ABEM, Sweden, (www.abem.sc) and the data has been interpreted using RES2DINV software. The survey revealed the location of waste sites, characterize the subsoil strata, depth of groundwater occurrence and flow direction. Based on this outcome and with the help of soil and ground water analysis data, footprint of contaminants have been identified rationally.
- Electrical Resistivity Tomography or Electrical Imaging is now gaining importance in sub surface investigations. This method involves low cost, fast field survey and high

resolution imaging of electrical properties of the sub surface. Now a day this technology is widely used for contaminated site investigations.

- It appears that the geophysical investigation faced a serious limitation as a significant portion of UCIL premises was covered under concrete structures, plants remains, sheds, roads, dense bushes, water logging etc. The HERT technology could not be applied in this area. It is therefore necessary to clean-up the area by decontaminating, decommissioning and dismantling of the plant site, clearing of bushes before reassessment. Re- investigation may reveal more dumpsite in the premise.

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ASSESSMENT AND REMEDIATION OF HAZARDOUS WASTE CONTAMINATED AREAS IN & AROUND M/S UNION CARBIDE INDIA LIMITED-BHOPAL- NEERI REPORT (2010)

1. Ms Union Carbide India Limited, Bhopal (UCIL) used to manufacture Carbaryl (SEVIN pesticide) as well as associated chemicals during 1969-1984 in its unit. After the leakage of Methyl Isocyanides (MIC) in 1984, the plant was closed. The solid, liquid and tarry wastes generated during the manufacturing of the pesticides and other associated chemicals were dumped within the UCIL premises. Several decades have been passed but no significant remedial measures have been taken in the past except few studies regarding status of the contaminated site.
2. A Task Force was constituted by the Hon'ble High Court of Madhya Pradesh. Based on the directive of the Task Force, the Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTR&RD), Govt. of Madhya Pradesh requested NEERI (National Environment Engineering Research Institute), Nagpur and National Geophysical research Institute(NGRI), Hyderabad to undertake a joint study on assessment of level of contamination and to fix the problem.
3. NEERI reviewed all the historical information including its own report (1994-96) and NGRI report (1994-96). Various apprehensions/issues raised in other reports of other organizations namely, GTZ, NGOs, MPPCB etc (Page 4-9 of this report) also reviewed. A joint study was carried out by NEERI and NGRI in 2009-10. The study involved a reconnaissance survey and geo physical and hydro geological investigation cum soil and groundwater sample analysis in and around UCIL.

Objective and scope of the study:

The objective of the present study (2009-10) was to re-assess the extent of contamination and to delineate strategies for remediation of the contaminated areas (if found) after preliminary site clean up by MPPCB through M/s Ramkey Ltd., a consulting firm. The salient points of the scope of the work outlined in three phases are as follows (Ref Para 1.3, pg 10-11 of report):

Phase I: Detailed geophysical and hydro geological assessment of the UCIL site and the surrounding area

Phase II: Detailed sampling and the analysis of dumped site and groundwater

Phase III: Developing risk based remediating strategies for contaminated areas

Salient Observations:

Approach and methodology:

Approach and methodology followed in the following study was based on analysis of exhaustive data available from the past study (1994-96). In the present approach, the reconnaissance survey of the plant area and the outside was included. Disposal area detected in the past and additional hot spots were revisited. Based on the available ground water flow direction, upstream sampling points were selected for soil and ground water and considered as background sample. Sampling and analysis were done following the widely accepted national and international protocol (referred in Table 5 of the report). The present status of contaminated site was confirmed through geophysical investigation and geo-hydrological study. The remediation strategy delineated is based on review of available remediation technology options and site conditions.

Reconnaissance survey:

During the reconnaissance survey the joint team revisited in and around the plant. The observations of the joint team are summarized:

- Remains of various manufacturing units, machinery, building and shades in the premises were observed in a dilapidated condition.
- Decontamination, decommissioning and dismantling of this plant were not done as per the terms of reference. Cleaning of dense bushes was to be done. As per TOR, cleaning of these works was to be completed before initiation of NGRI and NEERI study.
- Existence of number of dump sites were observed in the open areas near disposal areas 1 & 2 . Excavation and recovery of wastes from dump site were incomplete.
- Existence of one Solar Evaporation Plant (SEP) and abundant land fill site were observed outside the UCIL plant.

Field study:

The study includes geophysical and geo-hydrological investigation (e.g. by electrical resistivity profiling, bore hole drilling, monitoring well etc.) followed by sampling and analysis of field sample of dump site, subsurface soil and ground water.

Outcome of NGRI study:

Geophysical investigation: The geophysical investigations through electrical resistivity profiling indicated the presence of subsurface black cotton soil underlain by silty soil, soft fragmented sand stone and hard sandstone (16-69m). Possible dump site were also

revealed in the suspected site. **In the present study High Resolution Electrical Resistivity Tomography (HERT) survey was carried out for nine sites within the premises which revealed possibility of existence of dumps at three sites as follows:**

Site I: North of formulation plant,

Site III: South of storage tank and police post,

Site V: Between neutralization tank and SEP including tarry waste dump in northern part.

These dumps are mostly to a depth of 2 meters except one dump that may be at a depth of 4-8 meters spread over a small area. These dumps are isolated from each other.

Hydro-geological study:

Hydro-geological study indicates that entire area of UCIL premises is occupied by layer of black silty clay and yellow silty clay to a depth of 22-25 meters below ground. The ground water is available to a depth of 25 meter as confined layer. The groundwater flow direction is towards south-east of the study area and dynamic in nature. A mount formation was also noted in the centre of the UCIL premises which may change the water flow direction from north-east to south-east depending on the approach of the flow. Series of lithological characteristics of the soil profile and the Fence diagram drawn in the report support the observation.

Assessment of contamination by NEERI (soil and groundwater):

Vertical and lateral assessment of contaminants for soil and groundwater were undertaken in and around UCIL. USEPA method and APHA Standard method were followed for sample collection. Three rounds of soil samples were collected and average values were reported. Parameters selected for monitoring are based on the process operation followed in past in the plant and apprehensions raised in various reports. These parameters include:

Semi volatiles/ pesticide: Carbaryl, aldicarb, alpha-napthol, hexachlorocyclohexane (HCH) & isomers and naphthalene

Volatile organics: Carbon tetrachloride, chlorophorm, methylene chloride, 1,2-dichlorobenzene, chlorotoluene and toluene

Heavy metals: Mercury, cadmium, nickel, chromium, cobalt, lead, zinc and copper.

Soil data: Soil data in upstream of UCIL premises used as control sample and revealed none of the volatile and semi volatile compound are present. **Subsoil collected from five bore wells shows the. presence of contaminants e.g. HCH isomers, aldicarbs, carbaryl, alpha-napthol and mercury up to the depth of two meters. Soil samples collected from possible dumpsites are also contaminated by the above contaminants. Soils in and around SEP located outside the UCIL premises were also found contaminated with some of the above contaminants.**

The comparison of upstream data with the soil collected from UCIL premises and SEP area indicates clearly that the soils of these areas are contaminated with aldicarb, carbaryl, alpha-napthol, HCH, dichlorobenzene and mercury as none of these parameters are present in the upstream soil samples.

Contaminated soil volume:

The total volume of contaminated soil has been estimated by NEERI as **6,50,000 cubic meters which is equivalent to 11,00,000 metric tons of soil requiring remediation.**

Groundwater:

Groundwater samples collected from constructed bore wells and existing bore wells (near entrance to the UCIL) do not show the presence of any volatile and semi volatile contaminants in the sample. This is due to the impermeable thick clay layer (approximate 22-25 meters) under the ground surface which has restricted the movement of contaminants to reach the ground water. Sampling and analysis of the bore well samples could not be carried out because bore wells were **found tampered at the site.**

Groundwater collected from five wells in the vicinity of the UCIL premises indicated isolated contamination. Since some of the wells are in the upstream of ground water flow direction, the possibility of contamination due to seepage through sub surface strata to aquifer is ruled out. The possibility of contamination **may be attributed to surface runoff from the UCIL dumps and improper management of SEP and abandoned landfill. Remaining groundwater samples did not show any contamination with respect to the contaminants generated from the UCIL.**

Remedial measures:

Considering the extent of contamination in various site conditions, **the NEERI has recommended immediate as well as long term remedial measures as follows:**

Immediate measures:

- Proper fencing and security to UCIL premises and SEP area for preventing unauthorized access and use of these areas by public.
- Immediate sealing of five contaminated wells so as to prevent use of water from the wells for any purpose by the residents.
- Excavation and recovery of dumped materials need to be completed with all precaution. The incinerable part of the waste may be disposed off in authorized TSDF at Pithampur, MP. The high volume non- incinerable wastes to be disposed in on- site secured landfill facility as planned for long term measure.
- Decontamination and decommissioning of plant, machineries and building prior to remediation of contaminated soil and groundwater should be completed on priority.

Long term measures:

Under long term measures, remediation of contaminated soil and groundwater was recommended. **For remediation of contaminated soil, an on-site secured land fill facility was recommended. For contaminated ground water "pump and treat" system was recommended.**

Cost of Soil & Groundwater Remediation:

The cost of soil remediation through secured land fill is estimated to be in the range of Rs. 78 Cr to 117 Cr. The capital cost for such pump and treat unit shall be in the range of 25-30 lacks. The operation and maintenance cost of such units is in the range of Rs. 10-15 Lacks per annum including cost of activated carbon and its disposal.

Comments:

- While reviewing the earlier studies on UCIL, it has been noted that the residues of hazardous chemicals generated during process operation in UCIL, its poor handling and storage practices for a long time, have led to the release of contaminants at site which has posed serious concerns. It is **not contaminated due to MIC release during accident occurred in 1984** as expressed by NEERI categorically in its report. Therefore, identification of this suspect site through assessment of extent of contamination is the fast step which has been rightly followed in this report.
- The objective and scope of the work of the present study is quiet focused. Assessment of contamination and site remediation generally begin with site reconnaissance and scoping and followed by subsurface investigations. The site reconnaissance has been done to assess the ground truth. Entire study has been

designed in two parts, firstly, to know the physical characteristics of subsurface strata, identification of chemical dump site in and around UCIL premises and secondly, the sampling and chemical analysis to identify the presence of contaminants and its lateral and vertical spread.

- Geophysical and geo-hydrological investigations have been taken in to consideration based on electromagnetic profiling with the help of most modern technologies i.e High Resolution Electrical Resistivity Tomography (HERT) technique, which has helped in identifying the waste dump site(Hot Spot). The hydro geological study has identified the nature of the sub soil through lithological characteristic and presence of ground water and its flow direction. These data have been used in interpreting the contaminants movement and extent of contamination in various compartments in the environment e.g. soil and groundwater. **The resistivity profiling has indicated the presence of deep black clay layer underlain by the soft rock and rock in the study area. This thick clay layer generally restricts the vertical movement of any contaminants as shown under the UCIL premises. This observation could be further strengthen through identification of clay mineralogical composition of this clay layer by X-ray diffraction study because the type of clay mineral present in this layer determines the fate of pollutants. The TCLP test of undisturbed core soil sample could also indicate the leaching potentiality of the subsurface layer for confirming the geophysical observation(not done).**
- Regarding selection of parameters for soil and ground water, my apprehension is that **there may be presence of some more secondary derivatives of main stream pesticide chemicals (used or manufactured) and some unintentional industrial chemicals like PCBs (an engine oil transformer/capacitor etc.) in the area. The presence of asbestos, and insulating materials generally used in the industry cannot be ruled out. The presence of Dense Non-Aqueous Phase Liquids (DNAPL) has also been reported as a contaminant in the study area. Therefore, list of parameters (toxic chemicals) could be rechecked.**
- In the context of soil sampling, particularly in a heterogeneous system, there is a need for statistical design for optimizing the sample program. A sufficient number of samples need to be collected to represent the statistical confidence limits required. Analytical protocol followed for soil and groundwater analysis is based on USEPA methods and Standard methods which are acceptable worldwide. For determining the concentration of hazardous constituents in contaminated soil and dumpsite waste samples "Toxicity Characteristics Leaching Procedure (TCLP)" could also be adopted as per ASTM-D5233-92 procedure. NEERI being premier research organization under CSIR, its laboratory undoubtedly follows QA/QC program.

Quantification of contaminant load in soil and ground water:

Soil Load:

Total contaminated soil load in UCIL premises has been estimated based on several assumptions. Some of these assumptions are based on the results of geophysical and geo hydrological investigations and soil and ground water analysis. Others are based on logic. These considerations are:

- Major contaminants: BHC, Aldicarb, Carbaryl, Alpha- Napthol and mercury
- No. of contaminated sites: 3 sites (Site I, III & V) out of nine sites as shown in the site map in the main report (NGRI study) and some additional dump sites. Total contaminated area is about **7 hectares**
- Depth of contaminated soil is 2 m. (Site I & V) and 4-8 m depth at site III (NEERI Report). Due to restriction of clay barrier further deeper movement of contaminant has been ruled out which was confirmed by lithological studies.
- Area likely to be contaminated during decontamination and decommissioning (not completed during joint reconnaissance survey) would be **about 9 hectares**.
- Contaminated land area near SEPs and secured landfill sites outside UCIL premises is **about 14 hectares.**
- Contaminated area near Site III of 8 m depth is **about 0.6250 ha** thus total contaminated land area in and around UCIL is **approximately 31 hectares**. Total volume of contaminated soil is **about 6,50,000 cubic meters**. Considering bulk density approximately 1.7 gm/cc, the total quantum of contaminated soil would be **about 11,00,000 metric tons**.
  This is an approximation. At the time of soil remediation work, it is apprehended that quantum of contaminated soil will increase.

Ground water:

Quantum of ground water contamination:

Data revealed no trace of contamination present in groundwater located below 25 m depth. Some stray cases of pesticide contamination have been reported near UCIL in north east and east directions may be due to surface runoff from the dump sites. **Due to isolated nature of the contamination, total groundwater contamination could not be quantified in the report. Before implementation of this report, the quantification of total volume of contaminated groundwater needs to be completed for planning and cost estimation for adopting the "pump and treat" system locally.**

Remediation strategy:

- The selection of remediation process has to satisfy a number of conditions including clean up standard set by regulatory body, availability of fund and need for local community. In the present case, the remediation of contaminated soil is necessary; a comparative assessment of remedial alternatives needs to be done to select the appropriate technology. The assessment of alternate technology also requires cost benefit analysis, development of clean up schedule among others. **Detailing needs to be worked out.**
- Natural barrier of impermeable clay later has restricted the spread of identified contaminants from its vertical movements within 2 meters depth and in very few cases to a depth of 8 meters. Groundwater contamination to a depth of 25 meters is practically impossible in most of the wells. Soil is mostly contaminated within the UCIL premises and in few cases near SEPs and abundant land fill sites. **Total soil mass contaminated has been approximated as 1100000 metric tons. Ground water in five wells was found to be contaminated in the vicinity of the UCIL which needs to be quantified. In addition, significant quantum of wastes would be generated during detoxification and decommissioning of the plant, needs to be quantified and disposed.**
- **The NEERI has recommended immediate as well as long term measures which need to be implemented in all seriousness. It is surprising to note that more than two decades have passed and no programmed remedial action has been taken up to clean the site. The BGTRRD should immediately take up the following issue without loss of time:**

  Immediate Actions:

  - Area should be cordoned off to stop any access of the public and stray animals to the contaminated sites in the UCIL premises near SEP and abundant land fill areas on priority.
  - The contaminated wells should be sealed immediately to stop use of these wells.
  - Excavation and recovery of dumped materials containing tarry wastes, off specification products should be completed in a time targeted manner with all care and protection. If there is need of any pre treatment that should be done. The collection, storage, classification of the wastes and their disposal should be done based on the Hazardous Waste (Management, Handling and Trans boundary Movements) Rules, 2008 and CPCB guideline. For disposal of off

specification products, guidelines prepared by UNEP/USEPA could be also be consulted.

- **It is not clear how the waste materials generated at site will be classified as incinerable and non-incinerable wastes. Detailing is required before sending the waste load to government authorized incinerator having efficient emission treatment system including constituents like dioxin and furan as per CPCB guide line and Hazardous Waste Management Rules,2008. It is not known whether Pithampur TSDF system is updated to that extent. It is also to be examined whether the existing TSDF has the capacity to accommodate the huge quantum of toxic soil load of unique character. Because of the sensitivity of the matter, It is not advisable to move such huge quantity of contaminated soil to Pithampur TSDF about 150 km away.**

Long term Actions:

- **Technology selection:** Regarding long term remediation the NEERI has recommended some long term remedial measures with an objective to remediate the contaminated land and ground water in the suspect site below the risk based clean up levels. It should be noted that there exits lot of technologies in the market but all these technologies are not necessarily effective at treating all the contaminants of different contaminant groups (needs to be grouped based on the property of each contaminant). **In this context, it is suggested to consult "Remediation Technologies Screening Matrix and Reference Guide" prepared by Federal Remediation Technology Roundtable publication (FRTR,1994) (Ref:www.frtr.gov/matrix2/section2/2_intro.html). Therefore, more detailing is necessary in technology selection for long term remediation of contaminated soil in and around the UCIL premises.**
- In the mean time for taking immediate measures NEERI's recommendation could be followed for treatment of 11,00,000 metric tons of soil by on-site treatment and disposal. The existing land fill facility may have some limitations because of this additional load. Therefore a secured land fill may be constructed within the premises of UCIL (as suggested by NEERI) as per the guideline of CPCB. This TSDF may be constructed at the existing disposal area to take the advantage of the site. It is to be noted that the secured landfill will be used as storage of the contaminated soil so that no contaminant is

leaked out. But feasible pretreatment technologies may be selected based on "Technology Screening Matrix" referred above.

- The contaminated ground water in some places could be remediated through **pump and treat system** as recommended by NEERI. **Detailing should be done through proper investigation of the quantum of groundwater contaminated and selection of site Specific and cost effective technologies. The level of treatment should be to the background level in the area.**

Cost estimation for remediation of soils and groundwater:

Soil remediation: It has been assumed that the cost of construction for secured land fill facility varies from Rs 600 to 900 per cubic meters of waste volume. NEERI has calculated the cost based on 6,50,000 cubic meters of contaminated soil to about 78 crores to 117 crores including the pre treatment like solidification and stabilization. It has rightly considered the 20% variation because of further additional contaminant loads and pre treatment needs. The operation and maintenance cost for secured landfill facility should also be computed which has not been included in this report.

Groundwater remediation cost: More detail work is required before cost calculation for pump and treat unit. The capital costs estimated by NEERI (25 to 30 lacks) and operation and maintenance cost 10-15 lacks per annum appears low.

Engagement of skilled professional contractors: The contaminated site remediation work is a highly scientific and technical work which needs a competent and skilled contractor having a group of knowledgeable and professional team having experience in such kinds of highly sensitive and vulnerable works.

The bid document for this work should include all minute details engineering design of the selected remediation technology, site plan, detail specification and detail programme schedule. This should be overseen by the expert organization like IICT, NEERI and NGRI.

Regional screening level:

In absence of any cleanup standards for hazardous waste contaminated sites in the country, risk based remediation level has been used based on the USEPA's "Regional Screening Level (RSL) Summary Table USEPA 2009" for the present study. Assuming the use of ground water for drinking purpose and possible future threat of human health by contaminated groundwater due to natural calamities, screening standards for industrial soils and groundwater protection for identified contaminants in UCIL sites have been used.

USEPA has developed the screening levels by using risk assessment guidance of EPA which is generally used for US Superfund sites. The concentrations mentioned in the Table 38 (Para 3.4.1) is derived from standardized equations combining exposure information assumptions with EPA toxicity data.

It is considered to be proactive for the human over a life time. However, screening levels are not always applicable for a particular site or non human health end points, such as ecological impacts. The screening level standards are not de-facto cleanup standards and should not be applied as such. If the contaminant present below screening level, no further actions are required otherwise further evaluation of the potential risk by site contaminants is appropriate. Its role in site "screening" is to help identifying areas, contaminants and conditions that require further attention before cleaning a particular site. The screening levels are calculated under the assumption that only one contaminant is present. But in presence of multiple contaminants target risk will change and target hazards quantum may be modified and needs to be considered (www.epa.gov/reg3hwmd/risk/human...table/userguide.htm may be consulted).

Regulatory framework:

- **There is a need for developing a national frame work for contaminated site and remediation.** The systematic approach should include i) identification of contaminated soil through a classification process; ii) assessment of sites; iii) comparison of site condition to generic environmental guideline; iv) determination of site specific remediation based on either guidelines based approach or risk based approach; v) development of remediation action plan to achieve the goal and its verification; & vi) continuous monitoring after remediation.

- **In absence of any clean- up criteria in the country, there is a need for development of such criteria for soil and groundwater so that all the clean- up programs should comply with those criteria**. Contaminated site criteria developed by various countries using risk assessment techniques are used as general targets in site remediation. Separate criteria can be developed or adopted for soil and ground water. Often, a distinction is made between industrial (least stringent criteria), commercial, residential and agricultural (most stringent criteria) for soil. Examples for such criteria can be found in the German Federal Soil Protection and Contaminated Sites Ordinance, The Swiss Soil Burden Ordinance and the Canadian Environmental Quality Guidelines (www.ccme.ca) The UNEP has also prepared guidelines for destruction and decontamination of POPs (www.unep.org/stapgef). **The ministry may also establish the Contaminated Site Remediation Fund to assist and clean up the contaminated sites throughout the country.**

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PROFESSOR C.N.R RAO
CHAIRMAN

GOVERNMENT OF INDIA
SCIENTIFIC ADVISORY COUNCIL
TO THE
PRIME MINISTER

SAC-PM/07/10- 599
29 July 2010

FAX: 011-24362222

Mr. Jairam Ramesh
Hon'ble Minister of State for Environment and Forests
Paryavaran Bhavan
CGO Complex, Lodhi Road
New Delhi 110 003

Dear Mr. Ramesh,

Thank you for your letter no. D.O.No.-7(161)/2004-HSMD (Part-II) dated 13th July 2010 regarding report of NEERI on the situation in the Bhopal plant site. I have gone through that. I believe that much importance is being given to the debris scattered around the area and for physically protecting the area. I feel that this is less important than actually making sure about the contamination in the soil and in the water around the site. To what extent, and how far has the chemical contamination, if any, has spread? This requires a detailed chemical study. NEERI may have the ability to do this. They could use the expertise of IICT and the National Chemical Laboratory as well for this purpose and carry out a profile analysis both in terms of breadth and depth. It is possible that now, poisonous units like cyanide and cyanate may hydrolyzed or got transformed to something else. Even then, there may be other types of undesirable chemicals present in small concentrations in various depths, extending to fairly long distances. This has to be determined and ways found to eliminate them. Removing harmful chemicals and other objects from the surface and cleaning up the place may be an easier thing to do.

With best wishes and personal regards,

Yours sincerely,

(C.N.R. Rao)
National Research Professor
&
Linus Pauling Research Professor

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के. कस्तूरीरंगन
सदस्य
K. KASTURIRANGAN
MEMBER

योजना आयोग
योजना भवन
नई दिल्ली–११०००१
PLANNING COMMISSION
YOJANA BHAWAN
NEW DELHI-110 001

D.O.No. PC/M(KK)/E-2/2010
August 2, 2010

Dear Shri Jairam Rameshji,

Kindly refer to your communication of July 13, 2010, regarding the reports submitted by NEERI, NGRI and IICT on decontamination and remediation of the Union Carbide plant site in Bhopal. I have gone through the NEERI document which incidentally also refers to the study conducted by NGRI and to some extent IICT. Even though, I am primarily referring to the NEERI document for my comments, in my view, it could also encompass conclusions that may be pertinent in the context of the other two reports too.

2) In my view, the NEERI report is comprehensive and analyse the most important two issues related to the soil contamination and the ground water contamination. The approach involves reconnaissance of the site to understand the condition of the plant machines and buildings including the study of their contamination, number of existing waste dumps as well as associated elements outside the UCIL premises such as Solar Evaporation Plant and abandoned landfills. The study further involves hydrogeological investigations including geophysical studies and analysis of field samples from dump site, sub-surface soil and ground water.

3) I am broadly in agreement with the various conclusions and recommendations given in Section (5) of the report. It is clear that contamination of soil and ground water in and around the plant premises is solely due to the dumping of various wastes during the period 1969-84 and the Methyl Isocyanate gas tragedy had no relevance to it. I am not repeating the conclusions and recommendations covered in pages 75-80 except for the fact that the decontamination and safe disposal of all the parts of the plant including machinery and abandoned

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manufacturing units as well as clearing of dense bushes from the plant premises are yet to be completed. To that extent the area occupied by these elements is not included in the present study. In my view, subject to the appropriate procedures being adopted for decontamination and clearance of bushes, the conclusion presented in this proposal may not undergo major changes at the fundamental level.

4) However, I have the following observations to make for your kind consideration, may be for future:

a) The technique of using radioactive traces for mapping the flow of water from one location to another could be a way to assess whether contaminants from a potential source could reach other locations especially in the context of drinking water.

b) There are many specific aspects, such as (mapping of slope, tone and texture of soil, nature of vegitative cover etc., that could be studied with good resolution (of the order of 60-70 cm) using today's space based systems.) It is worth investigating whether such tools could be useful for studying these types of accidents.

Further, on the lines of the above suggestions, there may be other innovative tools that could be identified from Space, Atomic Energy, DRDO and other scientific endeavours that could be integrated in developing future strategies. A separate assessment of the same may be worthwhile to carry out.

Lastly, knowing your own outlook, I venture to suggest that the various documents that have come out of the studies about this tragedy could be very critically gone through (of course, in the context of future) using the Indian National Science Academy (INSA). You have already made a very interesting beginning in this direction in the context of Bt brinjal.

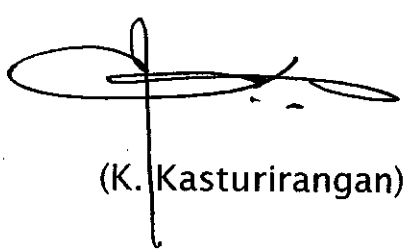
INSA for example, has the best of the academicians in chemistry, chemical engineering, geology, hydrology, sensors and instrumentation and mathematical modeling. President of

INSA could be asked to constitute an Inter-disciplinary Committee of Academicians who could go through various study reports and recommend to you what more we should do in the case of such eventualities in future.

Before I close, I may like to point out that, it is not clear how do you propose to use the land occupied by the chemical plant? Would it be possible to identify certain types of plants and other types of vegetative growth which over the years can clean up the soil and water through certain type of chemical reactions? Periodic monitoring of the same through Hyper Spectral images from space is a possibility. There is no precedence to this suggestion to the best of my knowledge, so some experts have to study and comment on the same.

With my warm personal regards,

Yours sincerely,



(K. Kasturirangan)

Shri Jairam Ramesh
Hon'ble Minister of State (IC)
Ministry of Environment & Forest
Paryavaran Bhawan
CGO Complex, Lodhi Road
NEW DELHI - 110 003.

R.K. GARG

Retd. Chairman, Recruitment & Assesment Center, DRDO
CMD, Indian Rare Earths Ltd.
Director, Chemical Engg. Group, BARC

4, Vikram Jyoti, Deonar, Mumbai-88

2nd August, 2010

Dear Honorable Jairam Rameshji,

I received your letter of 13th July, enclosing a copy of the report submitted by NEERI on "Assessment and Remediation of hazardous waste contaminated areas in and around UCIL, Bhopal", and inviting my comments there on. My comments on the report are enclosed as Annexure B to this letter.

With Regards,

Yours Sincerely,

R.K. Garg

Annexure

COMMENTS ON NEERI'S REPORT ON ASSESSMENT AND REMEDIATION OF HAZARDOUS WASTE CONTAMINATED AREAS IN AND AROUND UCIL, BHOPAL, JUNE 2010

By R.K. Garg

This report is based on the geophysical and hydrological investigations carried out by NGRI, Hyderabad and sampling and analysis of soil and ground water samples carried out by NEERI.

The salient points brought out in the report are as follows:

1. The lithology of the area as determined by NGRI has revealed the existence of black and yellow silty clay upto a depth of 22 to 25 m below ground level. The ground water in the area exists confined below a depth of 25 m from the ground surface; the general water flow direction is towards the east.
2. Sampling and analysis of soil samples by NEERI was conducted from selected areas. Samples of soil were collected from 27 locations (suspected to be contaminated) within UCIL premises, out of which 5 locations were close to the bore holes drilled by NGRI in highly contaminated areas. Samples were collected from the surface as well as sub surface (30 cm). In addition soil samples were collected from 8 locations outside UCIL premises, 4 in upstream and 4 in downstream direction, from surface as well as at 30 cm and 60 cm depth.
3. Ground Water samples: A large number of samples of ground water were collected from nearby wells, bore wells and hand pumps (total 29 locations) ranging in distance from UCIL site of 0.22 to 2.7 km. From the site 6 samples were drawn, 5 from the bore wells drilled by NGRI and one from an existing borewell.
4. Soil samples were analyzed for Aldicarb, Carbaryl, α- napthol, HCH (different isomers), Dichloro-benzene and Hg and the results were as follows:
   Aldicarb: not detected in any surface sample. In sub surface samples in 7 locations (including 5 bore-hole locations) from 3.7 to 923 mg/kg were detected.
   Carbaryl: A number of surface and sub surface samples showed concentration varying from 0.038 to 10729 mg/kg
   α - napthol: a number of samples have shown, in the range of 0.511 to 1460 mg/kg
   HCH: α, β, γ isomers range in concentration from 0.148 to 19.82 mg/kg
   Dichloro-benzene: only in a few sub surface samples with concentration range of 0.000013 to 0.165 mg/kg
   Hg: traces of Hg are present in many surface and sub surface samples varying from 0.10 to 4.17 mg/kg.
5. Out of all the ground water samples outside and inside UCIL premises, only 3 wells have shown contamination. They are close to the solar evaporation pond and the abandoned land fill and are in a low lying area. As per the report, this could be attributed to surface runoff from the dumps.

6. NEERI's recommendation on Soil Remediation: from the above findings, NEERI has recommended that 16 ha of area in UCIL premises, which has shown contamination, needs remediation. All the soil from this area upto a depth of 2m (quantity 320,000 cu.m.) should be removed and taken to a secured land fill. In addition 14 ha of land outside UCIL, covering the solar evaporation pond and abandoned land fill need to be remediated. Soil upto 2m depth will come to 280,000 cu.m. Another 50,000 cu.m. soil will have to be removed from area having contamination upto 8m depth. Thus a total of 650,000 cu.m. of soil (equivalent to 11,00,000 MT) need to be removed and deposited in a secured landfill to be constructed in disposal area II at site. Including any binders to be added, the landfill quantity may come to about 13,00,000 MT. A secured landfill of this capacity has been proposed to be constructed at site, with arrangement for leachate collection etc.

   It has also been recommended that decontamination of the equipment lying in the plant should be first carried out before remediation, since some of the soil/material in the plant area may also need land filling. For immediate action, certain measures have been recommended.

COMMENTS ON THE RECOMMENDATION IN RESPECT OF REMEDIATION

While considering the recommendation of NEERI, the following points need discussion:

i. The criteria for disposal in a secured landfill seems to have been adopted on the basis of screening standard of USEPA for ground water protection, which is apparently thousand times more stringent than the industrial soil (table 38 of report). This needs to be reviewed in view of the fact that no contamination of the groundwater under UCIL site has been detected even after 25 years of existence of contaminated soil. This is no surprise in view of the impervious nature of the strata under the site. Whatever small contamination has been detected, in 3 wells near the site, has been attributed to surface water runoff. This means proper arrangements to arrest surface runoff from the contaminated areas may provide adequate safeguards against contamination of ground or surface water.

ii. The contamination of soil has been assumed upto 2m (except a small area where the contamination is assumed upto 8m). Whereas sub surface samples seem to have been mostly collected upto 30 cm only. It is observed that in some cases, particularly where surface samples have shown very high values, sub surface at 30 cm depth have shown drastic reduction in concentration.

    In NEERI's own report in 1996, a reference to which is made in the present report (p6), it was stated that the extent of contamination requiring remediation is ((0.3 ha x 60 cm) + (0.32 ha x 30 cm) + (0.08 x 30 cm)), which amounts to only 3000 cu.m.

iii. Apart from the cost of construction of the secured landfill for the 650,000 cu.m. of soil, which will be more than 100 crores, it will use up about 10-12 hectares of land which will be unusable for all time. The cost of removal of the soil, mixing with binders, transfer to landfill and recurring cost of leachate collection and treatment have also to be taken into consideration.

iv. The adoption of a combination of modes of soil remediation as against the only mode recommended by NEERI, needs to be considered. For soils with higher concentration of contaminants, secured landfill may be adopted. This quantity may perhaps be not even 10% of the quantity presently proposed (1996 NEERI report gave a figure of about 0.5% of present quantity). For the remediation of the rest of the soil with concentration of hazardous constituents in the range of a few ppm, bioremediation may be seriously considered.
A preliminary discussion with an expert suggests the feasibility of this option.

v. It may be mentioned that for decontamination/remediation of the Hg contaminated soil in Kodaikanal (TN) soil removal has been limited to about 20ppm Hg. In case of UCIL site, Hg contamination is ranging from 0.1 to 4.17 ppm.

vi. Bioremediation is reported to be much cheaper and will provide a green cover in an area of 30 ha, apart from reducing the carryover of contaminated soil to the outside, through surface run off. It may be mentioned that one project on bio-remediation of copper tailings from a copper concentrator in MP has been already in progress under the guidance of Prof. Gautam, presently Chairman of CPCB. Prof. Prasad of Hyderabad University is another expert in this field and has carried out an extensive study on bioremediation. NEERI itself has a group on bio-remediation who have carried out a project on bio-remediation of Manganese ore mine overburden near Nagpur. It is suggested that an expert group may be constituted to give concrete shape to this combined mode of remediation viz. secured land fill and bio-remediation.

vii. The recommendation of NEERI to carry out decontamination and dismantling of the equipment in the closed down plant before carrying out soil remediation and the other immediate measures suggested in the report may be favourably considered.

डा. आर. चिदम्बरम्
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एवम्
डी.ए.इ. - होमी भाभा प्रोफेसर
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No. Prn.SA/443(O-1)/10
29th July, 2010

Dear Shri Jairam Ramesh,

Kindly refer to your letter of 13th July, 2010 regarding the decontamination and remediation of the Union Carbide plant site in Bhopal.

I had requested Director, BARC to get the comments of Waste Management Division in BARC. I have received it from him and enclose the same here.

With warm regards,

Yours sincerely,

R. Chidambaram

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Sub :- Comments on the report "Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd. (UCIL), Bhopal".

The report essentially deals with the results from the environmental survey studies and geophysical and hydro-geological investigations of the affected area. Based on the earlier records and the studies conducted, extensive work has been carried out by NEERI and NGRI to define the contaminants and delineate the contaminations spread out.

These works have clearly established that the contamination of the soil has been confined to UCIL premises and their two facilities viz. Solar Evaporation Pond and Secured Landfill located outside UCIL premises. Contamination of soil was found to be restricted up to a depth of 2 mtrs excepting a few hot spots where contamination was up to the depth of 8 mtrs. For the monitoring of the ground water, a number of bore wells were constructed within and outside the premises of UCIL. Sampling and analyses of the ground water from different depths have confirmed that there is no contamination of water from the releases during the plant operation and from the waste dumped at the secured landfill sites.

The immediate issue is to ensure containment of the contaminated soil and water so as to avoid their spread to nearby inhabited area followed by suitable remediation action. The report addresses various measures to be taken to avoid public access to the contaminated sites and prevent further spread of contamination.

The remediation should be preceded by decommissioning of the plant structures and equipment. The report vide Section 4, outlines the strategy for remediation of the soil and the ground water. The contaminated soil within the UCIL premises to the depth of 2 mtrs and in some places 8 mtrs has been recommended to be removed and disposed off in secured landfill. The report proposes adoption of pump-and-treat system for the contaminated water. This, seems to be okay in our opinion.

However, the following points could be considered while undertaking remediation action:

1. Efforts could be made to reduce the quantity of the contaminated soil to be dumped in secured landfill sites. Various methods like soil sieving, washing, scrubbing may be employed to separate the non-hazardous material from the bulk mass.

2. As the report brings out that there is no contamination of underground water in and around UCIL premises and near by sites, its remediation by pump-and-treat system may not be required. However, as surface water is likely to get contaminated by the run off from the contaminated soil, access to the water bodies within the plant premises should be guarded/sealed off for public use. Provision should also be made to avoid run off water from the UCIL premises to get into the nearby water bodies.

3. Possibility of setting up of an incineration facility within the UCIL premises rather than transporting the incinerable material 150 Kms away to TSDF at Pithampur may be looked into.

4. Monitoring and surveillance of the underground water and the soil within and around the plant should be continued.

LIMITATIONS OF SAMPLING

It is understood that the stored waste at the UCIL site is accumulated across almost the life of the plant itself. During the period of generation of the waste, this plant would have produced multitudes of pesticides (formulae) – resulting in absolutely uneven and heterogeneous waste characteristics. It will be also fair to assume that no one would have studied the data (existence and availability of which itself is doubtful) related to the raw material used as well as the intermediate & finished goods produced by this facility across the life of this plant to corroborate the waste analysis result.

This cross check is very relevant since the waste generated is nothing, but a heterogeneous mixture of raw material, intermediates, final products (both quality passed and rejected) heaped randomly.

A waste dump open to atmosphere, that has weathered 26 (minimum and certainly many more) years of thermal cycle and surface aspiration /reaction and rain-enforced leaching would have certainly undergone physico-chemical transformations that are not so easily detectable by the sampling.

If the samples were drawn from the surface strata alone, it certainly will not be representative of the middle and bottom layers.

("THUS ASSUMING THAT A STANDARD INCINERATOR WILL THERMALLY OXIDSE AND DETOXIFY THE WASTE STORED AT UCIL MAY NOT BE A RIGHT ASSUMPTION".]

DESIGN OF THE INCINERATOR

In order to incinerate a highly toxic waste with unpredictable characteristics composition and proportion, the incinerator should ideally be a custom built one. It should take care of :

1. A furnace volume design allowing sufficient residence time (minimum one hour for solids in primary combustion chamber and minimum 2 seconds in secondary combustion chamber)
2. Maintenance of temperature within maximum and minimum levels (to be decided, based on the waste characteristics) with absolute control, using auxiliary firing system and combustion control system.
3. Air supply calculated based on theoretical demand and sufficient provision for excess air.
4. A very well designed gas cooling tower, with gas Scrubber and dioxin capture system.
5. Incinerator should have a very advance and sophisticated control system.
6. Absolutely no leakage of gases.

IT IS QUITE UNLIKELY THAT ANY WASTE INCINERATOR, CURRENTLY WORKING IN THE COUNTRY WOULD SATISFY THE ABOVE PRE-REQUISITES. EVEN IF ONE WERE TO DESIGN AND MANUFACTURE A CUSTOM-BUILT ONE, MUCH MORE ELABORATE AND ACCURATE WASTE DATA WILL HAVE TO BE GENERATED.

APPREHENSION ABOUT INCINERATING THIS WASTE :

- The waste characteristics indicated to us based on the limited sampling itself contain Chlorinated Benzene derivatives. During incineration and the cooling stage thereafter, in the presence of heavy metals, there is very high potential for dioxin generation. The dioxin produced if not captured fully, will pose a major health hazard for the human and animal population in the surrounding areas.

- The sample data shows very high concentration of heavy metals, of which mercury alone is in excess of 1000 ppm. Being very volatile and semi-volatile in nature these heavy metals will get vaporized during the process of incineration. If not condensed and captured totally these vapours will lead to hazards of catastrophic proportion.

CHOICE OF INCINERATION AS A METHOD TO DESTROY THE WASTE SHOULD BE ARRIVED AT ONLY AFTER A THOROUGH STUDY.

ALTERNATIVE OPTIONS

1. Plasma destruction: The best technique currently available to destroy a heterogeneous waste with unknown ingredients will be deployment of plasma technology. This is not well developed in our country and we certainly will have to take the help from either America or Germany.
2. Immobilization: Chemical and physical immobilization technologies are well developed and are practiced by waste management companies specialized in hazardous waste treatment from the West and will be able to advice on the suitability of this technology.

Sent by M.S. Unnikrishnan
Chief Technical Officer
Thermax Ltd, Pune
(unnikrishnan.ms@thermaxindia.com)

Bhopal UCIL Assessment and Remediation

Summary Review and Recommendations - July 21, 2010

Blacksmith Institute Technical Advisory Board:
Ira May, Senior Geologist and former head, US Army remediation programs
Dr B Sengupta, former Member Secretary, CPCB
Other input from other Blacksmith TAB members

Summary.

The Technical Advisory Board above reviewed existing on-line literature regarding the Bhopal site. It is broadly recommended that additional study needs to be done at the site before remediation activities should be undertaken. Specifically, the full extent of contamination needs to be better defined so as to clarify a scope of work for remediation contractors. In addition, lower cost solutions for remediation are available than those presented in the existing literature.

It is envisaged in general that site work would remove existing structures, remediation of contaminated soils and waters, and turning the location into a remembrance park.

Detailed Suggestions.

Assumptions that these suggestions are being made:

Clean up of the site needs to be done to international standards, in a secure manner and within a foreseeable time. However, short-term low cost solutions might be available to cut done on the present risks from the site to the population.

The assessment team would organize the assessment in five different sections. Those would be 1) what is still at the site in buildings, tanks, etc. 2) what is in soils, 3) what is in groundwater/surface water 4) what is in the air and 5) recognized available treatment technologies for the chemicals indentified.

The team should apply standard Site Assessment techniques to the problem and then prioritize based on potential exposures and number of people exposed. A modification of the US EPA Federal Facilities Remedial Site Inspection Summary Guide, 2005 http://www.epa.gov/fedfac/pdf/ff_si_guide.pdf could be used by the team as their operating guide.

Assessment Phase

Some of this information may already be complete, but not available in the on-line literature. Broadly speaking the following questions need to be answered by an appropriate technical team.

Step 1. What is the current situation at the site? What is still at the site?
At the Bhopal plant, parts of the former pesticide factory remain, including some of the production plants, storage and disposal areas, and various buildings. These buildings need to be assessed as to what chemicals remain in the tanks, piping, and other containers and then to develop a plan for proper disposal.

The site is secured with a fence, a wall, and security service but is easily accessible by people from neighborhood. The team needs to assess if security is sufficient to prevent direct contact with hazardous chemicals. Diverse laboratory chemicals are likely to be present and PCB in transformers and asbestos in roof and wall coverings may exist. These possibilities need to be assessed.

Visible wastes remain on the ground in many places. The team needs to assess proper disposal and/or temporary secure storage of these wastes.

The plant is surrounded by settlements. The team needs to assess how many people are living in close proximity to the plant, where their drinking water is coming from and where their foods supply is in relation to the site.

Step 2. What is in the soils at the site and in the near vicinity?
The plant was reported to have at least disposed of liquid wastes from the pesticide production into at least three lagoons (or solar evaporation ponds), which needs to be assessed as to the amount of the contamination in the soil zone. The team also needs to assess if there are other large-scale disposal areas in the plant besides the lagoon. It is assumed that there will be significant residues from the production of pesticides such as temik, hexachlorocyclohexane (HCH), sevin, naphthol, naphthalene and mercury. Solvents such as dichlorobenzene, carbon tetrachloride, and chloroform are highly likely to be present in the soil.

Step 3. What is in groundwater and surface waters?
The ground water is likely to be contaminated by solvents, pesticides, and some heavy metals. The team needs to assess the regional geology and groundwater flows to identify present and future potential risk pathways. All wells and surface waters with a 2 km radius need to be identified.

The team needs to assess where waters are presently being used as drinking water and/or livestock water and should focus on these ground and surface waters.

Step 4. What is in the air?
The air and the dusts blowing from the site are likely to be contaminated by solvents, pesticides, and some heavy metals. The team needs to assess if this is correct and if this is a significant potential pathway for risk.

Step 5. What are the objectives for remediation of this site and what technologies are available?

- Site remediation should be done with proven and low-risk technologies.
- The disposal of wastes has to be carried out with the best available technologies according to international standards.
- The team needs to assess what disposal options present exist nearby in India and what remediation has already been accomplished at this site.
- The team needs to assess what are the risks from the use of ground and surface water as drinking water and propose low cost solutions before the groundwater can be fully cleaned up.

Remediation Phase – Likely Efforts, and Potential Blacksmith Support

The Blacksmith team recommends that remediation will be based on building of a hazardous waste and non hazardous waste landfills on site. Chemicals found in the production lines and buildings would be transported to existing waste incinerators for disposal.

- Blacksmith technical experts could be made available to review the plans for the landfills and incinerators to bring international experience to these problems.

Contaminated soils most likely could be land-filled on site.

- Blacksmith technical experts could propose some alternative technologies for the contaminated soils, especially for the soils under the former lagoons (SEP's) where we believe the most dangerous contamination exists.

Either in-situ treatment, or a pump and treats system for pesticide contaminated ground waters will be needed.

- Blacksmith technical experts could assist both in the design of a pump and treat system and/or insitu bioremediation alternatives for the groundwater cleanup.

The team has very little discussion of the potential contamination of surface waters in the vicinity, especially during the monsoon season.

- Blacksmith technical experts could take a more detailed look at this potential pollution pathway.

The team has little discussion of risks to human health and bioaccumulation pathways.

- Blacksmith technical experts could take a more careful look at these pathways and Blacksmith public health experts could look more carefully at the existing human health situation

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Indian Institute of Technology Kanpur

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DIR/IITK/2010/
July 29, 2010

Shri Jairam Ramesh
Honorable Minister of State (independent charge)
Environment and Forests
Government of India
New Delhi 110 003

Subject: Review of reports provided by NEERI, IICT, and NGRI on decontamination and remediation of the UC plant and its site in Bhopal

Dear Sir:

A committee comprising Professors D. Kunzru, Mukesh Sharma and K. Muralidhar reviewed the documents provided to us on the above subject. Their comments are appended with this letter.

If there are specific issues to be addressed, please let us know.

With best regards

Sincerely

Dhande

Sanjay G. Dhande

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IIT KANPUR

COMMENTS ON THE REPORT

prepared by Indian Institute of Chemical Technology on

Detoxification, Decommissioning and Dismantling of the Union Carbide Plant

in Bhopal

Scope and Content

This report contains the technical details of all the equipment, the plant layout, and the condition of the equipment at the Union Carbide site in Bhopal. The equipment and machinery that need to be detoxified are listed. Chemical analysis of the material present at the site has been carried out and reported in considerable detail. The material samples were collected from the two manufacturing facilities of the plant. The report comprehensively describes the methodology required for detoxification, decommissioning and dismantling of the different units. The central idea is to decontaminate the equipment in their original form, followed by cutting into small pieces and eventual disposal. The process flow diagrams for the detoxification of the different units have also been extensively reported. All the additional equipment, instruments and machinery needed to carry out the detoxification operations are carefully brought out. The treatment of wastewater formed during the clean-up process is also addressed. The document is thorough and addresses all the concerns associated with its objectives.

The report also contains the details of the bidding document that would help in identifying parties to implement the suggestions and procedures.

Highlights

i. The tender document is very detailed and seems to cover all aspects.

ii. The procedure for detoxification of each unit has been given in detail including process flow sheets.

Weaknesses

a) The procedure recommended for detoxification is elaborate and very much on the conservative side. The committee feels that the cost of the entire operation may turn out to be excessive. The authors of the report would have been served better with some quantitative analysis that would have brought caution to a realistic level. Simulation packages such as FLUENT could have helped in mathematical modeling of the clean-up process.

b) (No estimate of the total cost of the detoxification, decommissioning and dismantling of the plant has been given.)

c) At some places, there are references to Indian Standards but the details are not specified.

d) (Subsequent disposal of the detoxified scrap is not discussed.)

e) On pg145 of the bidding document (Clause 5.1, Section V), the report details the detoxification methodology of each unit. Further, the bidder is also asked to *suggest methods for detoxification which meet the international standards and guidelines*. The committee feels that the task at hand is specialized and IICT should serve as a watchdog over all the operations.

COMMENTS ON THE REPORT

prepared by National Environmental Engineering Research Institute on

Assessment and Remediation of Hazardous Waste Contaminated Areas in and around the Union Carbide Plant, Bhopal

Scope of the work

M/s Union Carbide India Ltd, Bhopal manufactured pesticides and the associated intermediate products during the period 1969-84 and dumped the solid, liquid and tarry toxic industrial waste generated during manufacturing on their own premises. Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTRRD) sponsored a project to NEERI, Nagpur and NGRI, Hyderabad to undertake a study on assessment of contamination and strategies for the remediation of the contaminated areas in and around the plant.

Highlights/Strengths

NGRI established the lithography of the site and then used state-of-the-art techniques such as electric sounding and electric resistivity profiling to assess the vertical and horizontal extent of contamination in soil, where the waste was dumped. NEERI analyzed several environmental samples from the contaminated soil (at various depths and downstream) and ground water (both upstream and downstream of the site). The chemical analysis carried out included physicochemical and organic pollutants, specific to the chemicals those were dumped at the sites. While the dumped sites were heavily contaminated, fortunately, in general, ground water was not contaminated by seepage. NEERI has suggested an onsite secured landfill for the disposal of contaminated soils. This suggestion is in the right direction since *ex-situ* treatment of an estimated 1.1 million tons of soil is not feasible.

Weaknesses, points of concerns and suggestions

1. Some assessment of the first clean up effort (excavation and recovery of waste) undertaken by Madhya Pradesh Pollution Control Board through M/s Ramkey Ltd should be done to know as to why this was abandoned. This could assist in technology evaluation.
2. Several waste chemicals dumped over the last 25 years might undergo chemical transformations. Some assessment of these transformed chemicals could have been useful, as the parent chemical may show a non-detect but the site could still be contaminated.

3. Upstream and downstream measurements of contaminants (with respect to the site) are an important aspect of this study. On page 31, ground water flow is stated as south east and on page 38 it is stated as north east. It is unlikely that the direction of flow can change dramatically and, therefore, one should reconcile as to which is the correct direction of flow and then decide on what lies in the downstream.
4. In Table 10 (details of ground water samples), one should specify the starting point for measured distances and directions with respect to plant, in addition to latitudes and longitudes.
5. Tables 17 and 18 need better statistical analysis (of chemical concentration) to ascertain if the downstream sites are more contaminated, indicating contribution from the plant premises.
6. In Table 20 (carbaryl concentration), results are inconsistent. Some values are higher at the surface and some at subsurface levels. For example, at S-2, surface concentration is 10729 mg/kg and at subsurface it is ND, whereas the trend is reversed at S-9. Some insight is required into these inconsistencies.
7. Has the form of mercury (inorganic/organic) established? The toxicity of the two forms is very different.
8. Although it has been reported that the Hg was deposited at the site, the other metals (Pb, Cd, Ni, Co, Cr) seem to show much higher concentration (Table 27). Possibly these metals were also dumped through impurities (in the dumped chemicals) or through other sources.
9. For all analysis, the lowest detection limit (LDL) must be specified, as many samples are indicated as ND (not detected). LDL can influence the interpretations.
10. If the ground water meets BIS water quality standards (in respect to metals and other parameters), is it necessary to treat the ground water? Else, this may require perpetual treatment of ground water.
11. If the excavation of contaminant sites is undertaken to fill it in the secured landfill, extreme care should be taken for the workers who could otherwise be exposed to high contamination levels. In addition, the sites are very old and during excavation it may release some toxic gases. All possible care should be taken for safety of all concerned.
12. The overall cleanup plan should also include refilling of excavated soil and development of a proper landscape.

To: Shri Jairam Ramesh
Minister of State
Ministry of Environment & Forests
CGO Complex, Lodi Road
New Delhi 110003
Via Email

6 August, 2010

Sir:

Subject: Comments on reports on assessment of contamination and hydrogeological conditions in and around former UCIL Factory, Bhopal, by NEERI and NGRI

First of all, thank you very much for allowing me to comment on these proposals. I hope that such a transparent method of handling with assessment of contamination, and identification and execution of remediation options could be made routine for all such contaminated sites in India. Further, three recommendations are particularly disturbing.

First, the proposal to incinerate the above-ground toxic wastes (obsolete pesticides, including organochlorine chemicals) in the facility in Pithampur is fraught with danger. The Pithampur facility is run by Ramky, which has had serious problems in several of its incinerators, including the Pithampur facility itself. The facility violates the Ministry's own siting guidelines. Several experts, including Mr. S. Unnikrishnan, CEO/MD of Thermax, and Dr. Eckhart Schultes, a hazardous waste management expert who consults with GTZ-Germany, have stated categorically that Indian incinerators and operators are not technically or experientially equipped to handle such complex organochlorine wastes. I would like to submit that the Oversight Committee consider the option of safely packaging the above-ground wastes and exporting it to an OECD nation for appropriate treatment and disposal.

Second, the proposal to bury 1.1 million tonnes of wastes onsite. As an option, this raises several disturbing questions. If a landfill is envisaged, this location violates key siting criteria, located as it is in the midst of a densely populated neighbourhood. Further, no arguments have been presented to make this option the most desirable and least hazard prone. In fact, like with the incinerator recommendation, no other options have been explored or presented.

Third, the consultants propose that the factory be decontaminated, dismantled and demolished. It is an oft-repeated demand of Bhopal survivors that significant and salvageable sections of the plant be decontaminated and preserved as part of the memorial that is to be constructed onsite.

My other comments are as below:

General Comments:
The reports are generally of poor scientific quality. Many of the assumptions are crippling, and throw into question the integrity of the recommendations. The reports can at best be treated as yet another indicative study. The need for a thorough, systematic and comprehensive assessment still remains as a necessary pre-requisite for proper clean-up as these studies do not make the mark as a comprehensive study.

1. NEERI/NGRI's studies fall far short of presenting a comprehensive and credible assessment of

depth, spread and nature of soil and groundwater contamination in and around the former UCIL factory premises.

2. There are noticeable flaws and inadequacies in methodologies, including sampling methodology, and quality control.
3. Thes report leave several questions unanswered. A comprehensive report would seek to fill all gaps in existing information. But these reports neither identify the key gaps in information by performing a thorough desk study of all data generated till date, nor address crucial issues, such as the number, spread and dynamics of aquifers, the source of reported groundwater contamination, the discrepancies between NEERI/NGRI's findings and former studies that report widespread contamination.
4. The NEERI report recommends disposal option without thorough characterisation of the wastes, and without presenting various options for treatment/disposal and arguing the case for the chosen options.

Specific Comments

1. The reports do not anywhere identify the number of aquifers in and around the factory site. While only a generalised flow direction is given, the flow gradients of individual aquifers have not been identified.
2. NGRI's testing results contradict the consultants' claims that the aquifers are protected from contaminant leachate by a thick layer of impermeable clay. The hydraulic conductivity was found to be much higher than the 10-9m/s. This makes the claim by NEERI ruling out groundwater contamination because of the low-permeability clayey layer unsupportable.
3. Page 11 of the NEERI report states that the apprehensions raised by other studies on possibility of existence of other contaminants has been considered. But no details have been provided as to how this has been "considered." Evidently, the parameters chosen for analysis are very limited, and no effort has been made to verify the findings of previous studies. For instance, the 1999 Greenpeace study reliably identified 10 organochlorine compounds in various groundwater samples taken from inside and outside the factory. Only chloroform, carbon tetrachloride and 1,2-dichlorobenzene from among these 10 have been reported. This lapse fails to give confidence that other contaminants reported in the other studies do not exist in the groundwater.
4. In a similar vein, the sampling protocol is severely compromised on a number of different fronts:

a) No systematic approach has been adopted to identify the sample sites. The entire factory site has not been covered in a representative manner, and neither have the surroundings been covered in any representative manner. Grid sampling could have addressed this requirement for representative sampling, but as the consultants themselves admit in page 17 of NEERI report, areas that were covered with thick vegetation were not covered in the sampling exercise.

b) Borewells, handpumps and other groundwater sources sampled by Greenpeace, Srishti, MPPCB and CSE have not been included in NEERI's study of groundwater quality. In the absence of a verificatory study, the validity of the reported contamination in many of these groundwater sources cannot be ruled out.

5. NEERI admits to having averaged the results of analyses of water samples taken on different occasions. This is irregular. Presenting the results individually allows one to understand seasonal differences and to appreciate if there are times when the contaminant levels peak or dip.
6. The conclusion that groundwater in the five contaminated wells was contaminated by surface water run-off is without basis. More importantly, it exposes the fact that the consultant failed to take precautionary quality control measures to mitigate the influence of run-off water

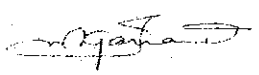
contaminating the groundwater sample (say, by purging).

7. On page 31, NEERI states that the groundwater flow direction is generally towards the Southeast. Ten pages later, on page 41, it claims that the flow is towards Northeast. But as stated earlier, these are only general flow directions. No local-specific flow directions of different aquifers has been provided, and this is a crippling limitation of the study.
8. The number of intrusive hydrogeological samples taken do not seem adequate to construct an accurate model of the geology underlying the factory and its immediate surroundings.

Given the severe limitations in the design and implementation of the NEERI/NGRI studies, the key conclusions relating to quantum of contaminated soil, and the isolation of the surface and sub-surface contaminants from the groundwater aquifers are untenable.

It would be very important to have a high-quality scientific assessment of depth, spread and nature of contamination in and outside the UCIL factory site to arrive at the various treatment and disposal options, and estimate costs of the entire exercise.

Sincerely,



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Decontamination and Remediation of Union Carbide Plant Site in Bhopal

Dear Shri Jairam Ramesh:

I thank you for your letter dated 16 July, 2010 (D.O. No. 1-58 MOS (UC) E&F/10) related to Union Carbide Site at Bhopal and the copy of NEERI Report. During a short visit to Hyderabad, I have had opportunity to have a brief book at the Report prepared by IICT. I learn communications similar to mine have been received by others.

The Task Force BGTRRD has sponsored these studies. It will be of value to receive the objectives outlined by the Task Force and the planned manner in which portions of the site could be put to use after Decontamination and Remediation by the State Government and the City of Bhopal. The NEERI preamble records the MIC Gas Tragedy in 1984 has no relevance to the contamination of soil and groundwater in and around UCIL premises. It is solely due to dumping of wastes generated during the manufacture of Carbomate Pesticides and the associated intermediate chemicals at their Bhopal Unit from 1969 to 1984 within their premises by UCIL.

The NEERI Report refers to several previous studies. Dr A.P. Mitra, Director General had arranged for a Special CSIR Cell for Bhopal Affairs to bring together all the scientific and technical data and the results of investigations by CSIR laboratories in two Volumes with consultations of several laboratories and some scientists of Public Sector Companies. Volume I with a Preface dated 25 May, 1987 by Dr Mitra contains summary of work by CSIR Laboratories with details in Volume II. These were marked RESTRICTED in 1987 on account of legal cases pending in courts. Copies of the Volumes are in the CSIR Office Library and Laboratories, which made essential contributions. A Report entitled Bhopal Toxic Gas Leakage was placed in Parliament in December 1985. A copy is enclosed for ready reference.

With increasing population, growth in Agriculture Industry and Education there is demand for land and water especially adjacent to cities and planning requires attention to outlining standards, objectives and treatments for reuse. The Central Pollution Control Board has provided expert guidance. Summaries of any studies on UCIL site or other similar ones will be

valuable. The Cities in Madhya Pradesh are being given water for different purposes and the State Pollution Control Board may be evolving standards on steps for reuse economically. Manufacture of Chemicals, Fertilisers, Ferrous and Non Ferrous Metals and special ores from mining require efficient use of water and the State Board would have been successful. Information on these will be of use in any meetings. I will be happy to provide any further information.

With kind regards:

Yours Sincerely

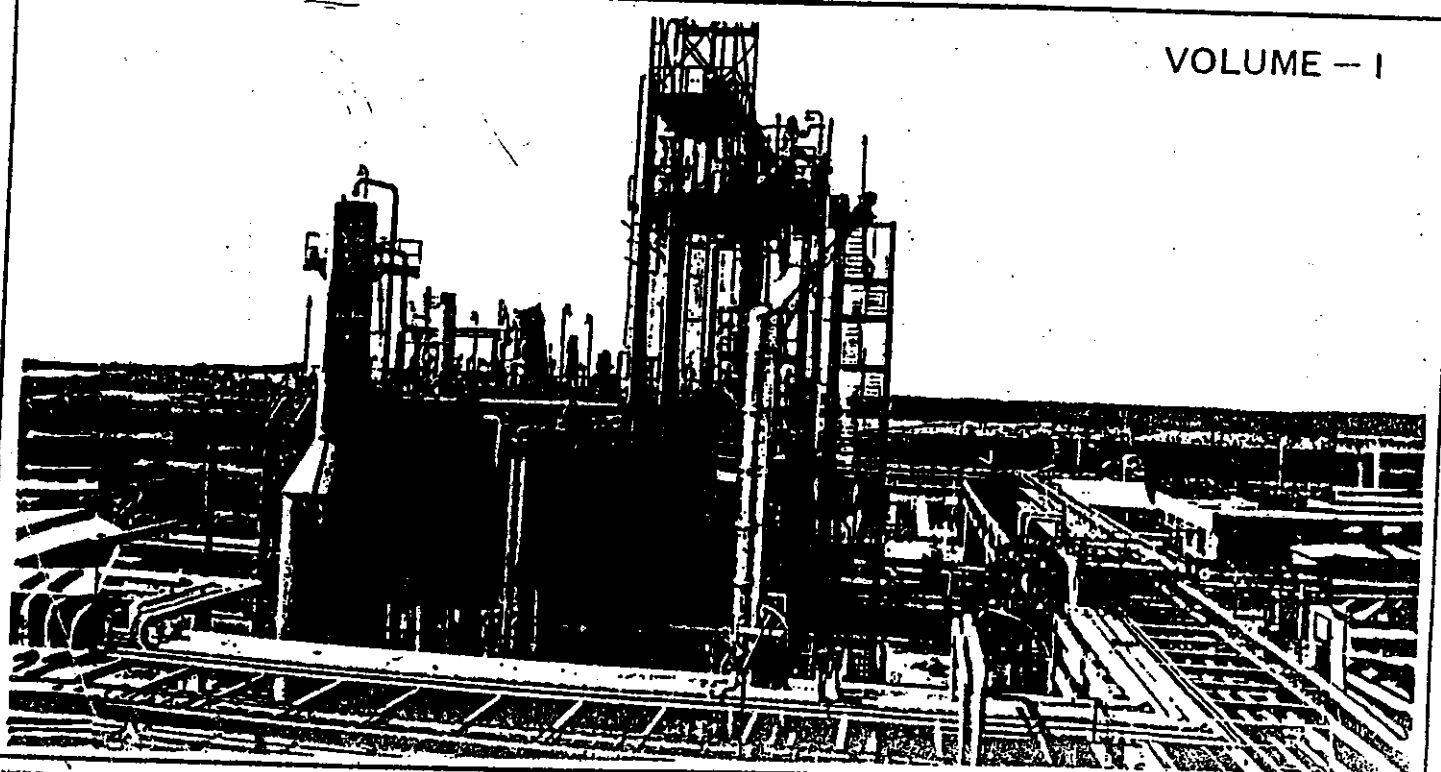
S. Varadarajan

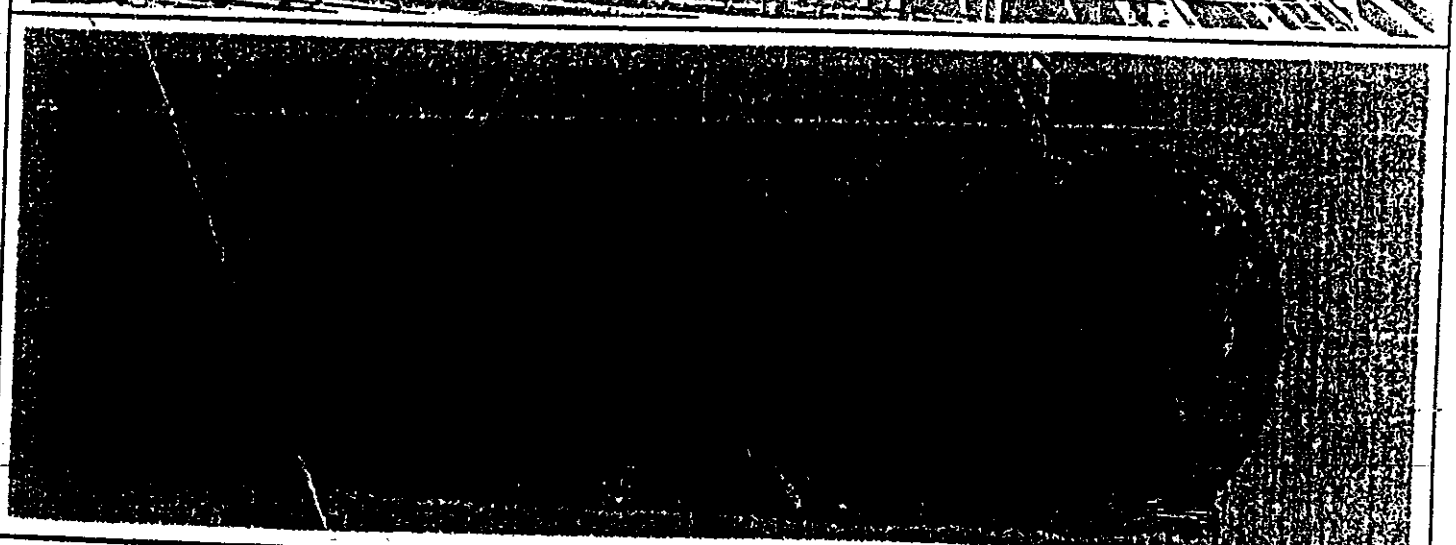
Shri Jairam Ramesh
Minister of State (Independent Charge)
Environment and Forests
Government of India
Paryavaran Bhawan
CGO Complex
Lodhi Road
New Delhi – 110 003

Encl: as above

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

VOLUME – I





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

RESTRICTED

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

VOLUME – I

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

PREFACE

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

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

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

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

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

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

New Delhi
25.05.1987

A. P. Mitra
(A.P. MITRA)
Director-General

CONTENTS

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

MEASURES TAKEN AT BHOPAL

Introduction

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

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

General Conditions in Bhopal

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

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

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

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

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

Action Taken-

The actions taken cover the following-

i) Examination of the environment immediately to see whether toxic material was present,

ii) If so what further precautions should be taken and advice given to the STate Government and through them to the public,

iii) Action to be taken to estimate the probability of further leakage of toxic material and if possible to prevent such an event;

iv) In the event of leakage occurring, precautions to be taken on minimising the damage to those present in the factory and to public outside including possibility of evacaution of population.

v) Actions on safe disposal of the remaining MIC and any other toxic material found in the factory;

vi) Immediate examination of post-mortem cases, animal carcasses as well as those affected otherwise so that full scientific observations could be made at this critical time for future examination.

viii) Coordination of all scientific efforts and arrangements for information release so that only authoritative data is given to press, to the State and Central Governments to avoid confusion and panic.

Notes on all these are recorded below-

(i) Safety of environment

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

(ii) Precautions to be taken

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

(iii) Estimating the probability of further leakage

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

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

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

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

Based on these discussions and on the general knowledge of chemistry of MIC, it was surmised that the leakage of material could occur by substantial quantity of water reacting with MIC. This is an exothermic reaction. Reaction with a part of the material could raise the temperature well above the 30°C, the boiling point and the remaining MIC could evaporate as a gas rapidly. By calculations, it was noted that 4.5 tonnes of water would be needed to react with 45 tonnes of MIC present in tank 610. However, it was pointed out by Dr. Varadarajan that 1.5 tonnes of water could be sufficient to react with one-third of the MIC and the heat produced from such a reaction could be sufficient to evaporise the remaining 30 tonnes. The reaction of large quantities of water with MIC could produce Tri-methyl Biuret (TMB) or Di-Methyl Urea. (DMU).

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

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

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

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

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

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

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

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

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

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

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

iv) **Action for minimising damage due to further leakage-**

Since it was clear that there was potential

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

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

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

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

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

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

v) **Action for Safe Disposal of Material of MIC:**

The following alternatives were considered for safe disposal of MIC:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

At one stage there were reports from some investigators, not forming part of the team, that cyanide levels in air in excess of permissible limits were detected. A large investigation was carried out to see if this could be verified by using special tubes for detection of minute amount of cyanide, flown in from IPCL Baroda along with appropriate experts. Throughout the period, no cyanide was detected in the air. The liquid level indicator in tank 611 and the empty tank 619 were not functioning and it was learnt that these were sealed by CBI. The estimates of MIC were made from the records provided by the factory management. However, after the first day operation on 16th December, it was possible to judge quickly from the gas pressure of tank 610 that the material present in tank 611 was in excess by about 4 tonnes. Adequate arrangements were made to ensure availability of alpha naphthol for conversion of the additional material. Similarly note was taken of the MIC material (about 1.2 tonnes) stored in sealed drums. Special arrangements were then instituted for drawing material from such drums. The tank 619 was also found to contain over 2 tonnes of material. This was also withdrawn and converted. The operations had therefore to be extended by about 2 days. About 3-4 tonnes could be processed each day. The transfer of MIC from tank was done during day light hours and conversion to carboryl was carried out throughout the night. Representatives of Scientists' team were present throughout this operation day and night and operations for each transfer of material were approved by Dr. Varadarajan and the team. Trial reactions in the factory laboratory were carried out with material in tank 611, 619 and drums separately to ensure these materials would fully react with alpha naphthol. Transfering of bulk materials were approved after such trials in each case.

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

(vi) Assistance to health and medical authorities

Scientists from All India Instt. of Medical

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

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

(vii) Collection of materials for future examination

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

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

(viii) Coordination of efforts:

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

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

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

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

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

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

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

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

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

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

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

Concluding remarks

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

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

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

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

New Delhi, the 9th January, 1985.

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

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- Dr. Lata Singh
- Shri M.V. Ramakrishnan

Regional REsearch Laboratory (CSIR), Bhopal
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- Dr. M. Patel
- Dr. C.B. Raju
- Dr. A.K. Ray
- Dr. (Mrs.) M. Maheswari
- Mr. Amrit Phale
- Mr. B. Kujur
- Miss A. Gupta
- Mr. A.C. Karara
- Mr. A. Khare
- Mr. J. Jain
- Dr. Ravi Prakash
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- Dr.N.R. Iyangar
- Dr. O.G.B. Nambiar
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- Dr. M.U. Beg
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- Dr. S. Sriramachari

Institute of Pathology, New Delhi.
- Dr. H.M.K. Saxena

National Institute of Occupational Health, Ahmedabad.
- Dr. S.K. Kashyap

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- Dr. Y.P. Singh
- Dr. A.E. Nivsarkar
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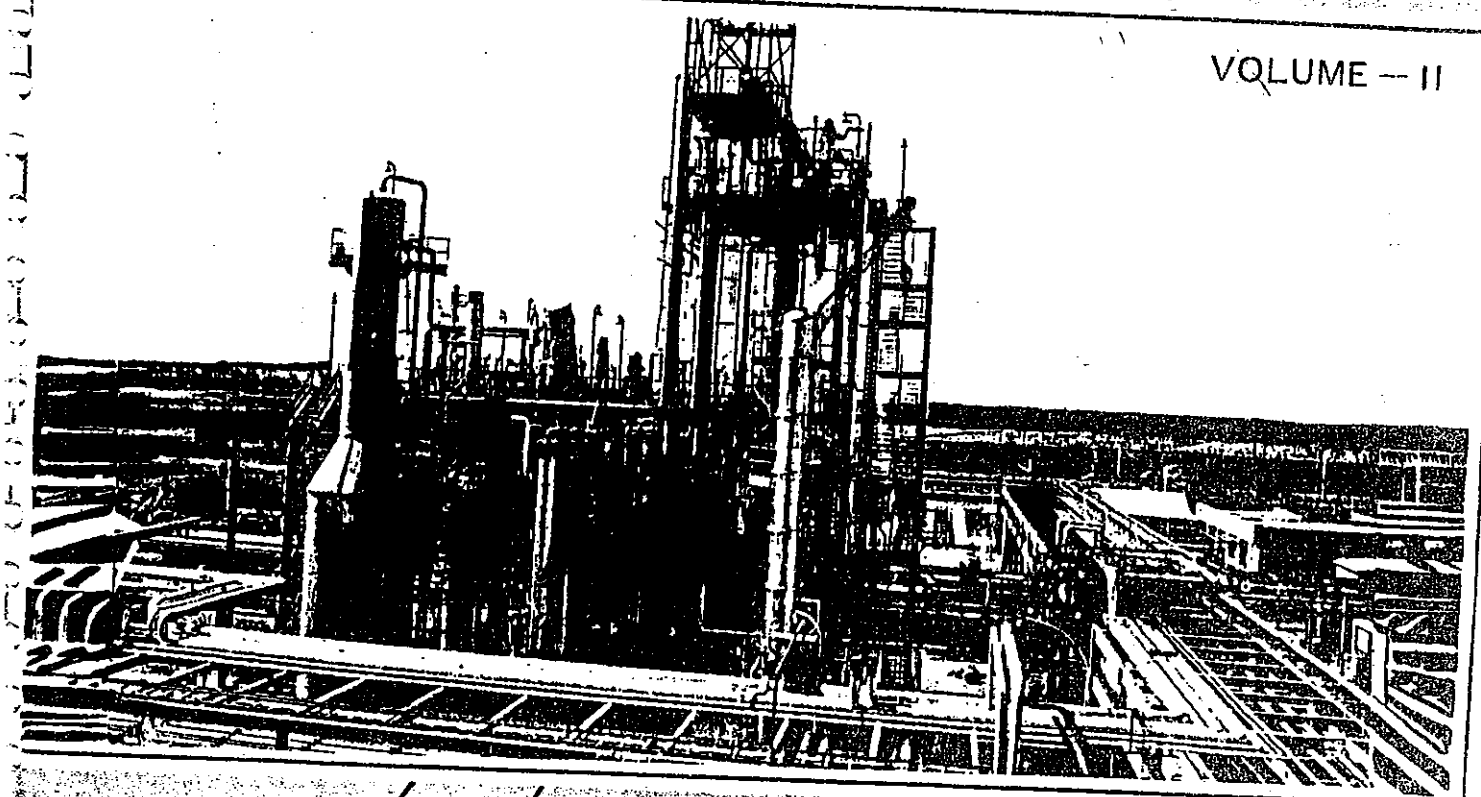

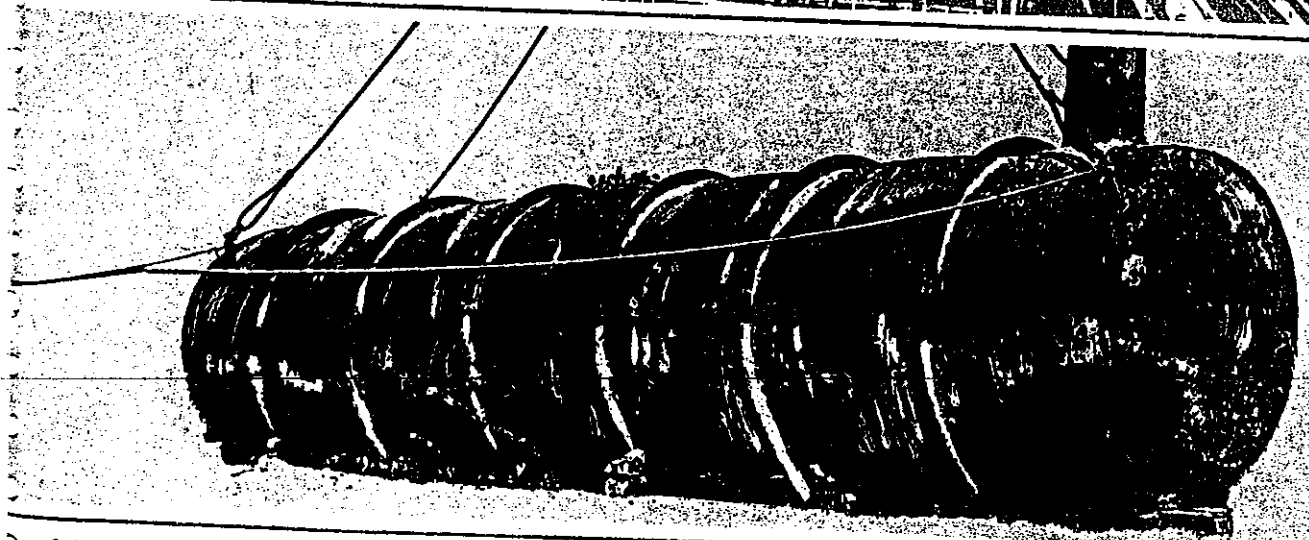

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THE CHEMICAL PHENOMENA LEADING TO THE TRAGIC TOXIC GAS LEAKAGE AT THE UNION CARBIDE PESTICIDE PLANT, BHOPAL AND AFTERMATH

VOLUME — II

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

DECEMBER 1985

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

DECEMBER, 1985

This Report results from Studies

by

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ABSTRACT

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

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

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

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

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

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

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

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

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

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

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

1.0 INTRODUCTION

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

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

1.1 The Bhopal Pesticides Plant

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

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

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

1.1.1 MIC manufacturing process

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

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

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

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

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

MIC PLANT

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

1.1.2 MIC storage system

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

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

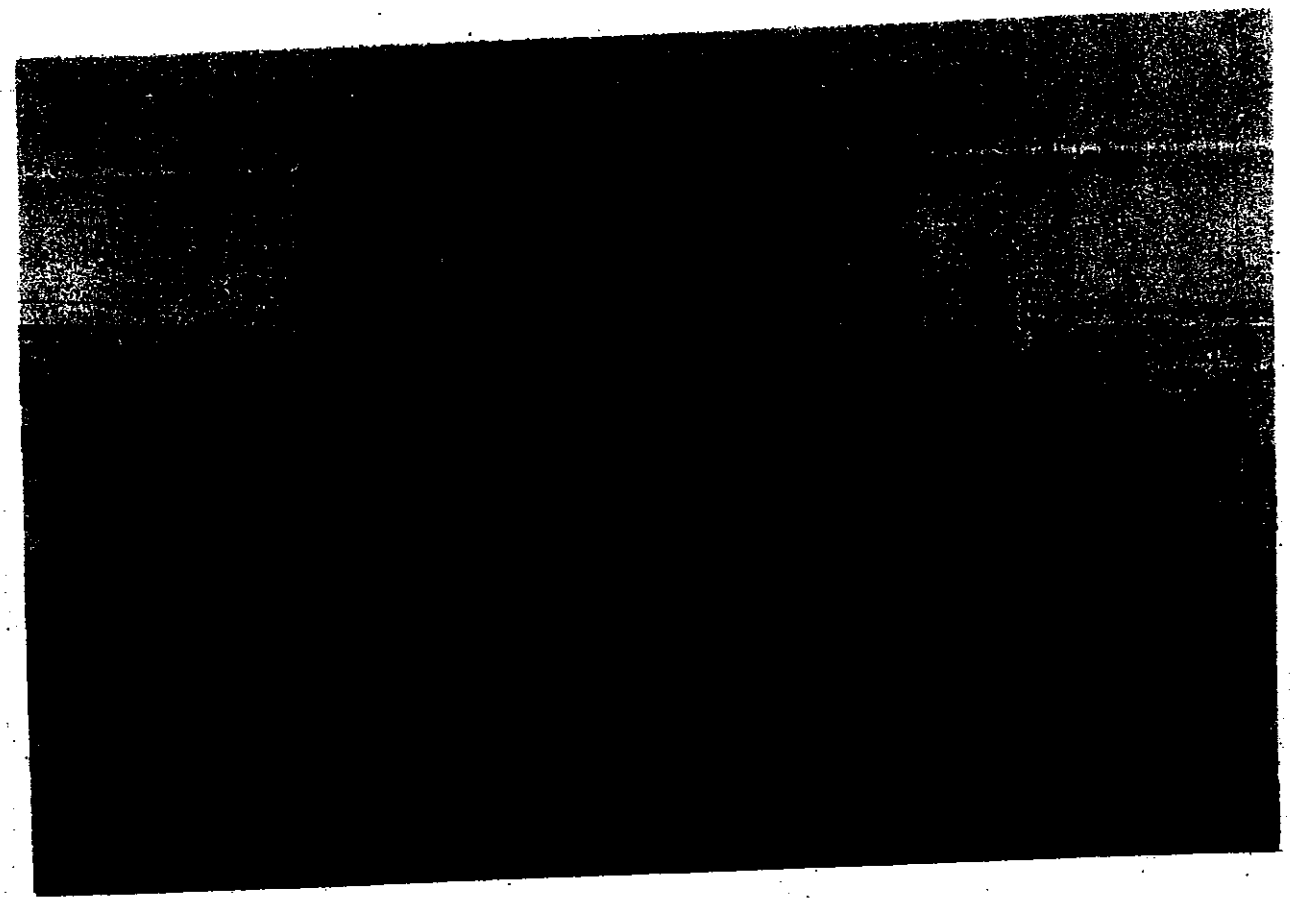
The schematic layout of the three MIC storage tanks with common headers is shown in Figure 1.1 MIC from MRS condenser in the MIC production facility (MIC structure) is led by a long common line of stainless steel to the MIC storage tank area and then branches off just before entry to the individual storage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

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

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

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

VIEW OF MOUNDED MIC STORAGE TANKS FROM GROUND LEVEL



VIEW OF TOP OF MIC STORAGE TANKS

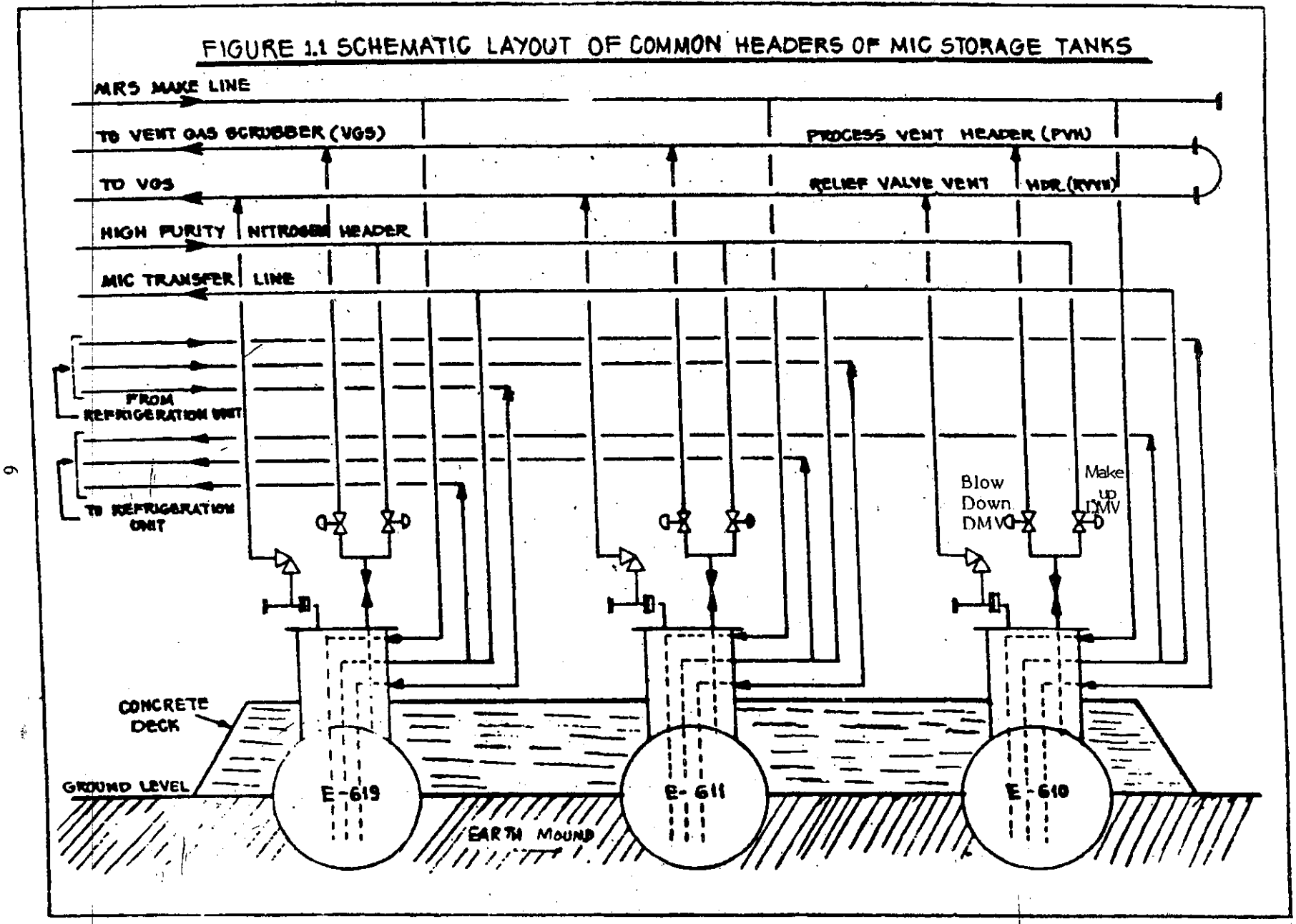


FIGURE 1.1 SCHEMATIC LAYOUT OF COMMON HEADERS OF MIC STORAGE TANKS

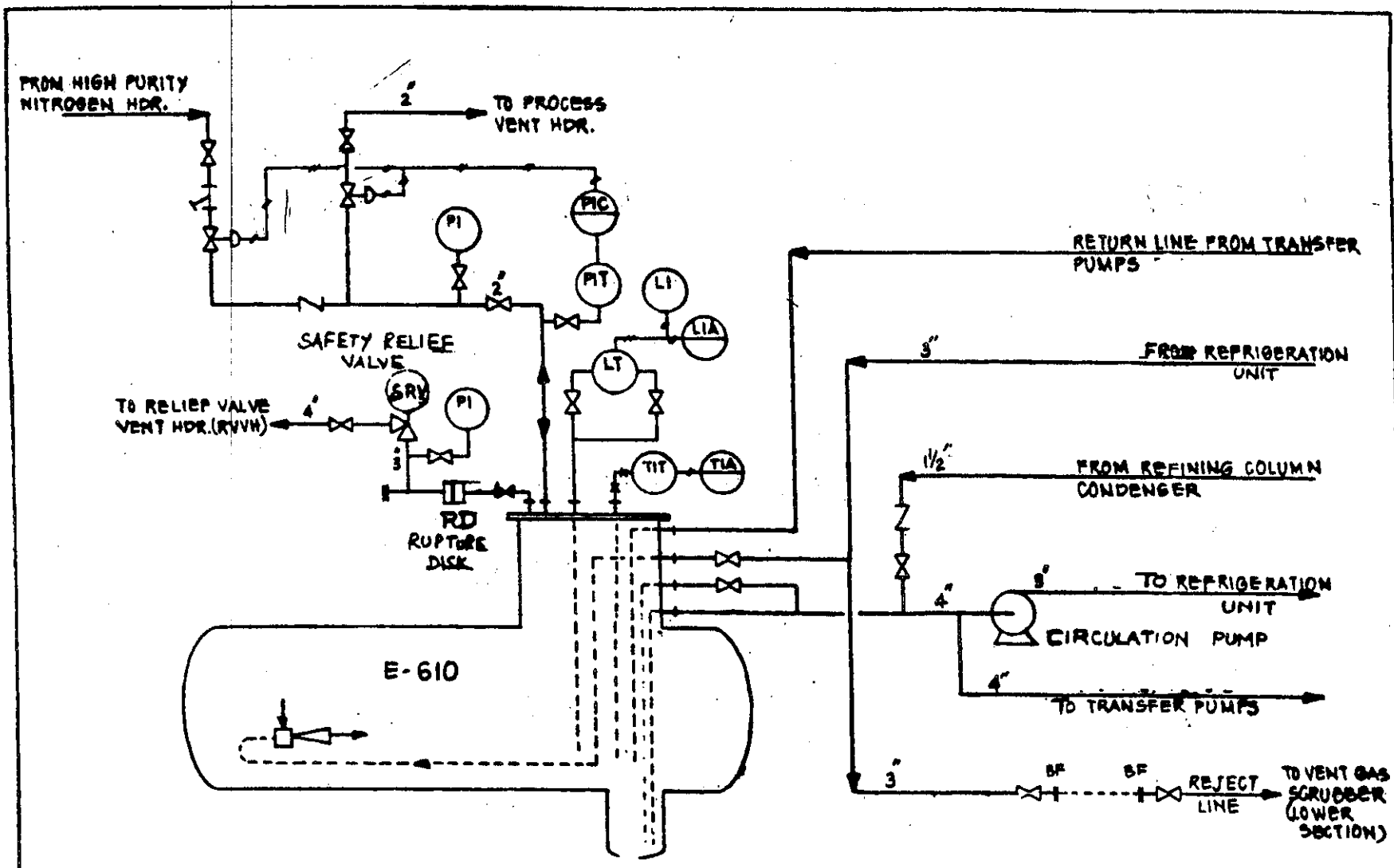


FIGURE : 1.2. MIC STORAGE TANK

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

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

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

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

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

1.1.3 **Vent gas scrubber :**

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

VENT GAS SCRUBBER

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

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

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

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

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

1.1.4 Flare tower :

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

1.2 The Event

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1.3 'Operation Faith'

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

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

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

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

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

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

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

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

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

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

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

or MCC. The relevant reactions are listed below :

$$COCl_2 + H_2O \longrightarrow 2HCl + CO_2$$

$$CH_3NHCOCl \xrightarrow{H_2O} CH_3NCO + HCl$$

$$2\,CH_3NCO + H_2O \longrightarrow \begin{matrix} CH_3NH \\ CH_3NH \end{matrix}\!\!>\!CO + CO_2$$

$$3\,CH_3NCO + H_2O \longrightarrow CH_3NH\!>\!CO \cdots + CO_2$$
$$CH_3\,NCONH\,CH_3$$

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

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

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

The measures introduced included of the following :

i. **Ultimate safe disposal of MIC**

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

ii. **Safeguards against entry of contaminants**

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

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

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

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

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

iv. Stabilisation of MIC

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

v. **Disposal of MIC**

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

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

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

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

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

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

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

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

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

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

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

2.0 EXAMINATION OF TANK 610 AND ITS CONTENTS :

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

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

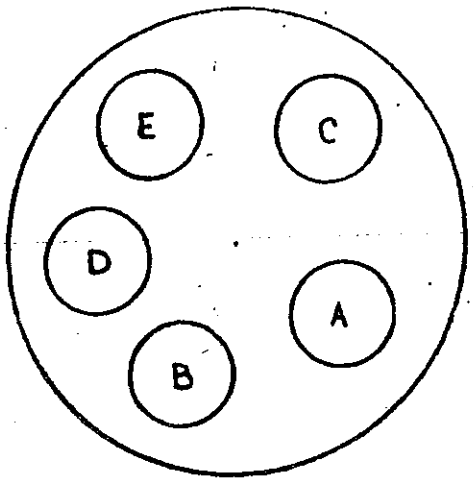
During March 1985, the concrete mound over the tank, which had already cracked during the event, was removed and excavation work around the tank completed to provide access to and enable inspection of the external wall of the tank.

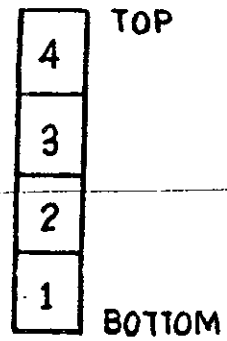
It was decided to cut windows at specific points on the tank wall and examine the metal as well as samples of the residue throughout the length of the tank. In April 1985, tank 610 was evacuated first and then purged with nitrogen to remove volatiles and minimise odour. Plates were then cut at predetermined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

2.1. Sampling

2.1.1. Core samples from the manhole nozzle :

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



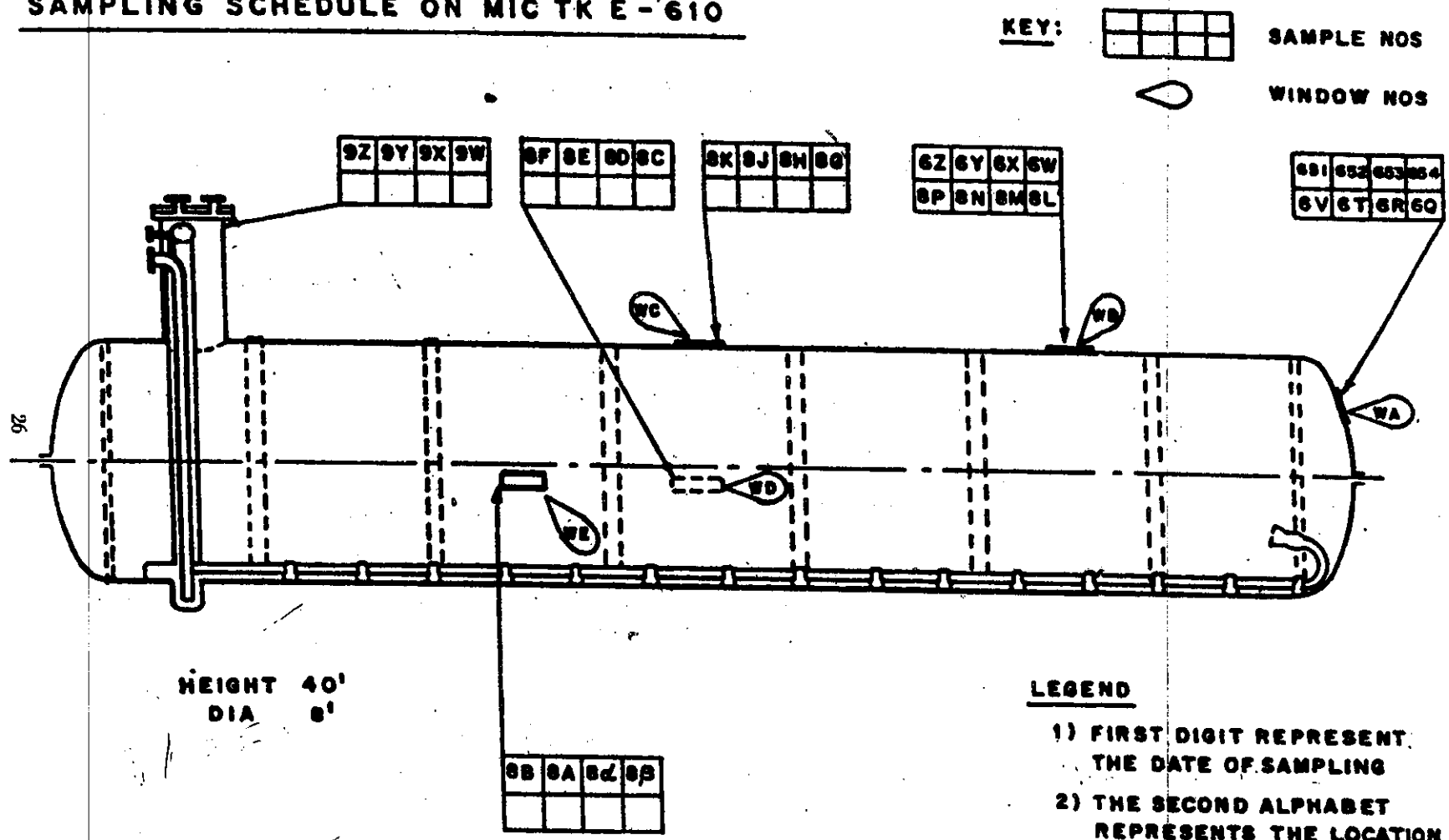


CORE SAMPLE

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

FIG. 2-1, SAMPLE IDENTIFICATION

SAMPLING SCHEDULE ON MIC TK E-610



LEGEND

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

FIGURE - 2.2

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

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

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

2.1.3. **Samples from pipelines :**

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

2.1.4 **MIC samples from tank 611 :**

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

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

2.1.5. Metal pieces cut from Tank 610 :

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

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

2.2 Chemical Analysis

2.2.1 Physical appearance of samples of residue :

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

2.2.2. Solubility Characteristics :

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

2.2.3. Qualitative Analysis :

Smell : The samples showed a strong smell of amines.

Acidity or alkalinity : The samples were highly acidic.

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

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

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

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

2.2.4. Analytical Procedures :

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

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

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

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

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

2.2.5. Analytical Results :

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

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

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

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

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

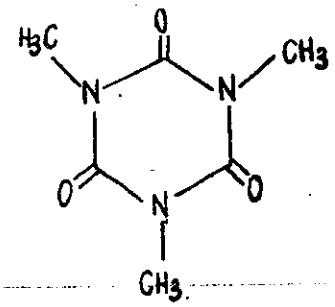
homogenised. This sample was prepared by mixing equal quantities from 22 different residue samples. These samples represent the bottom portions, middle portions and top portions at different axial positions along the 40 feet long storage tank. Two such samples were prepared initially, each of which was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

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

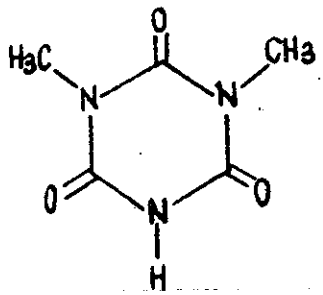
The total identified compounds in the sample add up to about 95%. As indicated earlier, the residue samples contain about 3-6% of un-identified tarry materials.

2.3.1. Product distribution :

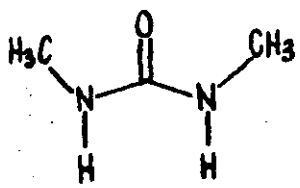
Besides the presence of various metal and chloride ions, the residue contains 10 organic compounds. These are presented as kg moles in the last column of Table 2.9. The tank residue contains 40.7 kg moles (or about 7000 kg of MIC trimer). The next highest molar concentration is that of DMI with 17.0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



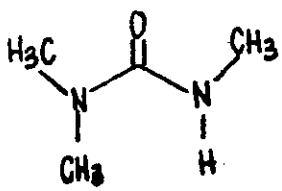
MICT
MW = 171



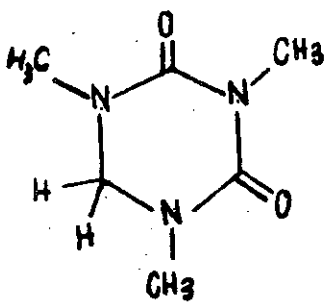
DMI
MW = 157



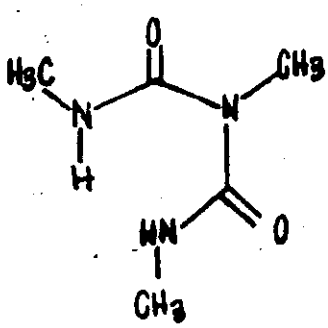
DMU
MW = 88



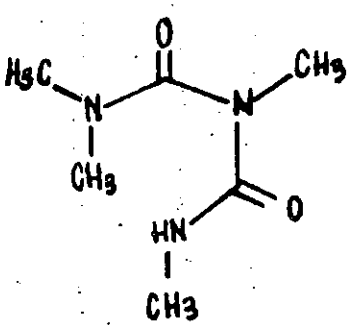
TMU
MW = 102



Dione
MW = 157



TMB
MW = 145



TRMB
MW = 159

FIG. 2.3 - STRUCTURES OF COMPOUNDS IN TANK-610

TABLE 2.1

ANALYSIS OF LIQUID SAMPLES FROM RVVH/PVH

Sl.No.	Sample	Chloride % Cl^- w/w	Acidity % HCl, w/w	Alkalinity, % w/w Na_2CO_3	$NaHCO_3$
1	2	3	4	5	6
	A. Samples of February,1985				
A1	From PSV downstream bleeder of dryer.	1.37	-	-	-
A2	Side-stream cooler PSV d/s bleeder.	15.61	11.98	-	-
A3	RVVH drain bleeder on desuperheat on second level.	5.01	4.38	-	-
	B. Samples of May, 1985				
B1	PVH No. 7	1.42	Nil	13.62	13.31
B2	RVVH from bleeder on 2nd level B.F. towards Sevin.	1.50	-	7.67	12.06
B3	RVVH VGS line bleeder	1.15	-	8.59	20.62
B4	RVVH VGS line bleeder	1.16	-	-	23.93

TABLE 2.2

ANALYSIS OF MIC SAMPLES FROM E-611

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

* As per Union Carbide Analytical Procedure.

TABLE 2.3

ANALYSIS OF CORE SAMPLES FROM THE MANHOLE NOZZLES

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

TABLE 2.4

ANALYSIS OF CORE SAMPLES FROM THE MANHOLE NOZZLES

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

Table 2.4 Contd.....

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

TABLE 2.5

ANALYSIS OF SAMPLES OF TANK RESIDUES AFTER OPENING THE TANK

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

TABLE 2.6

ANALYSIS OF SAMPLES OF TANK RESIDUES AFTER OPENING THE TANK

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

TABLE 2.7

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

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

TABLE 2.8

ANALYSIS OF AMINES BY GAS CHROMATOGRAPHIC METHOD

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

TABLE 29

ANALYSIS OF TOTAL REPRESENTATIVE CORE SAMPLE FROM E-610

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

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

* Tarry material (4.7%) not characterised.

ANNEXURE 2.1

Gas liquid chromatography (GLC)

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

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

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

Determination of MICT, DMI, Dione and Ureas

Sample preparation :

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

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

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

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

Standard solutions :

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

Instruments and chromatographic conditions :

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

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

GLC conditions :

Column - FFAP 10% on chromosorb WAW (SS column of 1/8" ID x 6')
Detector - Flame Ionisation Detector (FID)
Carrier gas - nitrogen (60 ml/min)
Column oven temperature - 180°C
Injection port temperature - 250°C
Detector temperature - 250°C
Injection volume - 0.4 µl
Total analysis time - 43 min.
Quantitation method - absolute calibration curve method 44.

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

GLC conditions :

Column - OV-210+OV-17 3-5% w/w on chromosorb W-HB 80/100 (glass column 2 mm ID x 180 cm)
Detector - Flame Ionisation Detector (FID)
Carrier gas - nitrogen (30 ml/min)

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

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

GLC conditions :

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

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

Standard solutions with internal standard :

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

Retention time data and order of elution :

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

TABLE A-2.1

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

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

(Conditions as given in pages 44 and 45).

TABLE A-2.2

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

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

(Conditions as given on page 44).

Determination of amines

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

Sample Preparation

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

Standard Solutions

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

Retention times of amines were as follows :

Monomethylamine	-	3.85 min
Dimethlamine	-	5.29 min
Trimethylamine	-	5.99 min

Reliability Tests

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

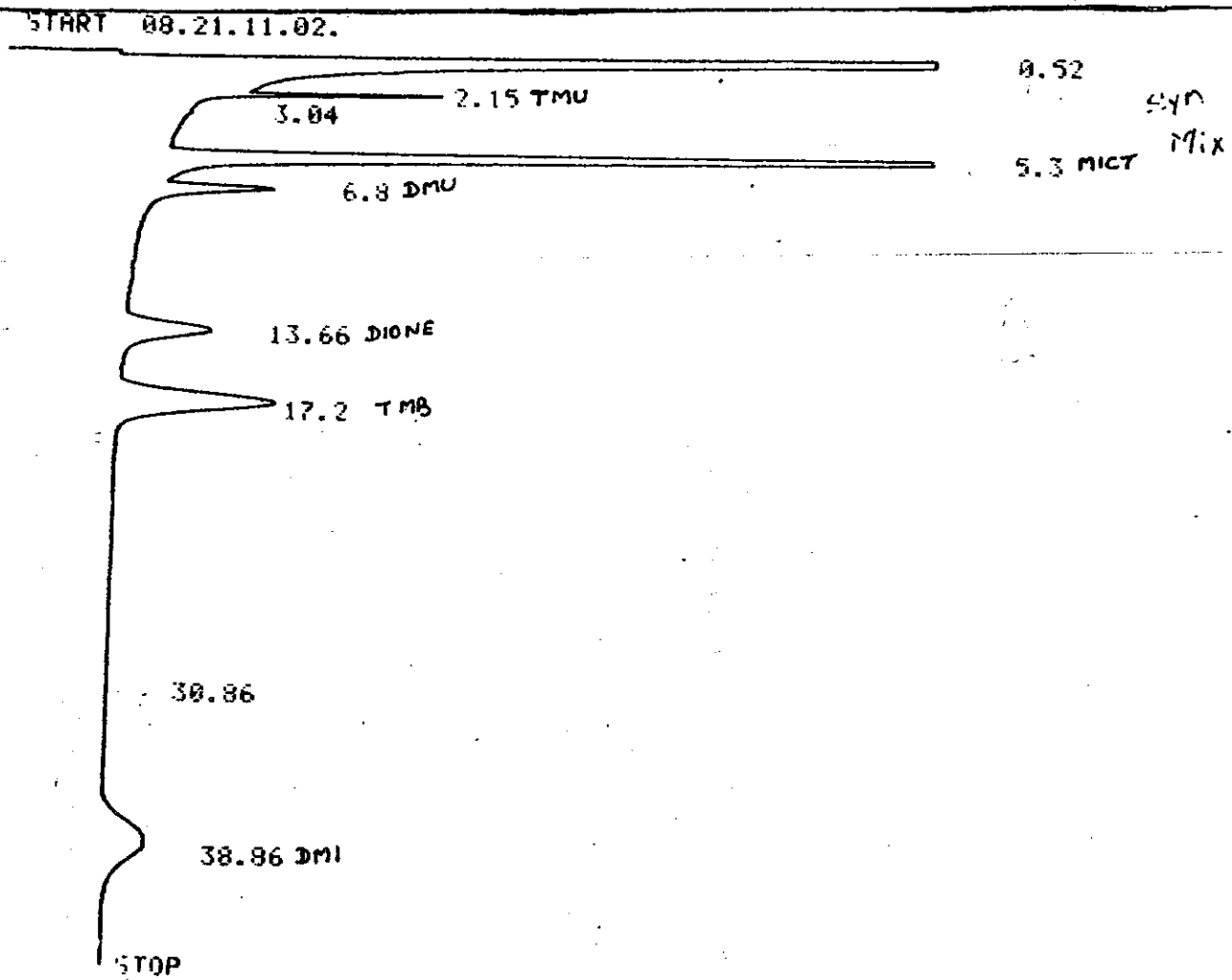

START 08.21.11.02.
0.52
2.15 TMU
3.04
syn
Mix
5.3 MICT
6.8 DMU
13.66 DIONE
17.2 TMB
30.86
38.86 DMI
STOP

FIG. A-1

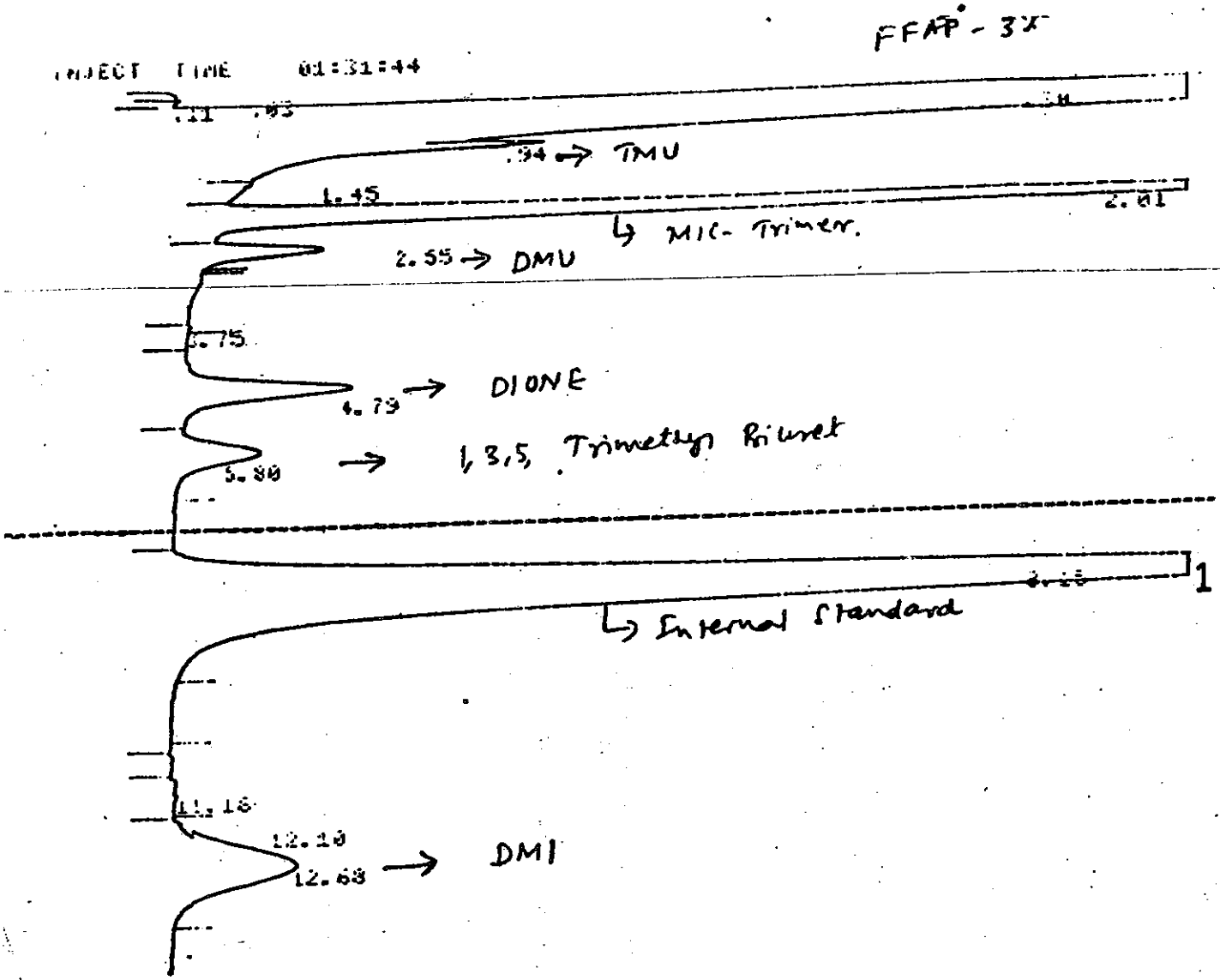

FFAP - 3X
INJECT TIME 01:31:44
.11
.93
.94 → TMU
1.45
2.01
↳ MIC- Trimer.
2.55 → DMU
3.75
4.79 → DIONE
5.80 → 1,3,5, Trimethyl Phenol
↳ Internal Standard
11.18
12.10
12.68 → DMI

Fig. A.2

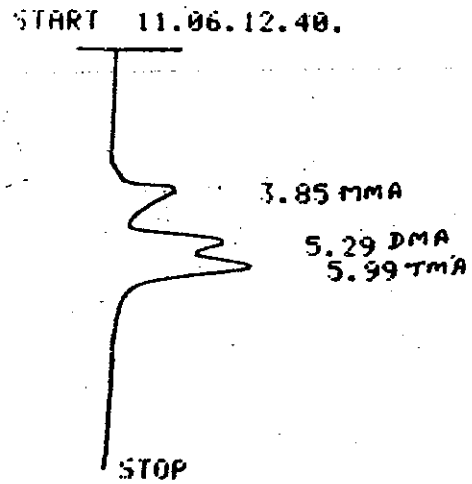


FIG A-3

Instrument and chromatographic conditions

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

GLC conditions

Column - 8% TEPA + 2% KOH on chromosorb 102
(SS column of 1/8" ID x 6 feet)
Detector - Flame Ionisation Detector (FID)
Carrier gas - nitrogen (50 ml/min)
Column oven temperature - 85°C
Injection port temperature - 150°C
Detector temperature - 225°C
Total analysis time - 15 min
Quantitation method - Absolute calibration curve method 44

Determination of Chlorides by Potentiometric Titration

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

Reagents and Appratus

A R Grade reagents were used for all the work.

1. 0.1 N silver nitrate was prepared by dissolving 85 g of silver nitrate in 5 litres of deionised-distilled water. The solution was standardised using sodium chloride as standard.

2. Mettler automatic titrator was used for all the titrations. ORION CHLORIDE ion selective electrode along with a double junction reference electrode was used as the indicator electrode system.

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

Procedure

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

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

1 ml of 0.1N $AgNO_3$ = 3.55 mg Cl^-

Preparation of Standard Compounds

Trimethyl Urea

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

1, 3, 5 Trimethyl Biuret

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

1,1,3,5 - Tetramethylbiuret

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

Dione

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

MIC Trimer

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

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

Dimethyl Isocyanuric Acid

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

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

Amine Hydrochlorides

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

3.0 CHEMISTRY OF FORMATION OF COMPOUNDS IN TANK 610:

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

3.1 Experiments:

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

Two sets of experiments were carried out:

a) In the first set, a few experiments were done with MIC which was taken in loosely stoppered pyrex tubes essentially at atmospheric pressure, and reacted with different reagents.

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

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

3.2 Observations:

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

i. MIC reacts with small quantities of water slowly at room temperature, with a half life of 3 to 4 hours.

ii. Addition of a trace of ferric chloride to the above reaction mixture at room temperature results in a vigorous reaction after an induction period.

iii. DMU and TMB are readily formed by reaction of MIC with water.

iv. MICT is formed readily from MIC. (Presence of MICT has also been noted in various parts of the plant). It can also be formed from TMB by heating. It is very stable product and is not easily transformed into other products.

v. The formation of DMI is not noticed below 200°C. TMB alone on heating to temperatutres above 200°C also gives DMI.

vi. Dione formation was noticed only above 200°C and the quantity increases as the temperature is raised.

vii. Presence of chloroform is considered necessary for the formation of Dione.

viii. It appears that part of the chloride present has come from chloroform present in MIC when the reaction temperatures exceed 200°C.

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

3.3 Discussion:

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

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

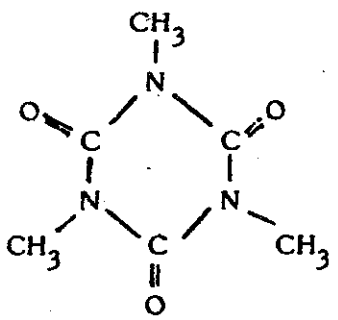
Assuming the residue composition, and the nature and quantity of each chemical entity present as given in Table 2.9, the following stoichiometric equations can be written for the chemical reactions involved :

$$COCl_2 + H_2O \longrightarrow CO_2 + 2\,HCl \quad (1)$$

$$2\,CH_3NHCOCl + H_2O \longrightarrow CH_3NHCONHCH_3 + 2\,HCl + CO_2 \quad (2)$$

DMU

$$3\,CH_3NCO \longrightarrow \quad (3)$$



MICT

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

MMA

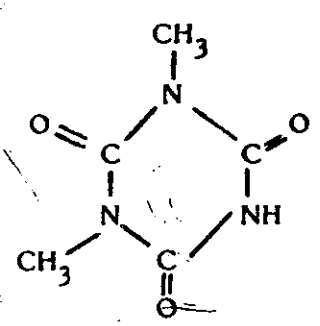
$$2\,CH_3NCO + H_2O \longrightarrow CH_3NHCONHCH_3 + CO_2 \quad (5)$$

DMU

$$3\,CH_3NCO + H_2O \longrightarrow CH_3NHCON(CH_3)CONHCH_3 + CO_2 \quad (6)$$

TMB

$$4\,CH_3NCO + H_2O \longrightarrow \quad + (CH_3)_2NH + CO_2 \quad (7)$$



DMA

DMI

$$CH_3NCO + (CH_3)_2NH \longrightarrow (CH_3)_2NCONHCH_3 \quad (8)$$

DMA **TMU**

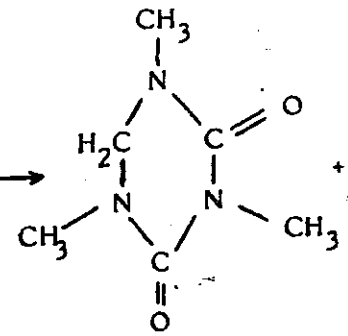
$$CH_3NCO+(CH_3)_2NCONHCH_3 \longrightarrow (CH_3)_2NCON(CH_3)CONHCH_3 + CO_2 \quad (9)$$

TMU — TRMB

$$7\ CH_3NCO+H_2O \longrightarrow 2\ DMI+(CH_3)_3N+CO_2 \quad (10)$$

TMA

$$3\ CH_3NCO+H_2O+CH_2Cl_2 \longrightarrow \text{Dione} + 2\ HCl + CO_2 \quad (11)$$



Dione

Assumptions

i. The above reactions represent initial reactants and final products without specifying possible intermediates.

ii. Chloroform present could enter into reactions only above 200°C. at which stage, all the water present would have been consumed by reaction with MIC. Chloroform or its thermal decomposition products could be available to react with DMU or TMB to produce the Dione.

iii. The formation of DMI takes place at high temperatures. It is assumed that N-alkylureas are converted to DMI with the simultaneous formation of alkylamines.

iv. The gaseous products emitted are assumed to be mainly MIC, carbon dioxide, methylchloride (CH_3Cl), methylene dichloride (CH_2Cl_2) and carbon tetrachloride (CCl_4). Some alkylamines may have been present in very small amounts.

v. Phosgene ($COCl_2$) and MCC ($CH_3NHCOCl$) present in very small amounts are readily hydrolysed with water to give hydrogen chloride.

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

3.3.1 Material Balance

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

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

3.4 Comments

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

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

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

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

3.5 Gaseous Products of Reaction of MIC

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

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

in a known quantity of dilute aqueous alkali. The valve was opened and the tube and contents were warmed up to 80°C to volatilise gases and low boiling materials. The gaseous products were thus trapped in the dilute aqueous alkali. The aqueous alkali was examined for the presence of cyanide by standard APHA methods. Cyanide was not detected.

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

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

TABLE 3.1

REPRESENTATIVE LABORATORY EXPERIMENTS WITH MIC & DERIVATIVES

Expt. No.	Reactants	Reaction Temp. °C	Time (Minutes)	GLC of Acetone Extract (Approx. %)
1.	MIC + H_2O + trace HCl	Rose 23 to 28	6	Not analysed. Temp. rose from 23° to 28°, remained at 28° for 15 minutes and started decreasing.
2.	MIC + H_2O + trace HCl + trace $FeCl_3$	1. Rose 23 to 29 2. 29 to 31 3. 31 to 45	3-5 60 in a few minutes boiled off	Residue was a solid mass which analysed for DMU, TMB and MICT qualitatively.
3.	MIC + $CHCl_3$ + H_2O	100	40	DMU (7), MICT (5) TMB(84)
4.	MIC + $CHCl_3$ + H_2O	190	40	DMU (3), MICT (60), TMB (36) Dione (Trace)
5.	MIC + $CHCl_3$ + H_2O	200	15	DMU (1), TMB (54), MICT (45), Dione (0.5)
6.	MIC + $CHCl_3$ + H_2O	250	45	TMU (2), DMU (14), MICT(41), TMB (2.5), DMI (6),Dione(3)
7.	TMB + MIC + $CHCl_3$	240	40	TMU (1), DMU (4.5), MICT(80) TMB (3), DMI (6), Dione (5)
8.	TMB + $CHCl_3$	245	45	TMU (2.5), DMU (40), MICT (6), TMB (4), DMI(9), Dione (2).
9.	TMB	250	45	DMI (4), Dione (nil) TMB(1), MICT (29), DMU (61), TMU (trace)
10.	DMU	280	45	DMU (100)
11.	DMU + MIC + $CHCl_3$	250	45	TMU (3), DMU (13), MICT (52), TMB (8), DMI (4), Dione (2)
12.	TMU + MIC + $CHCl_3$	251	45	TMU (10), DMU (1.5), MICT (47), TMB (3.5), TRMB (2), DMI (12), Dione (2)
13.	MICT + $CHCl_3$	280	45	MICT (100)
14	MICT + CH_3NH_3Cl	300	45	MICT (100)

TABLE 3.2

MATERIAL BALANCE

Chemical Reaction	Product	Kg. mole (kg.)	MIC Consumed kg.	Water Consumed kg.
1	2	3	4	5
$MIC+H_2O \rightarrow MMA+CO_2$	MMA	4.17 (129)	237.7	75.0
$MIC+H_2O \rightarrow DMI+TMA+DMA+NH_3+CO_2$	DMI	17.04 (2675)	3792.2	277.4
	TMA	7.17 (423)		
	DMA	5.47 (246)		
$3\ MIC+H_2O+2CHCl_3 \rightarrow Dione+2HCl+CO_2+CCl_4$	DIONE	2.49 (391)	425.8	44.8
$2\ MIC+H_2O \rightarrow DMU+CO_2$	DMU	1.83 (161)	208.6	32.9
$3\ MIC+H_2O \rightarrow TMB+CO_2$	TMB	0.81 (117)	138.5	14.6
$3\ MIC+2H_2O \rightarrow TMU+NH_3+2CO_2$	TMU	1.87 (191)	319.8	67.3
$3\ MIC \rightarrow MICT$	MICT	40.72 (6964)	6964.0	-
			12086.6	512.0

Overall reactions

$212.03\ MIC + 28.45\ H_2O + 4.98\ CHCl_3 \rightarrow 4.17\ MMA + 17.04\ DMI + 7.17\ TMA + 5.47\ DMA + 2.49\ Dione + 1.83\ DMU + 0.81\ TMB + 1.87\ TMU + 40.72\ MICT + 4.98\ HCl + 2.49\ CCl_4 + 4.64\ NH_3 + 28.45\ CO_2$

ANNEXURE 3.1

EXPERIMENTAL PROCEDURE :

a) The reactions at atmospheric pressure and room temperature were carried out either in a pyrex or stainless steel tube with a loosely fitting cork through which a thermometer was fixed to observe the temperature of the reaction. The rise in temperature due to the exothermic reaction was noted. In the reaction, wherein a trace of iron catalyst was added (Expt. No. 17 of Table A-3.1), after an induction period of about 1 hr a vigorous trimerization reaction set in. The temperature rapidly rose to 40-45°C, and MIC boiled off through the loosely fitting cork.

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

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

TABLE A-3.1

LABORATORY EXPERIMENTS WITH MIC & DERIVATIVES

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Wt of the product in gm Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
1.	MICT (2.00g), $CHCl_3$ (9.09g)	200	120	-	-	MICT (100)	-
2.	MICT (1.30g), $CHCl_3$ (3.00g)	200	120	-	-	MICT (100)	-
3.	MICT (0.41g), CH_3NH_3Cl (0.14g)	200	120	-	-	MICT (100)	-
4.	MICT (0.43g), CH_3NH_3Cl (0.29g) DMU (0.48g)	200	120	-	-	MICT + DMU(qualitative)	-
5.	MICT (0.52g), NH_4Cl (0.23g)	200	120	-	-	MICT (100)	
6.	DMU (2.20g), urea (3.00g)	200-230	300	-	-	DMI (1) + unknowns	-
7.	Methylcarbamoyl chloride (MCC) + Dimethyl Allophanyl chloride (DMAC) (0.50g) + Aq NH_3 5ml	27	30	-	-	MICT, DMU TMB (qualitative)	-
8.	MCC + DMAC (2.35g) + $MeNH_2$(excess) in solvent CH_2Cl_2	0-5	30	-	-	MICT, DMU, TMB (qualitative)	-
9.	MCC + DMAC (3.08g) + MIC (4.0g) kept at room temperature for 24 hr mixture treated with excess $MeNH_2$ in CH_2Cl_2	27	30	-	-	MICT, DMU, TMB (qualitative)	

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
10.	MICT (4.7g), $CHCl_3$ (0.22g), H_2O(0.1g), HCl 20% (0.05g)	200	120	-	-	MICT (100)	-
11.	MIC (3.0g), $CHCl_3$ (0.150g), H_2O (0.1g), HCl 20% (0.075g)	Mixture temp rose from 23° to 25°, was constant for 1/2 hr and then started decreasing		-	-	Not analysed	-
12.	MIC (2.5g), HCl 20% (0.075g), H_2O (0.1g)	Mixture temp went up from 23° to 28°, constant for 15 min. at 28° and started decreasing		-	-	Not analysed	-
13.	$CHCl_3$ (4.5g), H_2O (4.0g)	200	120	-	-	$CHCl_3$, CH_2Cl_2 (qualitative)	HCOOH detected
14.	MIC (3.2g), $CHCl_3$ (0.225g), H_2O (0.1g)	200	15	2.65	-	DMU (1.13),TMB(53.6) MICT(45),Dione(0.5)	Cl ions - nil, HCOOH-0.3%
15.	MIC (3.4g), $CHCl_3$ (0.35g), H_2O (0.1g)	240	45	2.31	1.23	MICT (84), TMB(2.0) Dione(1)	-
16.	MIC (2.5g), $FeCl_3$ (0.005g)	Temp rose from 23 to 29° in 5 min and then came down to 27°	-	-	-	Not analysed	

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Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in
		Rise in temp	Time				
17.	MIC (2.5g), $FeCl_3$ (0.04g), H_2O(0.05g), HCl(20%)(trace)	1. 23 to 30 2. 29 to 31 3. 31 to 45	3-5 60 in a few min. MIC boiled off	-	-	MIC evaporated at 45°C solid mass left analysed DMU, TMB,MICT detected qualitatively	-
18.	$CHCl_3$(4.5g), H_2O (4.0g)	200	120	-	-	$CHCl_3$, CH_2Cl_2 (qualitative)	HCOOH estimated (0.3)
19.	MIC (3.1g), $CHCl_3$ (0.22g) H_2O (0.1g), MCC + DMAC (0.34g)	200	45	3.24	0.52	TMU(0.64), DMU(15) MICT (53), TMB(12) Dione (0.5), DMI(2.3)	
20.	MIC (3.5g), $CHCl_3$(0.22g), H_2O (0.1g)	200	40	2.65	0.37	$CHCl_3$(0.1), CH_2Cl_2(1.06) DMU(1.5), MICT(66), TMB (30.4), Dione (0.25)	-
21.	MCC + DMAC (1.43g), DMA (0.68g) in pet.ether	10	15	1.85	-	TMU(17), MICT(8.76) Dione(3), TRMB (appreciable quantity), DMI (2)	-
22.	MICT (2.8g), $CHCl_3$(0.15g), H_2O (0.1g), HCl(trace)	245	45	2.84	0.1	MICT (100)	0.0126

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Wt of the product in gm Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in Water extract
23.	TMB (0.66g), $CHCl_3$(0.075g) H_2O (0.05g) HCl (trace)	245	45	0.2g	-	DMU(27), MICT(1.15), TMB(1.64), Dione(1.42)	0.02
24.	MCC + DMAC (0.45g), MIC (4.30g)	245	45	1.7g	0.08	TMU(traces),DMU(0.27) MICT(73.6),TMB(4.2) DMI(5.1),Dione(0.5)	-
25.	DMU (4.00g), MIC (4.8g) (Prepn of TMB)	120	120	6.8g (cryst from benzene)		TMB (100)	-
26.	MIC (6.8g), $CHCl_3$ + HCl (gas) (80 ml)	27	720	-	-	MCC+DMAC +MICT (trace) qualitative	-
27.	MIC (6.5g) MCC + DMAC (1.6g)	245	45	5.6g	2.02	TMU(trace),DMU (1.5) MICT(103), TMB(2) DMI(3.2), Dione (0.8)	0.05
28.	TMB(0.93g), MIC (3.5g), $CHCl_3$ (0.375g)	240	40	3.65g	0.5	TMU(1),DMU(4.68),MICT (90),TMB(3.1),DMI(5.6) Dione(4.7)	0.096
29.	TMB (1.12g), $CHCl_3$(0.35g)	245	45	1.25g	0.06	TMU(2.5),DMU(40),MICT (6.1), TMB(4.0),DMI(9.3), Dione (1.7)	0.004
30.	TMB (0.88g)	250	45	0.86	-	DMI(3.7), Dione(nil) TMB(1.36), MICT(29) DMU(61), TMU(trace)	-

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
31.	MICT(0.450g) + CH_3NH_3Cl(0.150g)	280-300	1 20	0.41	-	MICT (100)	-
32.	MIC(3.0g) + DMU(1.05g) $CHCl_3$(0.225g)	250	45	3.125	0.68	TMU(3.5),DMU(26),MICT (44.4), TMB(3.7), DMI(13.0), Dione (5)	0.04
33.	DMU (3.00g)	280	45	3.033	-	DMU(100)	-
34.	MIC(4.2g) + $CHCl_3$(0.225g) H_2O (0.2g)	250	45	3.420	0.056	TMU (1.94), DMU(14.03) MICT (41), TMB (2.35) DMI(6.1), Dione (2.79)	0.006
35.	MICT (0.55g) + $CHCl_3$ (1.5g)	280	45	0.63	-	MICT (100)	-
36.	MIC(4.5g) + DMU(1.05g) + $CHCl_3$ (0.225g)	250	45	4.05	0.052	TMU(1.6), DMU(18), MICT (76), TMB(6.9), DMI(4.5) Dione (3.05)	0.03
37.	MIC (3.1g) + $CHCl_3$ (0.3g) + H_2O (0.1g)	250	45	2.90	0.18	TMU(1.1), DMU(13), MICT(44), TMB(3), DMI(6.3) Dione(2.23)	0.3
38.	MIC (3.1g) + DMU (1.0g) + $CHCl_3$ (0.225g)	250	45	3.750	0.14	TMU(2.7), DMU(12.5), MICT(52), TMB(8), DMI(4), Dione (2)	0.02
39.	MIC (3.2g) + DMU (1.07g)	250	45	3.530	0.014	TMU(1), DMU(31.6), MICT(36), TMB (8.4), DMI(1), Dione (1)	Nil
40.	MIC(3.2g) + DMU (1.13g) + $CHCl_3$ (0.225g)	280-300	45	4.250	0.056	DMU(18), TMU(0.75), MICT(46), TMB(10) DMI(3) Dione(2)	0.006

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Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Wt of the product in gm Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
41.	MIC (3.4g) + DMU (1.02g) + CH_2Cl_2(0.225)	240-250	45	4.130	0.14	TMU(1.36), DMU(9) MICT(49), TMB(6.4), DMI(5), Dione (2.4)	0.01
42.	MIC (3.5g) + DMU (1.01g) + $CHCl_3$ (0.45g)	215	40	4.20	0.25	TMU(0.7), DMU(12), MICT(41), TMB(4.5), DMI(11), Dione(1)	0.07
43.	TMU(0.44g) + MIC(1.5g) + $CHCl_3$ (0.3g)	215	45	1.64	0.21	TMU(10), DMU(1.4), MICT(46.5), TMB(3.4), TRMB(1.7), DMI(12), Dione(1.6)	0.05
44.	MIC(3.5g) + $CHCl_3$(0.225g) + H_2O (0.1g)	100	40	1.09	0.02	DMU(7.4), MICT(5), TMB(83.5)	0.001
45.	MIC(3.5g) + $CHCl_3$(0.225g) + H_2O (0.1g)	190	40	2.64	0.02	DMU(3), MICT(70), TMB(36) Dione(traces)	0.005
46.	MIC(3.5g) + $CHCl_3$(0.225g) + H_2O (0.1g)	215-220	40	3.40	0.07	TMU(0.15), DMU(5.13), MICT(60), TMB(15), DMI(6), Dione(1.22)	0.005
47.	TMU(3.43g) + $CHCl_3$(0.3g)	220	40	2.50	-	TMU(64), DMU(13), TetMU (present)	nil
48.	MIC(3.2g) + $CHCl_3$ (0.45g), H_2O (0.1g)	215-220	40	2.91	0.08	TMU(1), DMU(7),MICT(52) TMB(14), DMI(5), Dione(1.6)	0.008

Sl. No.	Reactants	Reaction temperature °C	Time min	Wt of the product in gm Acetone extract	Water extract	GLC analysis of acetone extract (% w/w)	Wt in gms Cl ions in water extract
49.	MIC(3.4g) + DMU (1.04g) $CHCl_3$(0.6g)	220	40	4.48	0.23	TMU(0.6),DMU(10), MICT(44), TMB(6.5), DMI(8), Dione(2)	Nil
50.	Mic(3.6g) + $CHCl_3$(0.6g) H_2O (0.3g)	220	45	2.84	0.40	TMU(0.5),DMU(21), MICT(9), TMB(20), DMI(14), Dione (3)	0.1
51.	MIC (1.5g), TMU(0.47g), $CHCl_3$ (0.450g)	215	45	2.52	0.13	DMU(3.5), TMU(22) MICT(42.6), TRMB(2), TMB(5), DMI(4.3) Dione(1.5)	0.026
52.	MIC(5.0g), H_2O (0.2g)	20-29	48	1.02	-	MICT(1), TMB(52.3), DMU(49.4)	-
53.	DMU(1.55) + $CHCl_3$(0.3g)	220	60	1.33	0.04	DMU(96.9), TMB(2.02)	0.025
54.	TMB(0.208g) + CH_2Cl_2(0.15g)	220	60	0.197	0.019	DMU(39.3), TMB(50), MICT, DMI & Dione not seen	Nil
55.	TMB(0.820g) + CH_2Cl_2(0.45g)	250	60	0.68	-	TMU(0.92), MICT(12.9), DMU(39.4), Dione(4.4), TMB(30), DMI(1.5)	-

4.0 ANALYSIS OF DESIGN AND ENGINEERING FEATURES :

4.1 MIC and its Characteristics :

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

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

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

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

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

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

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

4.2 Storage Tank

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

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

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

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

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

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

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

4.3 Nitrogen :

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

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

4.4 Instrumentation and Control System :

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

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

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

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

- It is conceivable that gaseous MIC would be emitted due to a rapid reaction inside the tank. This gas is expected to be neutralised by circulating alkali solution in the packed section of VGS. This system is also grossly inadequate to handle quantities of vapourised MIC as large as were emitted during the event. Calculations show that even if the normal design load for VGS is taken into consideration, the VGS is inadequate to neutralise a discharge of 28 tonnes of vapourised MIC in about 2 hours.

- Therefore, neither the liquid nor the gaseous disposal system was capable of handling the event which occurred on the night of December 2, 1984.

- The relief valve design could not permit free flow of large quantities of gases, certainly at the level at which they were generated during the event. Thus, the tank contents were subjected to pressures much higher than 40 psig and correspondingly high temperatures.

- From the examination of the tank residue and from the conditions of formation of the residue, it is surmised that the temperature reached in the bulk storage tank may have been around 250°C. The total energy balance on the tank also indicate that the probable temperatures would be in the range of 200 to 250°C. Information from the mechanical examination of the tank indicate that the pressures may have reached 11 to 13 kg/cm^{2}g with the corresponding temperatures in the range of 200 to 350°C.

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

- The hydrolysis of MIC with about 500 kg. (1100 lb) of water by itself and in the absence of other contaminants is not expected to lead to thermal run-away conditions. The presence of this quantity of water would have possibly resulted in reaction with about three to four tonnes of MIC, generation of carbon dioxide, breaking of the rupture disc and release of CO_2. The temperature of the tank content would have gradually risen to about 60-70°C, below the boiling point of MIC at that pressure. It is surmised that no more than 50 to 100 kg/hr (110-220 lb/hr) of CO_2 along with small quantities of MIC, ca 100-150 kg/hr (220 - 330 lb/hr) would have been released. Such emissions will cease once the water has been consumed.

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

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

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

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

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

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

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

- The quantum of toxic leakage by violent chemical reaction is not related to the amount of metal and water which initiate the reactions but to the quantity of MIC stored in a single container. If 42 tonnes of MIC had been stored in 210 stainless steel drums of 200 litre capacity each, as alternative to a single tank, there would be no possibility of leakage of more than one fifth of a tonne and effects of even such a leakage could be minimised by spray of water or alkali.

- It has been reported that a large number leakages of MIC in comparatively small quantities have occured from storage vessels and tanks in Union Carbide. The causes for such leakages have not been made known. While Union Carbide product brochure refers to chemical properties and reactivity of MIC, including possibilities of violent reaction as well as of possibilities of spillages from drums and tanks during transport, no information is provided on the extraordinarily lethal toxic effects of inhalation. Public preparedness for eventualities arising out of leakage would have been substantially greater if information on these had been generally available. For instance, substantial care is exercised in the storage and transport of explosives or in handling even weakly radioactive materials or in the use of X-ray equipment, due to the awareness of hazards.

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

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डॉ. एम.एस. अनंत
Dr. M.S. ANANTH
निदेशक
DIRECTOR

DIR/2010
August 4, 2010

To
Shri Jairam Ramesh
Hon'ble Minister of State (Independent Charge)
Environment & Forests, GoI
NEW DELHI – 110 003

Dear Shri Jairam Ramesh,

This is in response to your letter dated 13th July, 2010. I requested my colleagues Dr. Indumathi Nambi, Department of Civil Engineering and Dr. Ravikrishna, Department of Chemical Engineering to give me their technical comments on the NEERI report. They work in the areas of contaminated soil remediation and mitigation of groundwater contamination. The comments received from them are attached.

If you need to tap their brains in the matter any further, I recommend that one or both of these colleagues attend the Technical Workshop that you propose to hold later in August.

With warm regards,

Sincerely yours,

(M. S. Ananth)

Encl: as above

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Review by two faculty members in IIT-Madras on the report on the "Assessment and Remediation Hazardous Waste Contaminated Areas in and around M/S Union Carbide India Ltd., Bhopal." Prepared by NEERI , Nagpur, India - Submitted to MoEF, June 2010.

a) Dr. Indumathi M. Nambi
Assistant Professor, Environment and Water Resources Engineering
Department of Civil Engineering, IIT- Madras, Chennai
Email: indunambi@iitm.ac.in
Website: http://www.civil.iitm.ac.in/people/faculty/EWRE-INDU2.htm
Research Interests: Assessment and remediation of subsurface environment (soils); Behavior of non-aqueous phase liquids in porous media; Waste treatments methods.

Comments:
The report summarizes the monitoring work done by various agencies in particular, NEERI, at Union Carbide plant in Bhopal. There are some serious concerns regarding the monitoring protocol which could lead to the elimination or significant reduction of certain toxic chemicals in the soil and groundwater samples. Some of the specific comments are:

1. The geophysical and hydro-geological investigations indicate a clayey zone in the top 30 m followed by alluvial aquifers zone and weathered zone and a final hard sandstone rock as the confining layer at the bottom. Soil samples were taken only from the top 30 cm depth in most of the locations. In some isolated borewells, soil samples were "taken up to a depth of 25-32 m depending on the occurrence of ground water", as mentioned in page 35. This is also just above the groundwater levels. When there are potential dense non-aqueous phase liquids such as chlorinated solvents and Mercury in the soil, they have a tendency to migrate below the water table and pool over the sandstone bed. It might be possible that the bulk of these compounds have been missed since the soil samples were not taken up to the sandstone level. Please see the reports on similar investigations.

2. Groundwater samples also were taken from borewells which were screened for the entire aquifer depth. Chlorinated solvents being very sparingly soluble would be giving away a very little mass into the groundwater flowing adjacent to the NAPL pools lying above the bedrock which could be easily diluted by the cleaner water flowing above. The very low diffusivities and lack of sufficient turbulence in the porous media can easily bring these concentrations to below detectable levels as mentioned in the report. A more appropriate way of sampling is to use multi-level water samplers which can pinpoint the zone of contamination. Also extreme precautions have to be taken while sampling due to the volatile nature of these organic compounds which could also result in misleading results.

3. There have been several reports about high concentrations of organic solvents (about 500 times more than their permissible levels) which has to be given priority in any investigations. The current report does not have any strong evidence to refute these reports due to the aforementioned reasons.

b) Dr. R. Ravi Krishna
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Research Interests: Contaminant Fate and Transport in the environment; Assessment and remediation of Contaminated sediments; Waste treatment methodologies.

The report addresses the history of monitoring of environmental parameters around the UCIL region since 1984 and sets up the background for the purpose of the current report and proposed work. The report delineates the efforts to trace the spatial extent contamination of soil in the UCIL and surrounding regions. The report also tracks ground water contamination with respect to the groundwater flow and the location of the UCIL. The report addresses many important issues of assessment and remediation with specific reference to the site and the vast history associated with it. In my opinion, the methods of chemical analysis described for the field data (concentrations and loading in water and soil samples respectively) are appropriate and adequate. These methods are standard methods acknowledged widely in the profession.

The following are some of my specific comments.

a) The report mentions that groundwater quantum cannot be estimated (section 4.3.2) ? Is there a reason for this? What can be done to estimate this since it will facilitate more efficient design of treatment options?

b) The report recommends "on-site ex-situ treatment" for contaminated soils (section 4.3.2). However the only 'treatment' option mentioned is the preparation of a secure landfill on site. This is not really a treatment of the waste. It is simply a transfer of contaminated material from its current location to a secure location within the same enclosure. Considering the evidence provided in the report, a secure landfill on site may not be as secure as desired (evidence of tampered or filled sampling borewells installed by NEERI/NGRI). An explicit separation of hazardous materials into a different medium (through extraction or equivalent process) can be attempted and then putting the 'clean' soil into the excavated area thus eliminating the need for a secure landfill for the entire material (and the need to monitor the secure landfill for a very long time). Even if the extraction may be financially expensive, in this specific case, it may be warranted given the history of the site. The concentrated waste stream can then be treated by incineration or any other advanced oxidation process.

Chairman, Bhopal Environmental Remediation Oversight Committee
and Minister of State, Ministry of Environment & Forests.
Paryavaran Bhavan, CGO Complex
Lodhi Road, New Delhi 110 003

August 05, 2010

Sub. Expert's Technical Review of NEERI and NGRI Reports on the environmental contamination in and around Union Carbide's abandoned factory site in Bhopal.

Dear Sir,

Enclosed please find a copy of the Technical Review of the reports published by NEERI, Nagpur and NGRI, Hyderabad by international experts on the contamination of soil and ground water in and around Union Carbide's abandoned factory site in Bhopal. This is in accordance with the decision taken at our meeting on July 9, 2010 at Bhopal.

We look forward to your responses and ideas about moving this process forward so that the ongoing issue of environmental contamination can be meaningfully addressed with the urgency it deserves.

Thanking you.

Yours sincerely,

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Children Against Dow-Carbide
Mob. 9826994797

Balkrishna Namdeo
Bhopal Gas Peedit Nirashrit Pension Bhogi Sangharsh Morcha
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Technical Review of NEERI & NGRI Reports:

'Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal' (NEERI)

and

'Geophysical Investigations to Assess Industrial Waste Dumped at UCIL, Bhopal' (NGRI)

Authors

Dr. Stuart Gray

Jarlath Hynes

Joe Jackson

Dr. Jurgen Porst

The contributions made by Will Nicholls of Beyond Bhopal and Colin Toogood and Tim Edwards of the Bhopal Medical Appeal, UK in coordination and preparation of the report is gratefully acknowledged by the Bhopal survivors' organizations.

Contents

Overall Comments

This document presents a critical review of the NEERI and NGRI reports published in June 2010. It is being submitted following the invitation for comments extended by the Chairman, Bhopal Environmental Remediation Oversight Committee and Minister of State, Ministry of Environment and Forests, Government of India to the Bhopal survivors' organizations on July 9, 2010 during a meeting held in Bhopal.

Both the NEERI and the NGRI report provide useful information, however, a number of key deficiencies have been identified in the site investigations and methodologies used. Critical results are misinterpreted, or missing, and a number of the conclusions reached, within the reports, are not supported by the evidence presented.

The scarcity of groundwater sampling, the absence of detailed investigation of the Solar Evaporation Ponds, false assumptions regarding groundwater flow direction, and the identified permeable nature of the black cotton soil all suggest that NEERI's conclusion that groundwater has not been contaminated from Union Carbide factory sources cannot be supported.

NEERI conducted a limited sampling campaign that was compromised and did not present analytical results for key contaminants of concern. Despite acknowledging the contamination found by previous investigations, NEERI did not follow-up these leads. Where groundwater contamination was detected, no explanation or theories were offered as to the source of this contamination.

Analysis of the geophysical data provided show that NEERI's attempt to quantify the soils requiring remediation based purely on the estimated fill depth is overly simplistic. At this time we still do not know how many aquifers there are, the groundwater flow direction in each, how they are recharged, and where they outcrop.

Overall, the current site assessment can only regarded as preliminary to a complete site investigation conducted to the highest international standards.

1.0 Introduction

This report is a review of the following documents:

- Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal. (Sponsored by: Bhopal Gas Tragedy Relief and Rehabilitation Department Govt. of Madhya Pradesh, Bhopal) By National Environmental Engineering Research Institute Nehru Marg, Nagpur;
- Geophysical Investigations To Assess Industrial Waste Dumped At UCIL, Bhopal (Union Carbide India Ltd.) By National Geophysical Research Institute, Hyderabad. Ref: GAP 401 28(VSS).

These reports are referred to here as the NEERI report and the NGRI report respectively.

The basis of this assessment is to consider the following:

1. Suitability of completed assessment;
2. Discussion of quality issues and constraints;
3. Suitability of Remedial proposals;
4. Identification of key issues raised by the report;
5. Recommendations for further work.

The NEERI/NGRI reports look at the contamination of soil and groundwater, in and around the Union Carbide factory premises, due to the known dumping of toxic wastes at the Union Carbide factory site during operations and subsequent to its closure. Thus a degree of separation is needed between this issue and the Union Carbide gas disaster of December 1984. There are significant 'legacy contamination' issues, caused by other chemicals dumped as waste, that still pose a significant threat to human health and the environment.

NEERI's report acknowledges that toxic wastes from production and related processes, were dumped both on the factory premises and just outside in three Solar Evaporation Ponds (SEPs). This information is consistent with the subsequent detection of these same substances in soil and water samples by other investigators (CSE 2009, BMA 2009, Greenpeace 1999-2004, Shristi 2002, Dikhshith et al 1990, MPPCB 2003-2006, Citizens Environmental Laboratory 1990) and strongly suggest that the groundwater has been, and continues to be, contaminated by these same substances.

2.0 Suitability of completed assessment

A review of the reports shows that the combined efforts of the NEERI and NGRI reports have broadly followed the following rationale:

- Summarise findings of selected historic reports;
- Geophysical (non-intrusive) investigation of selected areas to determine the depth of fill areas;

- Target shallow soil sampling based on the suspected dump areas revealed by geophysical survey (27nos. Surface and subsurface soil samples taken for analysis);
- Further soil sampling outside of Union Carbide factory (8nos. Locations and a total of 24nos. Samples collected);
- Drilling of 5nos. Boreholes (No's A to E) and soil logging, sampling and chemical analysis;
- Development and monitoring of drilled wells and a further 8 nos. Wells in the vicinity of the site;
- Preliminary testing of hydrogeological properties using slug tests in wells A to E
- Analysis of soil samples for contaminants detected in previous investigations, as discussed by NEERI. See Appendix 1.
- Define the hydrogeological regime at the site;
- Make recommendations for suitable remediation actions and provide a guide on potential costs of those actions.

2.1 Model Approach

The overall site assessment rationale does not conform to the approach generally adopted internationally, where a phased or tiered approach to site investigation and assessment is preferred (for example, in the UK, BS10175, 2001)

Particular elements of an investigation are managed pro-actively depending upon the findings of the previous phase. Subsequent phases can then be carefully targeted and this avoids unnecessary work being undertaken.

The phased approach typically consists of the following stages (BS10175, 2001):

Phase 1 Desk Study - Historical research and review of available information from sources such as archives, plans, records, previous study reports and test results. The desk study should examine the past activities at the site and assess them for potentially contaminative processes, determine the potential for the presence of contamination and identify the specific chemicals used/ disposed of at site, and collate existing evidence of any contamination. The report should also identify any potential receptors, e.g. humans, surface watercourses, aquifers, or ecological receptors and collate the information relating to the site's environmental setting i.e. geology, hydrogeology and the location of potentially sensitive waters (lakes, ponds, rivers, springs, aquifers). This information is then used to undertake a qualitative risk assessment through the development of a conceptual model for the site. The conceptual model identifies any Significant Pollutant Linkages that may be present. If Significant Pollutant Linkages are present then a Phase 2 site investigation may be required to quantify the risk. The gathered desk study information can be used to target potential problem areas and identify specific contaminants of concern. This may be formally provided as a Sampling and Analysis Plan for implementation at Phase 2.

Phase 2 Intrusive Investigation - An intrusive site investigation is undertaken to investigate each aspect highlighted by the Phase 1 desk study, historical research, and walkover survey. This comprises exploratory holes constructed using the most appropriate method for the site to investigate the local subsurface strata.

The Phase 2 intrusive contaminated land investigation is designed and implemented using a variety of in situ exploratory methods, depending on factors such as sensitivity of the area, ground conditions (anticipated geology, hydrogeology, the expected presence of old foundations or other obstructions, which may have an impact on the technique selected), size of site and type of contaminants identified by the desk study as potentially present.

A systematic, grid-based sampling regime is necessary to map the true extent of soil contamination. The vertical and horizontal extent of soil and groundwater contamination must be delineated prior to the design of any remediation strategy. Additionally, where water contamination is suspected, semi-permanent water monitoring stations must be established in local communities.

Chemical analysis of soil and water/ groundwater samples for common contaminants (and particularly any specific contaminants identified at the Phase 1 assessment stage) is completed to establish the concentration and extent of any contamination present. A risk assessment, using the 'source-pathway-receptor' model, would then be carried out and this assessment may be qualitative where pollutant linkages can be discounted, or quantitative where a pollutant linkage is evidenced or cannot be discounted.

Phase 3 Remediation (Design, Execution and Validation) - If remediation is deemed necessary (i.e. quantitative risk assessment has identified any unacceptable risk), then a site-specific remediation methodology should be produced. This can include delineation of contamination hot spots, further soil sampling, chemical analysis and additional monitoring if more information is required to supplement the data from previous investigations. A wide range of remediation techniques are available and the methods chosen, whether involving removal or *in-situ* treatment, are dependent upon a range of factors including: contaminant type and distribution; environmental sensitivity of the site; intended end use; cost and timescale. Finally the site is re-assessed (post-remediation) to ensure that the objectives of the remediation have been met. This is evidenced in a 'Completion Report', normally made available to the relevant regulatory authorities and key stakeholders, for approval.

Arriving at an appropriate, comprehensive and cost-effective remediation strategy must be a science-based decision, as selecting unsuitable methods can lead to incomplete clean-up and exacerbation of contamination issues

Whilst some of these best practice approaches may have been adopted, there remain critical discrepancies which detract from the assessment to such a degree that the conclusions arrived at by NEERI are compromised and cannot be scientifically supported. These discrepancies are summarised below.

2.2 Insufficient NEERI desk top study/ absence of Sampling and Analysis Plan

At a site such as the Union Carbide factory in Bhopal, with such a heavily contaminative past use, a detailed process review and potential contaminant inventory are essential pre-requisites to a full understanding of the situation. Some detail is provided in the NEERI report with a list of chemicals that were known to have been disposed of in and around the factory between 1969-1984 and possibly afterwards. Appendix 3 contains a list of the substances involved and the quantities dumped on the Union Carbide factory site. However, many of these specific contaminants of concern, which were known to have been used and/

or disposed of on, site have apparently not been tested for or have had no results reported. Appendix 4 lists substances that are normally associated with pesticide production, for which no formal sampling and analysis plan was developed.

The analytical methodologies quoted are to a high international standard and, if applied, an extensive array of substances could have been screened. However there remains doubt that much of this testing actually took place, as the results are not presented or discussed. Previous NEERI reports have only sought to identify the existence of certain functional groups (e.g chlorides), however the use of these referenced methods would indicate that accurate identifications were attempted. If so, this is extremely valuable information and the raw data should be released.

In addition, there is little discussion about the primary pesticide products, and their fate in the environment. As such, their isomers and break-down products may be present, and potentially harmful, but have not been tested for. For example, Carbaryl degrades to alpha naphthol (naphthol, the major degradate, is briefly discussed as a primary contaminant of the SEPs) but these minor compounds are not subject to analyses by NEERI. It is noted that the half-life of Carbaryl in soil is 12 days (Xu, 2000)

The NEERI desk-stop study has acknowledged, but not acted-upon, the findings of several credible contamination surveys performed by independent groups despite the fact that they contain numerous tests of the soil, surface water and the groundwater.

Chlorinated organic compounds, which were used as processing aids and solvents, on the Union Carbide factory site, are known to have been extensively dumped on-site, and have subsequently been detected in soil and water samples up to 3km away from the original source. The water sample test results strongly indicate the migration of contaminants, in one or other aquifers, in the form of a plume. NEERI has not followed-up on these previous findings and, despite presenting an extensive analytical methodology, only presents the findings for dichlorobenzene. Analyses for critical substances were either not performed or not presented.

Interestingly, where NEERI did find dichlorobenzene in water samples and sub-surface soil samples, they offer no theories as to the source of this contamination and instead simply dismiss the findings. There are no other local sources of dichlorobenzene or other chlorinated organics. NEERI's failure to fully investigate these discrepancies is a major deficiency.

The list of substances in Appendix 4 should be considered in light of the known products and processes associated with the site, and mindful of the results from previous investigations which were acknowledged by NEERI but never followed-up. Best practice demands conservatism in creating a sampling and analysis plan, i.e. to include a potential contaminant of concern rather than exclude it. The desk-top study should be used to cross reference the site history, and past activities, with the list of potential contaminants in order that the locations of the sampling and physical investigations are targeted accordingly. Site observations of suspected contamination, e.g. visual identification of 'tarry' wastes or olfactory evidence (such as the over-whelming odours reported by NGRI) should similarly be accounted for in a prescriptive sampling and analysis plan. In the NEERI study some consideration was given to areas of known historic dumping, but this was limited to accessible areas and did not consider, in necessary detail, past production/ storage areas that may be areas of concern due to inadvertent releases.

Since this figure was used to calibrate the numerical groundwater model, the model output is also invalid.

Physical characteristics. It is stated that the predominant near-surface geology is a clay with a hydraulic conductivity in the order of 10-9m/s. However the slug testing carried out by NGRI indicates a minimum hydraulic conductivity of 5.31m/d (equivalent of 6.15 x 10-5m/s), i.e. 4 orders of magnitude greater than the expected 10-9m/s. Since the well screens cross several different geological layers, the calculated transmissivity is not necessarily attributable to the 'sandy alluvium with pebble' layer only. It is recommended that shallower wells be installed at these locations to measure the transmissivity of the overlying 'silty clay' and the infiltration rate into this layer. Since there have been no subsurface investigations at the SEP outside the Union Carbide factory site, it is invalid to assume that a thick clay layer separates the pond and aquifer.

6. Potentiometric Surface. The potential surface of the groundwater has been reported (although there appears to be some confusion concerning the groundwater flow direction, being reported variously as southeast [p.31] or northeast [p.40]), based on the reduced level measurement of the wells. Surveying the absolute elevation of these wells is likely to be subject to error, over the large distances between wells, and potentially problematical due to the presence of buildings and vegetation interrupting line-of-sight measurements. Furthermore it is understood that some of the wells used for measurement are also routinely extracted from. This could cause a local cone of depression which may interfere with the true potentiometric surface being identified. The fact that there is variable pumping of existing wells is another reason why the groundwater level contour plots generally cannot be relied upon to indicate groundwater flow direction.

2.4 Quality Issues

Many of the key contaminants tested for are volatile or semi-volatile organic compounds but there are also some volatile inorganics such as mercury. It is possible that, unless collected and preserved correctly, the volatile fractions are liable to volatilise and thereby provide a 'false negative' reading (i.e. a contaminated sample may be reported as non-contaminated). This is prevented by use of amber sample glassware with no air spaces in water samples. Further quality assurance (QA) methods should also be employed, and whilst the sampling protocol has been quoted as an American standard, no further detail has been provided on sample collection and preservation. Greater comfort would be provided if a fuller description of the adopted protocols were included.

No original chemical certification was provided with the reports. It is generally considered best practice to attach the original laboratory certification and that should include full details of the testing laboratory accreditation.

There is no evidence of Quality Control sampling for soil or groundwater. As a minimum, it would be necessary to collect duplicate samples (1 in 10 samples) for analysis at the primary

laboratory as well as a secondary laboratory. In addition, laboratory quality control procedures have not been reported.

With regards to the water sampling and analysis, vertical delineation is required for groundwater, in addition to soil, since some of the contaminants of concern are Dense Non-Aqueous Phase Liquids (DNAPLs) and sink to the bottom of the aquifer. It is normally considered best practice to 'dip' potentially contaminated wells using a 'dual-phase' dip-meter to identify the presence (or absence) of any Non-Aqueous Phase Liquids (NAPLs): either lighter than water (LNAPL) which may be present as a layer floating on top of the water column; or DNAPLs which would sink through the water column until meeting a low permeability layer. Only when the absence of NAPLs is established should energetic purging take place (typically 3-5 well volumes), prior to sampling, thereby ensuring a representative sample is obtained. Where either LNAPL or DNAPL (or both) are present then selective sampling should be employed to assess the composition of any NAPLs as purging could expel LNAPL or fail to detect DNAPL. Many of the potential contaminants of concern at the site are DNAPLs and as such should be carefully assessed. This should also be considered in the well construction design (i.e. the monitoring wells should extend to a point at which DNAPL may be expected to accumulate [EPA 2000]).

This is an important concept, as it is well known from other, well investigated sites that chlorinated solvents can easily permeate to sub-surface groundwater where they become trapped, forming a plume, and causing persistent contamination of water supplies for decades. Where there is groundwater movement, the solvent plume can expand and migrate, spreading the contamination further than the original source.

It is noted that water analysis results were 'averaged'. All contamination testing provides a snap-shot of a dynamic system. Averaging of a series of results from the sample location is not considered best practice as it may 'mask' a spike in contaminant levels or other dynamic events.

The laboratory detection limits have not been reported. There is no comparison to any drinking water standards. As can be seen in table 4, Previous studies have found concentrations of solvents that greatly exceed limits set by WHO and EPA for safe drinking water.

The shallow soil sampling undertaken has focussed on both volatile and semi-volatile contaminants. It should be noted however that the nature of these contaminants is such that exposure to the elements (particularly wind and sun) would cause volatalisation even within the shallow soils (i.e. up to 0.3m+). The only chlorinated organic for which results were reported, dichlorobenzene, was detected in sub-surface soil and water samples, but not at the surface. The absence of VOCs and SVOCs in surface soils therefore cannot be considered conclusive evidence that VOCs and SVOCs are not present at depth. Further geochemical analysis of surface waters, SEP water and groundwater is required. It is possible to assess major cation (sodium, calcium, magnesium and potassium) and major anion (chloride, sulfate and alkalinity) concentrations to determine similarities between waters e.g. if a surface water and groundwater have a similar cation/anion signature, then it is likely that there is flow between them.

Finally, no 'leachate' testing has been completed. Leachate tests provide a good indication of how/ if soil based contamination may become mobile and leach out of the solid state and enter groundwater (BS 10175:2001) It is noted that the presence of over-grown and inaccessible

remediation, a detailed Remediation Options Appraisal should be completed before specific solutions are selected.

- *Decontamination and decommissioning of plant, machineries and buildings prior to remediation of contaminated soil and groundwater.*

As above this is likely to be an important pre-cursor to remediation, but given the significance of the plant structures, machinery and buildings as Modern Industrial Heritage and the survivors' organization's long pending demand that the plant structures, machinery and buildings be conserved as part of a memorial to the disaster it is critically important to involve experts from UNESCO (which has already expressed interest in this direction) and the Archaeological Survey of India (ASI) for the preparation of a plan for decontamination, reconstruction and conservation.

- *Under long-term measures, remediation of contaminated soil and groundwater was recommended. For remediation of contaminated soil, an on-site secured landfill facility was recommended. For contaminated groundwater, pump-and treat system was recommended.*

Again as above, a detailed options appraisal should be completed and alternative remedial measures considered, and trials conducted where necessary, before selection of the most suitable remediation methods can take place. The proposal to create an on-site landfill raises a number of issues which would have to be satisfactorily addressed. These are too numerous to mention within the scope of this review, but key concerns would include:

- Quality of design;
- Suitability of local geology (see above, the 'clay' has been measured to be quite permeable);
- Quality of construction and selection of materials;
- Monitoring and long-term after-care.

The NEERI proposal to pump water from the 5 identified contaminated wells is not sufficient as a course of action to address the water contamination issues. Without a full testing programme this course of action does not sufficiently address the contamination issues highlighted by other, previous studies. The results of these studies should be followed-up by an appropriate testing programme. This is an absolute pre-requisite to further understanding and action.

Furthermore, this limited pump and treat action does not acknowledge the possible existence of a contaminant plume and may lead to a change in the potentiometric surface of the water body, which in turn can lead contaminated water to migrate preferentially to other well locations, should such a plume exist.

Notwithstanding these issues, pump and treat is generally considered 'old' technology for groundwater remediation, due to low treatment efficiencies and ongoing costs, and other, more passive, options (not requiring pumping) such as containment barriers or permeable reactive barriers might achieve a better result.

NEERI should elaborate the reasons underpinning the decision to proceed with pump and treat, and should reveal what other types of remediation processes were considered, and why more advanced novel and/ or *in-situ*, methods were rejected

- *It is recommended that, BGTRRD should engage competent professional contractors for detailed engineering, and execution of various remedial measures recommended by NEERI.*

It is of paramount importance that the scheme is designed, built, managed and overseen by appropriate professionals. If the remediation contractors are to be responsible for all health and safety issues arising then this is a matter for concern. The NEERI proposal would necessitate an unprecedented removal of hazardous material that is likely to cause recontamination of the surrounding environment. Assurances would be required that this work is being conducted to the highest standards.

4.0 Identification of Key Issues raised by the report

The NEERI report makes a number of conclusions that are not appropriately evidenced by the information provided. Areas of potential misunderstanding of the sub-surface regime have been identified. Specifically

- *Total volume of soil contaminated is 650,000m3.*

As discussed above, the extent of contaminated soils cannot be fully delineated at this stage.

- *Groundwater is not contaminated due to seepage from Union Carbide factory dumps.*

The scarcity of groundwater sampling locations, the absence of detailed investigation of the SEPs, and the identified permeable nature of the black cotton soil, suggest this conclusion cannot be supported.

- *Contamination in wells attributed to surface water run-off.*

Groundwater contamination has been clearly demonstrated outside of the factory site boundary. Wells consistently in use would generally be purged of surface water run-off and in any event, as discussed above, best practice in groundwater sampling is to purge 3-5 times the well volume to remove the effects of any surface water that may have percolated within the wells. Ionic balance analysis may indicate the age (and therefore the source) of the well-water. At this stage, the suggestion that the presence of contaminants in groundwater is a result of surface water run-off cannot be supported.

- *Up-stream soils non-contaminated with metals?*

There is no identified mechanism whereby 'up-stream' soils (within the top 1m) could become contaminated with metals originating from the site. However this may not apply to other more mobile substances, and thus raises concerns over the conceptual site model and/ or understanding of the site by NEERI.

- *Site soils are not percolating to groundwater.*

As above, this conclusion cannot be justified, based on the scant data, absence of leachate testing and other factors detailed within this report. Of particular note is the absence of a suitable conceptual site model.

- *Contamination has not been found to be widespread.*

NEERI conducted a limited sampling campaign that was severely compromised, and did not present analytical results for key contaminants of concern. Despite acknowledging the contamination found by previous investigations, NEERI did not follow-up these leads. Where groundwater contamination was detected, no explanation or theories were offered for the source of this contamination.

5.0 Recommendations for Further Work

The work completed by NEERI and NGRI adds information of some value to the pool of knowledge regarding the former Union Carbide factory site. However it does not constitute a sufficiently detailed investigation to allow a suitable remediation approach to be adopted.

In terms of further work, reference should be made to the 'model approach' outlined above. The work completed to date (where fully evidenced with suitable lab certification etc.) can be assimilated into an assessment conforming to best practice. It is recommended that particular attention be given to the following areas (although not limited to):

- Detailed desk study, literature review and catalogue of all substances used on site, plus consideration of likely breakdown products of primary contaminants;
- Development of a Conceptual Site Model;
- Development of a formal Sampling and Analysis Plan (including details of all necessary Quality Control and Quality Assurance procedures, laboratory certification etc.), including provision for leachate testing and any other tests that may help inform the remediation method choice;
- Correct presentation of analytical results and release of all raw data;
- Detailed Health and Safety Plan for investigation and decommissioning of plant etc;
- Site investigation to consider the full shallow and deep soil horizon, with guidance drawn from the Conceptual Site model (this will determine how deep/ where to look for DNAPLs etc.);
- Site investigation to include an element of 'grid' investigation (it is not unusual for investigations of this nature to be based on a 25m or 50m grid);
- Dedicated monitoring wells to be designed and drilled solely for the purpose of investigating the groundwater body (or bodies), a number to be provided both inside and outside of the facility;
- Calibration of Conceptual Site model following site investigation;
- Risk based derivation of remedial targets;
- Remediation options appraisal (considering all potentially successful remediation methods) and trials as necessary.

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*Note: Conversion factors used for standardization, assuming solution density for water (1.kg/Litre), and that trace substances do not alter solution density.

1 microgram/Litre = 1 ppb

1ppm = 1000ppb

All detected substances are mainly processing aids that are all confirmed used during routine operations at the Union Carbide factory, and dumped subsequent to site closure (see Appendix 3)

Appendix 2

Environmental Protection Agency (US) test method standards for chlorinated organics and volatile organics:

Chlorinated organics

EPA Method-8081 http://www.caslab.com/EPA-Methods/PDF/8081a.pdf

EPA Method-8270 http://www.epa.gov/region9/qa/pdfs/8270.pdf

Volatile organics

EPA Method- 535 http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/5035.pdf

EPA Method-5021 http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/5021.pdf

EPA Method-8015 http://www.caslab.com/EPA-Methods/PDF/8015b.pdf

EPA Method- 5032 http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/5032.pdf

EPA Method- 8270C http://www.trincoll.edu/~henderso/textfi~1/416%20notes/8270c.pdf

Appendix 3

Chemicals reported to be dumped by Union from 1969-84.

S. No.	Chemicals	Quantity (MT)	Use in Factory	Nature of Pollution
1.	Aldicarb	2.0	Product	Air, water & soil
2.	Alpha-napthol	50.0	Ingredient	Air & soil
3.	Benzene Hexachloride	5.0	Ingredient	Air, water & soil
4.	Carbaryl	50.00	Product	Air, water & soil
5.	Carbon tetrachloride	500.00	Solvent	Air & water
6.	Chemical waste tar	50.00	Waste	Water & soil
7.	Chlorobenzoyl chloride	10.00	Ingredient	Air, water & soil
8.	Chloroform	300.00	Solvent	Air & water
9.	Chlorine	20.00	Ingredient	Air
10.	Chlorosulphonic acid	50.00	Ingredient	Air & soil
11.	Hydrochloric acid	50.00	Ingredient	Air & soil
12.	Methanol	50.00	Solvent	Air & water
13.	Methylene chloride	100.00	Solvent	Air & water
14.	Methyl Isocyanate	5.0	Ingredient	Air, water & soil
15.	Mercury	1.0	Sealant pan filter	Water & soil
16.	Monochloro toluene	10.00	Ingredient	Air, water & soil
17.	Monomethyl amine	25.00	Ingredient	Air
18.	Napthalene	50.00	Ingredient	Air
19.	Ortho dichlorobenzene	500.00	Solvent	Air
20.	Phosgene	5.0	Ingredient	Air
21.	Tri methylamine	50.00	Catalyst	Air
22.	Toluene	20.00	Ingredient	Air, water & soil

Metallic compounds (inorganic)

- copper-chromium-arsenates, copper salts, mercuric chloride mercuric oxide, mercurous chloride - used as preservatives, fungicides and antifouling products

Organometallic compounds

- Organotin
  - tributyl tin oxide1 - used as a wood preservative and antifouling product
- Organic arsenicals
  - organic arsenicals (cacodylic acid – used as a herbicide)

Organophosphorus

- dichlorvos, bromophos, diazinon, malathion – used as insecticides

Organochlorine

- aldrin, dieldrin, chlordane, DDT - used as insecticides
- lindane - used as an insecticide and for vertebrate control

Carbamates

- aldicarb - used as a molluscicide and soil sterilant
- aminocarb - used as an insecticide
- maneb -used as an insecticide, fungicide and antifouling product

Organonitrogen compounds

- substituted ureas
  - diuron, linuron - used as herbicides
- dinitroanilines
  - trifluralin, 2,4-dinitroaniline - used as herbicide
- other nitrogen derivatives
  - dinitrocresol, dinoseb - used as herbicides and insecticides, dinocap - used as a fungicide
- triazines
  - atrazine, simazine, propazine - used as herbicides

Phenoxyacids

- 2,4 dichlorophenoxyacetic acid, mecoprop, 2,4,5 trichlorophenoxyacetic acid - used as herbicides

Phenolics

- pentachlorophenol and other chlorinated phenols - used as wood preservatives

Metal carboxylates

- copper naphthenate, zinc naphthenate - used as wood preservatives and antifouling products
- zinc versatate - used as a wood preservative

Quaternary ammonium (diphyridils) compounds

- diquat, paraquat - used as herbicides

Pyrethroids permethrin - used as an insecticide and preservative

- resmethrin, bioresmethrin - used as insecticides

<u>Others</u>

herbicides benzoic acids, eg:

- chloramben
- anilides eg alachlor
- chlorinated aliphatic acids, eg sodium salts of trichloroacetic acid, dalapon (2,2 dichloropropanoic acid)
- amines eg picloram
- ammonium sulphamate

rodenticides pyriminil

- warfarin

molluscicide metaldehyde

<u>Other potential contaminants</u>

Dioxins Impurities in, for example, organochloride compounds, phenoxyacids, chlorinated phenols and benzenes, and may result from combustion of chlorinated organic compounds

Chlorates
Coal tar residues
Polychlorinated biphenyls (PCBs)
Asbestos
Fuel oils
Coal and ash
Effluent treatment chemicals sodium bisulphate, hydrochloric acid, phosphoric acid - used as pH adjusters
'Spent' activated carbon

Full details are available in the DoE Industry Profile for Chemical Works: Pesticide Manufacturing Works: http://www.doeni.gov.uk/

school95bjki-e-e.pdf

Comparison of Sampling and Analytical results of NEERI (2010) and previous studies.

Total Area UCIL, SPE and surrounds

Legend:

- / - Water sample detection
- / - Soil sample detection
- / - Vegetation (crops) detection
- / - Human breast milk detection

Table 1: Chlorinated organic compounds

Chlorinated organics	GREENPEACE 99-04	MPPCB 03-06	Shristi '02	BMA '09	CSE '09	NEERI
Chloroform	/	NA	////	/	NA	No results reported
Carbon tetrachloride	/	NA	NA	/	NA	No results reported
Dichloromethane	ND	NA	////	/	NA	No results reported
Chloroethenes	/	NA	NA	NA	NA	No results reported
Chlorobenzenes	//	NA	///	NA	//	No results reported
Dichlorobenzenes	/	/	/	ND	//	//
Trichlorobenzenes	/	/	//	/	//	No results reported

Note: NA - Not Analysed

ND - Not Detected

All detected substances are mainly processing aids that are all confirmed used during UCIL operations. The fate of these substances has not received sufficient investigation.

Only Shristi (2002) performed testing on vegetation and human breast milk samples.

Table 2: Pesticides

Pesticides	GREENPEACE 99-04	MPPCB 03-06	Shristi '02	CSE '09	NEERI
Aldicarb	ND	ND	NA	//	/
Lindane and isomers	/	ND	////	//	/
α-Naphthol	NA	ND	////	ND	/
Sevin (Carbaryl)	/	/	NA	//	/

Note: NA - Not Analysed
ND - Not Detected
Only Shristi (2002) performed testing on vegetation and human breast milk samples.
Only Isomers of Lindane include - α-HCH, β-HCH, γ-HCH, δ-HCH

Legend:
/ - Water sample detection
/ - Soil sample detection
/ - Vegetation (crops) detection
/ - Human breast milk detection

Table 3: Heavy Metals

Heavy Metals	GREENPEACE 99-04	Shristi '02	CSE '09	NEERI
Cadmium (Ca)	/	/	/	/
Chromium (Cr)	/	//	/	/
Mercury (Hg)	/	///	//	/
Nickel (Ni)	/	////	NA	/
Lead (Pb)	/	////	//	/

Note: NA - Not Analysed
ND - Not Detected
Only Shristi (2002) performed testing on vegetation and human breast milk samples.

Table 4 : Chlorinated organic compounds detected in water samples at radius up to 3km from UCIL site, and exceeding international drinking water standards.

Chlorinated organics	*Water analyses performed (ppb - normalised)*					*Drinking water standards Microgram/L = ppb**		
	GREENPEACE 99-04	MPPCB 03-06	Shristi '02	BMA '09	CSE '09	NEERI '10	WHO	USEPA
Chloroform	2590	NA	1359	259	NA	No results reported	200	100
Carbon tetrachloride	3410	NA	NA	3790	NA	No results reported	2	5
Dichloromethane	ND	NA	1666	19	NA	No results reported	20	5
Chloroethenes	250	NA	NA	NA	NA	No results reported	70	5
Chlorobenzenes	56	NA	29	NA	13	No results reported	300	100
Dichlorobenzenes	2875	93.11	ND	ND	0.8	2	300	75
Trichlorobenzenes	145	12.95	ND	17	0.2	No results reported	20	-

Note: NA - Not Analysed

ND - Not Detected

Conversion factors used for standardization, assuming solution density for water (1kg/Litre), and that trace substances do not alter solution density.

1 microgram/Litre = 1 ppb

1ppm = 1000ppb

Chairman, Bhopal Environmental Remediation Oversight Committee
and Minister of State, Ministry of Environment & Forests.
Paryavaran Bhavan, CGO Complex
Lodhi Road, New Delhi 110 003

August 05, 2010

Sub. Expert's Technical Review of NEERI and NGRI Reports on the environmental contamination in and around Union Carbide's abandoned factory site in Bhopal.

Dear Sir,

Enclosed please find a copy of the Technical Review of the reports published by NEERI, Nagpur and NGRI, Hyderabad by international experts on the contamination of soil and ground water in and around Union Carbide's abandoned factory site in Bhopal. This is in accordance with the decision taken at our meeting on July 9, 2010 at Bhopal.

We look forward to your responses and ideas about moving this process forward so that the ongoing issue of environmental contamination can be meaningfully addressed with the urgency it deserves.

Thanking you.

Yours sincerely,

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Children Against Dow-Carbide
Mob. 9826994797

Balkrishna Namdeo
Bhopal Gas Peedit Nirashrit Pension Bhogi Sangharsh Morcha
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SUBMISSION OF THE INTERVENOR BHOPAL GROUP FOR INFORMATION AND ACTION TO THE BHOPAL ENVIRONMENTAL REMEDIATION OVERSIGHT COMMITTEE ON REMEDIATION OF GROUND AND SOIL WATER, AND OTHER TOXIC WASTE, IN AND AROUND THE FORMER UNION CARBIDE FACTORY, BHOPAL IN COMPLIANCE WITH THE ORDER OT THE HON'BLE HIGH COURT OF JUDICATURE OF MADHYA PRADESH AT JABALPUR IN WRIT PETITION 2802 OF 2004 (ALOK PRATAP SINGH v. UNION OF INDIA & ORS.) DATED 21ST JULY, 2010

1. The intervenor, Bhopal Group for Information and Action (BGIA), to file the following submissions with the Bhopal Environmental Remediation Oversight Committee (hereinafter "Oversight Committee"), in compliance with the Hon'ble High Court of Judicature of Madhya Pradesh at Jabalpur Order of 21st July, 2010. The Hon'ble High Court allowed BGIA to place before the Oversight Committee reports and expert studies on the problem and the Operational Plan for the Preparation of Remediation Activities in and around the abandoned former Union Carbide factory at Bhopal.

2. The proposed Operational Plan is aimed at detailing the steps that need to be taken in three Phases over a period of two years for a thorough scientific assessment of the depth and spread of toxic contamination in the soil and ground water in and around the Union Carbide factory at Bhopal.

3. The proposed Operational Plan follows established international standards of assessment and is based on the opinions and suggestions of international experts in environmental assessment and remediation. It is submitted that the proposed Operational Plan offers the Oversight Committee with a feasible plan consistent with the principle that for remediation of hazardous waste, the best available technology must be used to avoid perpetuating the environmental harm while remediation. The plan is in keeping with the Order of the Hon'ble High Court of Judicature of Madhya Pradesh Order dated 23rd June, 2005, whereby BGIA, with other intervenor organisations, were accepted as intervenor to ensure a solution consistent with the community expectations and scientific consensus.

4. BGIA submits that similar to the disaster caused by the leakage of toxic gases on the night of December 2-3, 1984 from the Union Carbide factory, the ongoing environmental contamination in and around the abandoned factory site is an unprecedented situation that requires high degree of expertise and competence for its meaningful resolution.

5. That in adjudication of the scientific and technical issues this Honourable Court is expected to follow well established standards that require that "best available technology" is made available for the resolution of the ongoing unprecedented environmental situation in Bhopal. Courts in India have reiterated that for hazardous waste remediation, the best available technology must be used to ensure that there is no further environmental damage and risk to human life. In *Law Society of India v. Fertiliser & Chemicals Travancore Ltd.*, AIR 1994 KER 308, the Hon'ble High Court of Kerala held, in a public interest litigation brought against the possible leak of an ammonia storage tank in Willingdon Island area, Cochin, that:

> "On the findings and conclusions we have decoded from the mass of materials placed before us, we have to make our own final decision in the matter. We are fully aware of the fact that directing the first respondent to decommission the ammonia tank would certainly involve very far-reaching and serious economic issues as well as issues relating to loss of employment to

large number of persons. Certainly these issues involve vital and serious consequences. But we have to balance these issues with the real and intelligible potential possibility of a catastrophic accident to the ammonia tank resulting in extermination of all living beings in Willingdon Island, City of Cochin and nearby places. We have found that the catastrophic failure of the tank is not a remote possibility, but a credible and contingent possibility to be reasonably anticipated on the facts unfolded in the case. We feel that we have to discharge our obligation informed of the fact that the human population of Cochin City and Willingdon Island should not be compelled to remain under the dark shadow of a genocide. Life on earth can never be peaceful if it is shrouded in perpetual anxiety and fear of extermination on account of an avoidable human activity. It is the plain and clear negation of the most basic human right and gross violation of the fundamental right guaranteed under Article 21 of the Constitution of India." (para 191)

6. The pitfalls of using less optimal – quicker or disposal – means of disposal are demonstrated by the decision to dispose the stored 40 metric tonnes of lime sludge from the former UCC factory at a landfill in Pithampur, Dhar District, Madhya Pradesh. The disposal was recommended despite a lack of consensus in the technical sub-committee, and a failure to conduct appropriate studies. It was also conducted without consultation with the local community in Pithampur. The local community has since seen a spate of health problems related to the dumping of toxic waste, that have developed consequent to the transfer, and a full inquiry has been publicly promised.

7. The remediation plan being placed before the Oversight Committee was filed as part of an interim application before the Hon'ble High Court of Judicature, filed on 11st August, 2005 (IA 6809/2005). The Interim Application is still pending. The remediation plan is annexed hereto and marked as **Annexure 1.**

8. BGIA respectfully reiterates the following facts from its interim application (6809 /2005) filed before the Hon'ble High Court in WP 2802/2004.

Extracted numbered paragraphs from Intervenor's Application dated August 11, 2005.

21. That the **major reason for delay in responding to the environmental disaster was the active part in downplaying the assessment of hazard at the factory site by the government scientific agency NEERI,** which carried out a series of unscientific studies that produced conclusions favorable to Union Carbide.

22. That the National Environmental Engineering Research Institute **(NEERI) had insufficient experience and expertise** to characterize the waste remaining at the Union Carbide Factory site, or to assess the depth and spread of contaminants in soil and ground water in the nearby communities. An internal document [Annexure XLI] from Union Carbide describes NEERI's weakness in this area in the following words :

"NEERI's experience is mainly limited to Environment Impact Assessment of a new project or an Operating Plant. Investigation and remediation of a closed chemical plant site like Bhopal is a first of its kind in India and ***there is no one including NEERI having any experience for this kind of work.***"

26. That NEERI **enjoyed a special relationship with the Union Carbide Corporation** because NEERI's research was perceived by Union Carbide to be easily malleable and methodologically unprofessional in UCC's favor, and, that UCC chose to fund NEERI because NEERI is a Government agency whose research UCC understood would not come under intensive scientific scrutiny by monitoring agencies such as the MP Pollution Control Board. These facts are made clear from Union Carbide's internal documents.

> *" NEERI is a well known Government sponsored institute whose investigations are well accepted by monitoring agencies such as State Pollution Control Boards, as well as Government departments." [Annexure LI]*
>
> *"It was noticed that State Pollution Control Board did not question the investigations and recommendations of NEERI. If the work is carried out by any other agency, the Board follows up and examines the work critically, and more so if UCIL is involved. Strategy: from the foregoing, it is advisable to entrust the work to NEERI... " [Annexure LII].*

27. That Union Carbide Corporation understood and made use of NEERI's weaknesses in order to enable research that was beneficial to **Union Carbide, and was able to exploit** those weaknesses by hiring their own private consultants, the Arthur D. Little Company (ADL) to guide and advise NEERI on methodology..

> *"NEERI's Weaknesses*
> - *Not used to developing standards of contamination where not available*
> - *Likely to recommend unrealistic standards of contamination without sufficient back-up.*
> - *Found to ignore standard sampling procedures." [Annexure LI]*
>
> *"Hence, M/s A.D. Little, USA (ADL), who have vide been appointed as Consultant to UCIL, to advise and guide in investigation, development of EMP & carrying out remediation work to restore the plant site making it suitable for light engineering industry." [Annexure LI]*

The annexures in the application 6809/2005 are not reproduced as part of this submission and are available if necessary.

9. That the Intervenor- BGIA's purpose in presenting the above paragraphs is to highlight the need for thorough scrutiny of the competence and record of performance of scientific agencies to be selected for the purpose of assessment and remediation. In view of the fact that the issues raised in the August 11, 2005 application are eminently relevant to the subject matter under consideration. The Oversight Committee must consult all reports and studies and ensure that the remediation plan is consistent with the scientific consensus and represents the best available solution to solving the intractable problem of the contamination of the soil and ground water.

10. BGIA also reiterates the following reports for the reasoned consideration of the Oversight Committee in any consideration of a remediation plan for the consideration of the Hon'ble High Court in this matter.

11. The Centre for Science and Environment (hereinafter "CSE"), which has been filed before the Hon'ble High Court, one of the most respected scientific organisation in India, issued a report in December 2009, that concluded that not only within the factory site, but also outside, the soil samples contained toxic chemicals (chlorinated benzene compounds and organochloride pesticides and four out of the five heavy metals tested). The concentration of pesticides found in all water samples was upto 59.3 times the mandatory water standard affixed by the Bureau of Indian Standards (IS: 14543).

The report further concluded that not only is the UCIL the only source of the conta indentmination of ground water and soil, but:

> *"The topography of the area also points towards contamination of the ground water due to the UCIL".*

In addition, the CSE Report concluded that the closed UCIL factory continues to be a source of contaminants for the surrounding area. The report is annexed hereto as **Annexure 2.**

12. In 1999, University of Exeter undertook the collection of 33 samples of soil and 22 samples of groundwater from in and around the factory site. They found heavy concentrations of carcinogenic chemicals and heavy metals like mercury. Mercury was found at between 20,000 to 6 million times the expected levels: and elemental mercury was discovered to be widely distributed across the plant premises Twelve volatile organic compounds, most greatly exceeding EPA standard limits, were found to have seeped and continue to seep into the water supplies of an estimated 20, 000 people in local area. VOCs were registered in the following quantities in a water well of the Atal Ayub Nagar community in Bhopal, just north of the Union Carbide factory. Three water wells in this community, northeast of the factory, were discovered to have the most severe contamination. This report is annexed hereto as **Annexure 3.**

13. The toxic waste has been dumped around the Union Carbide factory between 1977 and 1984, when the Bhopal Gas Tragedy brought a tragic and abrupt halt to the operations of the plant. According to the German aid development agency (GTZ), a technical proposal entitled "Final and Complete Remediation of the Abandoned Factory Site of the Union Carbide", submitted to the Madhya Pradesh Pollution Control Board, Respondent No. 3 herein, approximately 25, 000 tonnes of contaminated solid material may exist at the site. A copy of the report is annexed hereto and marked as **Annexure 4.**

14. The Sambhavna Trust Clinic conducted a "Morbidity Survey Relating to Water Contamination" prepared in August 2006 which concluded that the soil and water contamination has resulted in an increase in the morbidity pattern among the population staying near the UCIL factory and surrounding area of the solar evaporation ponds, which were used in a shocking and reckless disregard of the consequences of such an act, to dump extremely toxic material around the factory site. A copy of the report is annexed hereto and marked as **Annexure 5.**

15. It is respectfully submitted that the below toxic waste disposal units - or other such environmental, health and safety regulations compliant facility - are recommended:

A. GTZ, Eschborn, Frankfurt, Germany

GTZ is active in over 120 countries in Africa, Asia and Latin America. The facility is already involved in an Indo-German collaboration with the Central Government for over 40 years that includes hazardous toxic waste management, dealing with obsolete pesticides, and environmental policy.

DEUTSCHE GESELLSCHAFT FÜR TECHNISCHE ZUSAMMENARBEIT (GTZ) GMBH
Dag-Hammarskjöld-Weg 1-5
65760 Eschborn

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Postal address
Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH
Postfach 5180
65726 Eschborn

B. **Ekokem Oy Ab, Helsinki, Finland**

This facility is owned by the Finnish government (34.1%), municipalities (28.2%) and industry (37.7%). It has ISO 9001, ISO 14001, EMAS, OHSAS 18001 and other key certifications and more than 20 years of experience. The plant utilises, renders harmless or safely disposes off some 120,000 tons of hazardous waste every year. The plant processes hazardous organic chemical waste, contaminated soil, inorganic hazardous waste and other industrial wastes. The company has much experience of disposing of obsolete pesticides from developing countries. The incineration of waste takes place in the kilns at a temperature of about 1300 °C with an oxygen surplus of at least 6 % in the kiln and its after-burning chamber. This ensures complete incineration.

The Finnish Funding Agency for Technology and Innovation and Finpro are planning with their co-partners to set up an innovation centre in India, the intention being to make the Finnish innovation system well-known and increase joint innovation activities between Finland and India

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C. Earth Tech, Alberta, Canada

The Swan Hills Treatment Centre owned by the government of Alberta and operated by Earth Tech Canada Inc has more than 20 years of experience.. The destruction and removal efficiency rate of the Swan Hills Treatment Centre exceeds the licensed requirement for DRE of 99.9999% for organic materials, typically operating at a DRE level of 99.999999%. It has been used to destroy dioxins and PCBs. The facility is networked with waste management service providers for onsite jobs such as waste collection, waste labeling/packaging, documentation or transportation of hazardous wastes. It is certified ISO 14001 OHSAS 18001. Earth Tech Canada has over 8,400 professional and support personnel in 150 offices worldwide, including the U.S., Canada, Mexico, South America, Europe, Australia, and Asia/Pacific.

EARTH TECH (CANADA) INCORPORATED
105 Commerce Valley Drive W
Thornhill, On l3T 7W3
http://www.shtc.ca/

16. That in conclusion the Intervenor organisation wishes to emphasize that transparency in the planning and execution of the work of scientific assessment of the depth and spread of contamination, participation of the victims and potential victims at all stages of the project and systems for long term scientific monitoring as well as monitoring by the neighbourhood community are vital to a sustainable solution to the problem of hazardous contamination in Bhopal.

Submitted on behalf of Bhopal Group for Information and Action

By Satinath Sarangi
Authorised representative

ANNEXURE - 1

Proposed Operational Plan for the Preparation of Remediation Activities in and around the abandoned Union Carbide factory at Bhopal

Introduction

Various Studies, Reports, soil and groundwater investigations have been performed and in some cases monitoring is currently ongoing. There should be enough and suitable data to draw a clear picture of the site and get an idea of the dimensions of the pollution. However, the existing data were never compiled and summarized completely and comprehensively, plus, existing gaps were neither properly identified, nor really filled. It is assumed, that there are still considerable gaps regarding the selection of appropriate, effective and suitable remediation methods and techniques, not to speak of the still incomplete picture of the status of real contamination of the site and its vicinity.

Therefore and as the primary step a comprehensive baseline summary including a **gap analysis** is recommended as basis for further action on site.

Some of the hazardous waste from the site such as chemicals, debris, tarry residues, other material (approx. 400 tons) were collected in 2005 stored in one of the sheds within the factory premises. The waste is contained in drums, big plastic bags and other containers. While these need to be disposed off currently this waste is secured, is not exposed to the elements and not leaching any contaminants in to the environment.

The expertise and services of UNESCO and the Archaeological Survey of India (ASI) will be very much required for the challenging task of dismantling, decontamination and reconstruction of plant structures, machinery and building. Already, UNESCO has shown interest in this direction. Further, and parallel to other actions, the site should be properly fenced (in particular the rear part of the site where uncontrolled access is possible) and secured by guards (not only the road entrance).

It may not be possible to dispose off hazardous and toxic or contaminated material, waste, or whatever will be found in Bhopal or Madhya Pradesh or even in India. It therefore might be appropriate to consider shipping for treatment in countries such as Germany, Canada and Denmark where the most appropriate and efficient facilities are available.

Even today it is not possible to select and decide on any specific remediation methods, techniques or strategies, since the data available on the extent and character of contaminants is not clearly known yet. However, as soon as a final site investigation would have been done, the base for action would be immediately clear and remediation techniques could be selected on the basis of a risk assessment study and a feasibility study, which may take only very few months. It would not be very difficult to propose options and carry out a feasibility study with proper and solid cost estimates.

A small variety of options is available in particular in Germany with a high experience gained in similar cases. However, given the current lack of knowledge on the extent and the type of contamination, especially with respect to ground water, appropriate, effective and feasible methods still need to be selected. A comprehensive site investigation and characterisation (detailed Phase II investigation – see below) is inevitable.

The operation plan for the holistic investigation of the abandoned Union Carbide factory site in Bhopal comprises of three steps or Phases.

- **Phase I** is a desk top study to establish a Baseline Document considering all available results
- Based on this study, available data will be compiled and checked for consistency and data gaps will be identified.
- During **Phase II** and **Phase III** data gaps identified during Phase I will be closed and missing data for the holistic understanding of contamination present will be obtained by additional investigation. A sampling and analysis plan will prepared, specifying the way data gaps will be closed. In a first step, additional investigation will address the direct Union Carbide site, in a second step the impacted surroundings of the site up to 5 km distance and radius will be included.

The operation plan considers also the decontamination, dismantling, reconstruction and conservation of plant structures, machinery, facilities and buildings still present on site.
Therefore the following scope is envisaged:

- Site cleaning, collection of any kind of waste still being present and removal of uncontaminated loose parts, plants etc. must be carried out. Existing vegetation especially grass, shrubs, tress should be cut and removed.

- A Health, Safety and Environmental (HSE) site management is absolutely important for safe performance of the planned action. The site management system should include all procedures and provide SOP's (Standards Working Procedures) for all works and processes. Training and education measures for staff working on the site and residents of neighbourhood communities must also be included. Enforcement of the HSE management on site must be provided by site supervisors.

- It is strongly recommended to establish an internationally recognized and accepted Health and Safety System (HASP) and adopt it to each step of the project.

Phase		Issue	Activities	Duration	Schedule
I	1.1	Collecting, reviewing and evaluating existing available data	Collect and compile all existing reports, studies, accounts, articles, verbal information from eyewitnesses and NGOs and other relevant data on the *site and the effected vicinity of the site regarding existing contamination*: e.g. biota, soil, ground and surface water, buildings, residual plant components, water supply	1 month	Month 1
I	1.2	Baseline summary	Compile evaluated data and prepare a baseline summary indicating the present state of knowledge on the contamination present (chemicals, extent in soil and groundwater, known and suspected contamination sources, pathways and receptors), from evaluated data start to produce a site conceptual model that can further be developed and completed with each of the following investigation steps. Identify the impacted site's surroundings and include them in the site conceptual model.	1 month (parallel to 1.1.)	Month 1
1	1.3	Plans for conservation of plant structures as Modern Industrial Heritage.	Invite experts from Archaeological Survey of India and UNESCO for an inspection and survey of the plant structures, machinery and buildings that need to be conserved as Modern Industrial Heritage.	1 month (parallel to 1.1)	Month 1
I	1.4	Gap analysis and Phase I Report	Identify and address data gaps and inconsistent data and recommend additional investigations for groundwater and soil wherever required, to obtain a holistic knowledge on the site and its surroundings regarding the extent and type of the contamination, the potential sources, pathways and receptors, prepare sampling and analysis plan for soil and groundwater based on the baseline study and the results of the gap analysis, prepare a report and stepwise complete the site conceptual model	1 month	Month 2
I	1.5	Inform all stakeholders and make decisions	Organise meeting(s) of all stakeholders and: Inform on findings from literature assessment (Report Phase I) Present and discuss work plan for PHASE II Achieve approval of work done and accordance on all further steps from all stakeholders	1 month	End of Month 2

Activities within Phase I can be started immediately.

After submission of the deliverables of Phase I to the High Court and the Remediation Group meetings are required among all relevant stakeholders such as survivors organizations, state and central government agencies, and NGOs for finalization of Phase II activities.

Phase		Issue	Activities	Duration	Schedule
II	2.1	Inventory of hazardous waste on site for later removal and disposal	Organise proper inventorisation and characterization of the waste.	1 month	Month 3
II	2.2	Organize proper packaging and labelling Organise proper transport Arrange disposal at a suitable TSDF (most probabaly in the EU)	Prepare removal and containment plans for the above waste for transport and eventual treatment of accumulated waste, get approvals for transport, disposal and if required export to another country (follow BASEL Convention requirements); identify private operator to carry out work.	1 month	Month 4
II	2.3	Supervision of removal and disposal activities	Supervise the removal and disposal activities for compliance with regulations, the contract and health and safety requirements	0,5 month	Month 5
II	2.4	Investigation and inventory of existing plant components	Plan and carry out: Detailed inspection, survey and analysis of all plant components that are still in place: containers, cauldrons, reactors, tanks, pipes, etc. on residual chemicals, contaminations and other material; quantification of items with the participation of experts from ASI and UNESCO.	2 month	Month 3 and 4
II	2.5	Investigation of existing buildings and building components	Plan and supervise:: Identify analyses and quantify all production residuals, raw materials and products left back in containments, vessels and tanks . Detailed analysis of contamination of buildings and building components: take samples and analyse; quantification of existing components Preparation of a decontamination, decommissioning, reconstruction and conservation plan for all plant structures, facilities and buildings with major help from ASI and UNESCO. Preparation of detailed Health and Safety plans (HASP) for the above work including Standard Operation procedures (SOP's) for all work steps.	2 month parallel to 2.1	Month 3 and 4
II	2.6	Preparation of tender documents (for subcontracting) for decontamination, dismantling, reconstruction and conservation work,	Prepare Tender Documents for decontamination, dismantling, reconstruction and conservation of facilities and disposal of residuals left back in tanks, pipes etc.	1 month parallel to 2.1	Month 4
	2.7	Supervising above work	Supervise the demolition, decontamination, reconstruction activities for compliance with regulations, the contract and health and safety requirements		Month 4 and 5
II	2.8	Health and Safety Planning	Preparation of detailed Health and Safety plans for the above work including Standard Operation procedures (SOP's) for all work steps.	1 month parallel to 2.4	Month 3 and 4

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II	2.9	Preparation of Tender Documents for sub-contracting, based on the sampling and analysis plan derived from the gap analysis, for Site investigation works including drilling of soil borings, groundwater monitoring works, sampling and chemical analysis	Prepare Tender Documents for site investigation work	1 month	Month 5
II	2.10	Investigation of biota, soil and subsoil on contaminations	Plan and supervise : Detailed analysis of biota; detailed analysis of soil: layer wise, sample collection each 0.5 m thickness: drill boreholes and take samples according to a drilling plan; analyse samples	6 months overlapping 2.1 and 2.4	Month 4 to month 9
II	2.11	Investigate all water bodies, investigate storm water discharge from site	Plan and supervise : Detailed analysis of Surface water bodies (nallahs, creeks, lakes, ponds, etc. if existing) according to plans;	3 months parallel to 2.8	Month 5 to month 7
II	2.12	Groundwater investigation	Plan and Supervise Detailed sampling and analysis of existing ground water wells, drilling of additional boreholes and installation of additional wells as per results of gap analysis and sampling. Set up a numerical fate and transport model for groundwater.	4 month parallel to 2.8	Month 7 to 9
II	2.13	Sampling of ground and surface water on regular bases (periodically 4 times/a)	Based on results from step 2.12: plan and carry out Ground water and surface water sampling and analysis every three months to find out trends and seasonal dependencies within one year	1 month per period	Month 8 to month 19
II	2.14	Prepare a holistic analytical report including risk assessment for the site and site conceptual model	Compile and assess all analysis and investigation results, evaluate results and draw conclusions (findings and recommendations) with respect to a holistic risk assessment, select and identify appropriate remediation technique and prepare final rehabilitation action plan and Health and Safety Plan (HASP) for onsite labours and neighbouring people	2 month	Month 9 to 10
II	2.15	Prepare Tender (for sub-contracting) for site remediation (soil and groundwater)	Preparation of Tender Documents for soil and groundwater, disposal/treatment of contaminated soil, Assist in tendering process, contract negotiation and prepare for site supervision during remediation works		

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II	2.16	Inform stakeholders on regular bases and make common decisions where required	Ongoing: Organise regular meetings of all stakeholders and: 1. Inform about progress of detailed investigations on Union Carbide factory area 2. Inform on preliminary findings and recommendations 3. Achieve accordance on **every further** step from, **all** sides		Month 3 to month 19
II	2.17	Inform all stakeholders and achieve accordance on further steps	Organise final meetings of all stakeholders and: 1. Inform about findings and recommendations from PHASE II 2. Present and discuss work plan for PHASE III 3. Achieve accordance of **all** stakeholders on all **further** steps 4. Discuss remediation objectives (status of site after remediation has ended)		Month 10 etc.

The activities of Phase III could run in wide parts parallel to and in close connection with the one of Phase II. Since the measures are similar and the equipment used and staff employed will be the same:

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Phase		Issue	Activities	Duration	Schedule
III	3.1	Prepare Tender Documents for subcontractors for a site investigation work in the vicinity of the Union Carbide factory site	Preparation of Tender Documents based on the sampling and analysis plan derived from the gap analysis, for Site investigation works including drilling of soil borings, groundwater monitoring works, sampling and chemical analysis	1 month	
III	3.2	Investigate biota, soil and subsoil on contaminations	Plan and supervise : Detailed analysis of biota; detailed analysis of soil: layer wise in strata of 0.5 m thickness: drill boreholes and take samples according to drilling plan; analyse samples	6 months	Month 8 to month 13
III	3.3	Investigate all water bodies and water types on contamination	Plan and supervise: Perform a detailed analysis on existing wells based on the results of the Baseline Summery under Phase I. Install new monitoring and pump wells if necessary and test (pump test packer tests, MIP tests, geophysics, hydro chemically and hydro mechanically) them accordingly. Investigate also deeper or different aquifers within the fractured bedrock, provide a detailed plume analysis and detect any DNPL/LNPL, if present. Set up a numerical fate and transport model for groundwater. Detailed analysis of surface water bodies (nallahs, creeks, lakes, ponds, etc.) according to sampling plans; Detailed sampling and analysis of ground water and well water.	3 to 5 months parallel to 3.2	Month 9 to month 11
III	3.3	Sampling of ground and surface water on regular bases (periodically 4 times/a)	Based on results from step 2.4: plan and carry out Ground water and surface water sampling and analysis every three months to find out trends and seasonal dependencies.	1 month per period	Month 12 to month 23
III	3.4	Prepare a holistic analytical report including risk assessment for the site and site conceptual models	Compile and assess all analysis and investigation results, evaluate results and draw conclusions (findings and recommendations) with respect to final rehabilitation work (remediation master plan)		Ongoing
III	3.5	Information meetings for stakeholders / decision making	Refer to Phase II steps 2.7 and 2.8: Include results from Phase III		Ongoing

OBSERVATIONS AND COMMENTS ON THE REPORT ENTITLED: "ASSESSMENT AND REMEDIATION OF HAZARDOUS WASTE CONTAMINATED AREAS IN AND AROUND M/S UNION CARBIDE INDIA LTD., BHOPAL"

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Background

Based on the directives of the *Task Force* constituted by the Honorable High Court of Madhya Pradesh, the Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTRRD), Government of Madhya Pradesh, Bhopal, sponsored a joint study in March 2009 to National Environmental Engineering Research Institute (NEERI), Nagpur and National Geophysical Research Institute (NGRI), Hyderabad for assessment of contamination and delineation of suitable strategies for the remediation of contaminated areas in and around the UCIL site. The Indian Institute of Chemical Technology (IICT), Hyderabad also contributed to the study. The study was conducted from March 2009 to May 2010 and the final report was submitted in June 2010. The final report of the above mentioned study was titled as: "Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal".

This report was studied and commented upon by the author of this note in response to the specific request from Mr. Jairam Ramesh, Honorable Minister of State (Independent Charge), Ministry of Environment and Forests, Government of India, New Delhi, vide his letter dated 19th July, 2010.

Although, there is no clear mention of the Terms of Reference (TOR) prescribed for the "NEERI-NGRI-IICT Consortium" (hereafter referred to as "the Consortium") by the sponsoring agency while commissioning the said study; the final report briefly outlines the objectives on page 10 and 11 in Consortium (2010). The first objective

of the study conducted by the Consortium appears to be "reassessment" of the extent of left over contamination at the UCIL site in the context of wash-out of the pollutants due to natural processes, even volatilization as well as degradation of some of them and episodic efforts to clean-up some of the contaminated zones, identified and characterized by the respective agencies. The second objective set forth by the Consortium was to identify "strategies for the remediation of the contaminated areas, if any, especially after the preliminary site clearing activities carried out by the Madhya Pradesh Pollution Control Board (MPPCB)".

It was clarified by the Consortium in their final report that the preliminary site clearing activities were not completed by M/s Ramkey Ltd. (the contractor appointed by MPPCB) and as a result, the Consortium had difficulties in carrying out site assessment related activities due to presence of vegetation, old dilapidated buildings and scattered machinery and equipment. The 15-month study conducted by the Consortium was divided by them in three phases *namely*:

Phase 1: Detailed geophysical and hydro geologic assessment of the UCIL site and the surrounding area,

Phase 2: Detailed sampling and analysis of dumpsite and groundwater and

Phase 3: Developing risk based remediation strategies for the contaminated area.

Five major prior studies were used as background material by the Consortium and the reports were cited in Consortium (2010). The oldest study was authored by the NEERI-NGRI in 1996. This report somehow could not be downloaded and was not available for us to study. The remaining three reports *namely:* Greenpeace (1999), Srishti (2002) and CSE (2009), could be downloaded and studied. It is in this context the final report, Consortium (2010), was studied and commented upon.

The author of this note has restricted his opinion to the facts and strategies presented in Consortium (2010). The final report of Consortium was studied carefully by the author and following four questions emerged in his mind:

- Whether the pollutants were appropriately selected in the site assessment exercise?
- What was considered important to be included in the site assessment exercise?
- What was learnt from the site assessment activity?
- Is the proposed strategy for site remediation appropriate?

The effort was made to search the answers for the above mentioned four questions based on the final report of Consortium and the past studies (whichever available). Those comments and concerns were articulated by the author and presented categorically along with the author's opinion in the following four sections. Finally, a summary has been given based on the salient points raised in the context of the above mentioned questions.

Whether the pollutants were appropriately selected in the site assessment exercise?

The Consortium report gives the names of the pesticides and intermediates manufactured by the UCIL, Bhopal, upfront on page 3 in the 'background' section *i.e.* two pesticides and one intermediate *namely*: carbaryl (trade name: Sevin), aldicarb (trade name: Temik) and butylphenylmethylcarbamate (intermediate). However, Table 1 (page 4) reports the yearly production quantities of carbaryl alone along with methyl isocynate (MIC) - which is yet another intermediate manufactured by UCIL, Bhopal. Incidently, prior studies (also cited in the Consortium report) have reported the third pesticide that was manufactured *namely*: gamma-hexachlorocyclohexane (trade name: Savidol) in (CSE, 2009; Srishti, 2002 and Greenpeace, 1999); of which production route, raw materials, intermediates or production capacity has not been mentioned in any of the reports cited above.

Table 1 Pesticide named as Savin (chemical name: carbaryl) and intermediate chemical called as methyl isocynate *i.e.* MIC* manufactured at UCIL, Bhopal and sold in market from 1977 to 1984. (Reference: Table 1, page 4 from the report by Consortium, 2010)

Year	Carbaryl *i.e.* Savin (MT/year)	MIC* (MT/year)
1977	321	0
1978	367	0
1979	1,468	0
1980	1,534	374
1981	2,658	864

Year	Carbaryl *i.e.* Savin (MT/year)	MIC* (MT/year)
1982	2,271	623
1983	1,727	535
1984	1,101	313
Total	**11,447**	**2,709**

* The MIC quantities indicated in this table are the quantities sold by UCIL. Total manufacturing of MIC at Bhopal site must have been the quantities required for in-house consumption of MIC for production of carbaryl plus the quantity sold as intermediate chemical for the given year.

It would have been useful if some efforts were made in collecting the facts about the products, their respective production capacities and the production of associated raw materials and intermediates. Such information will eventually be useful in determining the list of critical pollutants in soil and aquifer environment – which should be focused in sampling, analyses and strategy articulation.

Appendixes A, B and **C** show compilation of the useful information on three pesticides manufactured at the site of UCIL, Bhopal during 1968 to 1984 (*namely*: carbaryl *i.e.* Sevin, aldicarb *i.e.* Temik and γ-hexachlorocyclohexane *i.e.* Lindane). This is an indicative compilation of critical information on these pesticides and based on the three appendixes **Table 2** was expanded. It has been adapted from the original version as Table 6 (page 37) given by Srishti (2002) which gives compilation of names of chemicals dumped by UCIL at Bhopal site from 1969 to 1984 (which is yet another indicative listing to illustrate a point). Those all chemicals were considered as "potential pollutants" based on some knowledge about their fate, transportation and toxicity.

It should be noticed that the author of this report has not listed each and every chemical associated with the UCIL plant in Bhopal in the above table (Table 2). It is an indicative compilation of useful information related to the critical potential pollutants from the four categories *namely* products, ingredients, solvents, and wastes. This information helped the author of this commentary in arriving at list of critical pollutants that should be analyzed through systematic sampling of matrixes at the site of UCIL, Bhopal.

Table 2 Chemicals dumped by UCIL at Bhopal site from 1969 to 1984.

(Reference: Adapted from Table 6, page 37 in Srishti, 2002)

Sr. No.	Category	Chemical (potential pollutant)	Quantity dumped during 1969 to 1984 (MT)	Nature of Potential Pollution
Products				
1	Product	Carbaryl ## (Production Capacity Known)	50	Air, Water and Soil
2	Product	Aldicarb ## (Production Capacity NOT Known)	2	Air, Water and Soil
3	Product	Butylphenylmethylcarbamate (Production Capacity NOT Known)	?	? Nothing is known!
4	Not Identified as Product!	γ-HCH ## (Production Capacity NOT Known)	?	? Nothing is known!
Ingredients				
5	Ingredient	α-napthol ##	50	Air and Soil
6	Ingredient	benzene hexachloride	5	Air, Water and Soil
7	Ingredient	chloro benzoylchloride *	10	Air, Water and Soil
8	Ingredient	chlorosulphonic acid *	50	Air and Soil
9	Ingredient	hydrochloric acid	50	Air and Soil
10	Ingredient	chlorine gas (for carbaryl & γ-HCH)	20	Air
11	Ingredient	methyl isocynate (MIC)	5	Air, Water and Soil
12	Ingredient	monochloro toluene *	10	Air, Water and Soil
13	Ingredient	monomethyl amine	25	Air
14	Ingredient	napthalene	50	Air
15	Ingredient	phosgene	5	Air
16	Ingredient	toluene	20	Air, Water and Soil
Solvents				
17	Solvent	Carbon tetrachloride	500	Air and Water

Sr. No.	Category	Chemical (potential pollutant)	Quantity dumped during 1969 to 1984 (MT)	Nature of Potential Pollution
18	Solvent	Chloroform	300	Air and Water
19	Solvent	methanol	50	Air and Water
20	Solvent	methylene chloride	100	Air and Water
21	Solvent	ortho-dichlorobenzene ##	500	Air
Wastes				
22	Catalyst	trimethyl amine	50	Air
23	Filter Sealant	Mercury (Sealant) ##	1	Water and Soil
24	Impurity	α-HCH ##	?	?
25	Impurity	β-HCH ##	?	?
26	Impurity	δ-HCH ##	?	?
27	Impurity	ε-HCH ##	?	?
28	Waste	General Chemical Wastes & Tars	50	Water and Soil

* The author of this note does not know in which steps these chemicals are used.

Only these chemicals were monitored in the study reported by Consortium (2010).

Clearly, Consortium (2010) final report did not go as far as it should have gone in identifying "potential pollutants" and there is a shortfall between the desirable *versus* available information on potential pollutants.

In sum, in the context of site remediation, the inclusion or exclusion of the potential pollutants should be typically dictated on the basis of their environmental fate, relative mobility with water in aquifer, persistence at the interface of soil, sediments, minerals as well as their eco-toxicity and toxicity to humans. The report from Consortium (2010), however, does not discuss the basis for their selection and elimination of the variety of chemicals consumed and used by UCIL at the Bhopal site. All the chemicals handled by UCIL could have been deemed as "potential pollutants" and a careful exercise could have been performed to select the most critical ones based on the known information on the respective products, raw materials, solvents, byproducts and intermediates. As a result, it seems to be a

difficult task to determine if the list of pesticides, intermediates, raw materials and solvents chosen by the Consortium in their site assessment and sample analysis was adequate in the first place.

What was considered important to be included in the site assessment exercise?

Section 3.0 (pages 21 to 68) describes steps and results obtained by the Consortium members during 15 months of field investigation (March 2009 to May 2010) aimed at assessment of contamination at UCIL site, Bhopal. The UCIL plant site in Bhopal is of the shape of an arrow-head, the tip of the arrow-head pointed to south-east direction. The ground water, however, flows from south-west to north and north-east. A nearly straight railway line lays parallel to the edge of the plot. Somehow the size of plot was not clear from any investigation report including the Consortium (2010). May be it is mentioned somewhere but somehow it could not be located anywhere, in spite of the specific efforts. A close observation of the remotely sensed picture of the site suggests that the plot could be of the size of 100 to 120 hectors.

The Consortium team concluded that the sizes of contaminated zones add up to area of 16 hectors within premises of UCIL, Bhopal. The solar evaporation pond (SEPs) and the secured landfill located outside UCIL premises cumulatively cover an area of about 14 hectares.

The geophysical investigations were performed to define and delineate the contaminants present and the general extent and location of contamination. For this study Consortium used the most widely used surface geophysical technique "electrical Resistivity Method". The electrical resistivity method can be classified in two categories viz. 1) vertical electric sounding (VES) and 2) electrical resistivity profiling (ERP). The VES is typically used for delineating vertical variations of the subsurface, whereas ERP is used to detect lateral variations (page 22 in Consortium, 2010).

Based on this information and based on the 1996 experience the Consortium reportedly conducted a fresh geophysical investigation using "the latest technology of resistivity imaging namely High Resolution Electrical Resistivity Tomography

(HERT) was used by NGRI for obtaining two dimensional (vertical profile) as well as three dimensional (horizontal profile at different depth) distribution of resistivity of subsurface strata. An equipment, SAS4000 from ABEM, Sweden was used for the present study. The data were interpreted using RES2DINV (2005) software. The HERT was carried out across the selected areas based on background information about the site as well as physical limitations at site (existence of concrete structures, sheds, bushes, water logging, roads etc). Total nine sites within the UCIL premises were covered during the HERT survey" (page 23 in Consortium, 2010).

While drilling wells as well as making geophysical observations, samples of soils and ground water were also collected from the cores and production of the test wells. Further, the Consortium selected three different parameters to analyze the collected soil and ground water samples - which are listed below:

- ✓ Semi volatiles/pesticides (carbaryl, aldicarb, alpha naphthol, hexachlorocychlohexane isomers and naphthalene)
- ✓ Volatile organics (carbon tetrachloride, chloroform, methylene chloride, 1,2-dichlorobenzene, chlorotoluene and toluene)
- ✓ Relevant heavy metals (mercury, cadmium, nickel, chromium, cobalt, lead, zinc, and copper)

The Consortium analyzed the presence of above listed chemicals in soil and ground water samples collected from in and around UCIL site, Bhopal by using the relevant US EPA standards and protocols, as listed in Table 5 (page 35) in Consortium (2010).

Of the three methods of sampling typically employed for site characterization, *namely*: systematic, judgmental and random (or a mixture of these), it is not clear which was used by the Consortium. While random sampling is practiced to test statistical hypothesis and has the highest number of samples taken and analyzed, judgmental, which has smallest number of samples taken and analyzed, is based on knowledge of site condition and the experience of the assessor. In this report a clear plan for sampling and analysis is not provided.

Further, attempts to eliminate areas which are not contaminated, by sampling and analyzing the matrixes, are not detailed. In addition, extended sampling of areas that were deemed contaminated could have helped narrow down the areas and volumes of contaminated soil patches, thus providing a better estimate of the contaminated soil volume that needs treatment. It is the author's belief that a better

characterization of the contaminated area and volume would have helpful in a better estimate of the cost of remediation.

In sum, in all fairness it must be mentioned here that no clear opinion can be expressed on the basis of the cryptic details on protocols and processes used in site assessment activity described in the Consortium report and in the light of the fact that no code or standard protocol was followed (or at least it was not reported in Consortium, 2010). While it is not possible or practical in many instances to give all the details related to every step in the report, the final report of Consortium should have at least described their inclusions and exclusions in terms of protocols, matrixes, analyses of critical parameters and should have made critical comments to defend their choices related to site assessment so that the reader can make rational assessment of the effort. In this context, it was all the more important to describe what was not done and why it was decided not to do it?

What was learnt from the site assessment activity?

In the final report submitted by the Consortium in June 2010, the following proclamations and conclusions have been highlighted by them on the basis of their field work and interpretation of results from sample analyses conducted during the study period March 2009 to June 2010. Effort has been made in the following 11 bullets to bring all the major observations and conclusions nearly verbatim (except some minor editorial corrections shown in brackets) as drawn by the Consortium team in their final report (Consortium, 2010) because the author feels that some of these conclusions are important and useful and some of the conclusions are not convincing because the data were not found in the final report:

1) During the study it appeared that there existed a general misunderstanding among the public as well as various agencies and organizations that MIC gas tragedy in 1984 also resulted in contamination of soil and groundwater in and around UCIL premises (in Bhopal). However, it may be made clear that, contamination of soil and groundwater in and around UCIL premises is solely due to dumping of the solid, semi-solid, liquid and tarry wastes generated during the manufacture of pesticides and associated chemicals dumped by UCIL within their premises from 1969 to 1984, and MIC gas tragedy has no relevance to it.

2) The geophysical investigations carried out by NGRI indicated possibility of contamination only at three sites (Site I, Site III and Site V) out of nine sites (Fig. 4). The depth of contamination at these sites was limited to about 2 m, except at one dump (Site III) that could be deeper (4 – 8 m). These dumps were isolated and limited to few spots.

3) The lithology of the area, as determined through drilling of bore wells by NGRI, revealed existence of black and yellow silty clay up to a depth of 22 to 25 m below ground level. The clay has very low permeability (of the order of 10^{-9} cm/s) and acts as natural barrier to the flow (of) water / leachate to the aquifer (from the contaminated zone due to dumping). The groundwater in the area exists (~~under~~) confined below a depth of about 25 m from the ground surface.

4) Confirmatory sampling and analysis of subsurface soil (collected during drilling of bore wells) also indicated contamination of soil up to a depth of about 2 m. Major contaminants detected at the site include: BHC, aldicarb, carbaryl, α-naphthol and mercury.

5) The additional sampling and analysis of soil from the possible dump areas also indicated contamination of soil in terms of above mentioned contaminants. The total area of soil contamination is estimated to be around 7 hectares.

6) Since the plants, buildings, tanks and other equipment were not decontaminated and decommissioned prior to the commencement of study by NGRI and NEERI, the open areas around such structures could not be monitored by NGRI and NEERI during the present study. During decontamination and decommissioning, the area in and around these structures is likely to be contaminated. The quantum of this area is about 9 hectares.

7) With these considerations, the total contaminated area within UCIL premises amounts to 16 hectares. Considering an area of 16 hectares and an average depth of contamination of 2 m the total volume of contaminated soil to be remediated from UCIL premises is about 3,20,000 m^3.

8) The solar evaporation pond (SEP) and the secured landfill located outside UCIL premises cover an area of about 14 hectares. This area also needs to be

remediated. Assuming a depth of contamination of 2 m, the total volume of soil to be remediated in SEP area is about 2,80,000 m^3.

9) As stated earlier contamination (at) one location(s) co(u)ld be as deep as 8 m. A total volume of contaminated soil from such is assumed to be about 50,000 m^3.

10) The total volume of contaminated soil (within and outside UCIL premises) thus amounts to 6,50,000 m^3. Assuming a bulk density of 1.7 g/cm^3 of soil, the total quantum of contaminated soil requiring remediation amounts to 11,00,000 MT.

11) Monitoring of groundwater from the bore wells constructed by NGRI within UCIL premises and the existing wells around UCIL premises indicated that ground water in general is not contaminated due to seepage of contaminants from the UCIL dumps. However, isolated contamination in terms of pesticides was observed in five wells in the immediate vicinity of UCIL premises in the north-east and east direction. The source of contamination of these wells cannot be attributed to leaching of contaminants from the dumped waste and migration of aquifer, due to the fact that a thick (22 to 25 m) layer of clay is overlain on the aquifer. The contamination of these wells, was therefore, attributed to surface runoff from the dumps. The quantum of contaminated groundwater could not be estimated due to isolated nature of contamination.

As stated above, some of the conclusions (listed above) are extremely useful for articulation of strategies for dump sites. Those conclusions can be specifically listed as follows and credited to the Consortium team:

i. Lithology of the area confirmed the existence of black and yellow silty clay up to a depth of 22 to 25 m below ground level.

ii. Analyses of sub-surface soils from the suspected dump sites revealed that the contamination existed up to 2 m depth (except in one location where it was found to be 8 m deep).

iii. The Consortium team could not apparently work on several spots since the vegetation, buildings, tanks and other equipment were not decontaminated and decommissioned prior to commencement of the study. Even the open areas around such structures could not be monitored.

iv. It has been cautioned in the report that during decontamination and decommissioning, the areas in and around these structures is likely to be contaminated.

However, as mentioned earlier, some of the conclusions are not convincing because the data were not found in the final report: Those conclusions can be specifically listed as follows:

i) The ground water underneath dump areas has been found to be at a depth of about 25 to 32 m as depicted in Table 7 (page 36, Consortium, 2010). However, pages 28 and 29 (Consortium, 2010) placed the ground water table at various depths in the UCIL factory premises in the range 55 to 68 m except for well no. 2 which was shallow (9.5 m deep) based on the dug well survey. Interestingly, the Consortium (2010) final report documents yet another study conducted by NGRI, Hyderabad in the premises of UCIL, Bhopal, wherein reportedly " ..... the well hydrograph generated by NGRI indicated water level variation from 3.4 m to 23.37 m due to monsoon of 2008-09. The lowest variation of 3.4 m was observed in the shallow dug well outside the premises which may be a localized shallow aquifer. The remaining bore wells indicated similar behavior with a variation of about 9 to10 m, except for a well in the eastern part (23.37 m) which has very high abstraction (almost running for 24hrs)". Unfortunately, the Consortium study neither brings out these differences as the issue of concern nor does it flag the data gap and articulates a clear work plan for future further investigation – especially in the light of inconsistent data.

ii) As quoted above in bullet number 3, the clay has very low permeability of the order of $1x10^{-9}$ cm/s. It is true that typically clay has rather low permeability and hence acts as natural barrier between leachate and ground water present in deep aquifer. But, the value of $1x10^{-9}$ cm/s is alarmingly small value when compared with the realistic values (for example) of say $1x10^{-7}$ cm/s for very high quality compacted engineered clay liner installed underneath a landfill facility. Was the value of $1x10^{-9}$ cm/s measured in the field or was it a guess? What is the significance of this value in the light of the fact that the depth of ground water in the study conducted by Consortium and in the earlier studies varied significantly all over the place in UCIL premises?

iii) In this light, the tentative estimation of contaminated areas within the UCIL premises in Bhopal placed at about 16 hectares appears to be on much lower side. Since the exact area of the UCIL premises as well as cumulative area occupied by production plant, machinery, storage tanks as well as ware houses on the premises of UCIL is not known; a rough guess and estimate placed the premises area at 100 to 120 hectares and about two-third area of it occupied by buildings and other installations. As a result in addition to the 16 hectare contaminated area, 70 to 90 hectare area may also need serious decontamination. Thus, 80 to 100 hectare area within UCIL factory premises alone will have been brought under careful characterization, remediation and post remediation monitoring. Once MPPCB and/or (M/s. Ramkey Pvt. Ltd.) have finished removing the buildings, tanks and equipment; the area occupied by them will need environmental investigations based on the extent of contamination. The affected area will have to be remediated along with the 16 hectare area identified in this report. This is the least one could have concluded on the basis of the highlight of the results from field investigations depicted in the above mentioned 11 bullets.

In sum, the geophysical investigations as well as hydrological investigations conducted by the Consortium team have revealed certain important and critical facts about the subsurface strata and interaction of ground water with the dump sites. One of the major limitations of the site assessment exercise, as reported in the final report, stems from the fact that Consortium (2010) does not discuss the results obtained during this site assessment exercise as opposed to their observations of 1996 and the changes that have taken place on the site due to interventions of MPPCB (with the help of M/s. Ramkey Pvt. Ltd.) in terms of partially removing contamination and partially removing the vegetations from the premises. It would have been truly interesting and of relevance to the exercise of strategy articulation if Consortium (2010) could shed light on what was revealed to them in terms of natural decay, wash out due to surface run off and mobilization away from site as a result of more than 25 years of elapsed time.

Lastly, it deserves a special mention that the Consortium report did not critically discuss their findings related to solar evaporation pond (SEP), landfill site and the surroundings.

Is the proposed strategy for site remediation appropriate?

In a study of this kind, one expects clarity on following a comprehensive plan for dealing with the contaminated matrixes. This report identifies "land filling on site" as a viable option. Given this option, one would expect identification of location of on-site landfill, its geometry and capacity; keeping in consideration that many building components, fragments and debris generated as a result of decommissioning and dismantling of the 25-year junk machinery, process plants, reactors, over ground and underground storage tanks, warehouses, buildings and structures of manufacturing facilities including discarded, empty and partially filled containers of chemicals, solvents and products may also have to be placed into the secured landfill.

Where is such comprehensive listing of candidate materials that might have to be committed to the secured, engineered landfill and the plan for prioritization of the tasks and responsibilities to bring it into reality? In absence of any critical comment rooted into today's reality at the UCIL site in Bhopal, the suggestion of creating a secured landfill appears to be pre mature and/or generic.

The report identifies solidification of waste with 1:1 as the soil : binder proportion. The justification of using binder and the ratio of soil to binder has not been provided. It is well known that the presence of oil traces, solvents, heavy metals and several other constituents can potentially interfere with setting time and strength of the results produced during solidification and stabilization processes when cement is used as binder. It is entirely possible that the Consortium does not see the "treatability study" as an integral part of the assessment and strategy development activity and hence it was not addressed in the Consortium (2010) final report. But in that case, it would have been helpful to identify the "treatability study" as one of the important tasks in their articulated strategy.

Looking at the ground water table data and noting the fact that ground water rises to shallow levels as well as sinks to deep levels over different seasons and at different locations within the UCIL premises; it is not frankly clear that how one could make a rational argument favoring onsite landfill without addressing the varying depths of ground water in the premises.

In addition, the author has become curious about the ground water level data in Consortium final report, especially in the context of the ultra-low clay permeability

value of $1x10^{-9}$ cm/s (measured or estimated .... not clear). Is there any guarantee that water will not enter in the secured landfill? What will be the selection and elimination criteria for identifying land for development of secured engineered landfill within premises of UCIL, Bhopal?

There is no clear discussion on presence (or absence) of incinerable chemical wastes within premises of UCIL, Bhopal. If such wastes do exist, a clear plan for their storage, labeling, transportation and disposal will have to be developed. The final Consortium report should have either given such plan or clearly stated that this and similar tasks were deemed outside their perimeter and it would have been productive to include it in the strategy section for the benefit of implementation agency.

In sum, a detailed remediation plan along with the information gaps identified in the above paragraphs should have been included in the strategy section for the benefit of implementation agency. The overall report writing appears to be rather weak in terms of organization of facts, information and communication of results of various tasks undertaken during the site assessment exercise. As a result, even the available data and field verification results were not connected to the effort of strategy development. Similarly, as stated earlier, the results from several past studies were not used gainfully.

Therefore, the report in the present form first needs to be reorganized and rewritten to at least include and effectively communicate the results of work done by the Consortium. Second, there is a great need to compare results from past studies with the learning from the investigation undertaken by the Consortium. Third, the efforts should be made to identify the gaps of knowledge and left-over tasks in investigation need to be identified and undertaken as a separate study. Finally, a rigorous effort of connecting the findings of all the studies mentioned above will have to be undertaken so that the ground truth can be assessed in a more complete way (than what we know today based on the final report of Consortium) and develop a strategy for a remediation which is based on realistic understanding of the site and educated techno-economic evaluation of candidate technology for remediation becomes possible.

Summary

The author of this note has restricted his opinion to the facts and strategies presented in Consortium (2010). The final report of Consortium was studied carefully by the author and following four questions emerged in the mind:

1. Whether the pollutants were appropriately selected in the site assessment exercise?
2. What was considered important to be included in the site assessment exercise?
3. What was learnt from the site assessment activity?
4. Is the proposed strategy for site remediation appropriate?

The effort was made to search the answers for the above mentioned four questions based on the final report of Consortium and the past studies (whichever available). Those comments and concerns were articulated by the author and presented categorically along with the author's opinion in the preceding pages. Following are the salient points from those discussions:

a) The report from Consortium (2010) does not discuss the basis for their selection and elimination of the variety of chemicals consumed and used by UCIL at the Bhopal site. All the chemicals handled by the UCIL could have been deemed as "potential pollutants" and a careful exercise could have been performed to select the most critical ones based on the known information on the respective products, raw materials, solvents, byproducts and intermediates.

b) In all fairness, it must be mentioned here that no clear opinion can be expressed on the basis of the cryptic details on protocols and processes used in site assessment activity described in the Consortium report and in the light of the fact that no code or standard protocol was followed (or at least it was not reported in Consortium, 2010). In this context, it was all the more important to describe what was not done and why it was decided not to do it?

c) It is well known that typically clay has rather low permeability and hence acts as natural barrier between leachate and ground water present in deep aquifer. But, the value of $1x10^{-9}$ cm/s, as reported by Consortium (2010), is alarmingly small value when compared with the realistic typical value of (say) $1x10^{-7}$ cm/s, corresponding to very high quality compacted engineered clay liner installed underneath a landfill facility. Was the value of soil permeability (reported as $1x10^{-9}$ cm/s) measured in the field or was it guessed?

What is the significance of this permeability value in the light of the fact that the depth of ground water in the study conducted by Consortium and in the earlier studies varied significantly all over the place in UCIL premises? This information is critical for siting and designing secured engineered landfill facility on the premises of UCIL, Bhopal.

d) Dilapidated production plant buildings, tanks and other equipment have not yet been decontaminated and decommissioned on the factory premises. Unless they are decontaminated and decommissioned it would be difficult to undertake a task of remediation of contaminated sites around them. During decontamination and decommissioning of these structures and installations, areas in and around these structures is likely to be contaminated (Consortium, 2010).

e) The tentative estimation of contaminated areas within the UCIL premises in Bhopal has been placed in the Consortium report at about 16 hectares. In the opinion of author, it appears to be on much lower side. In addition to the 16 hectare contaminated area, 70 to 90 hectare area will also need serious decontamination which is currently occupied by production plant, machinery, storage tanks as well as warehouses on the premises of UCIL.

f) It deserves a special mention that the Consortium report did not critically discuss their findings related to solar evaporation pond (SEP), landfill site and the surroundings.

g) One of the major limitations of the site assessment exercise, as reported in the final report, stems from the fact that Consortium (2010) does not discuss the results obtained during this site assessment exercise as opposed to their observations of 1996 and the changes that have taken place on the site due to interventions of MPPCB (with the help of M/s. Ramkey Pvt. Ltd.) in terms of partially removing decontamination and partially removing the vegetations from the premises. It would have been truly interesting and of relevance to the exercise of strategy articulation if Consortium (2010) could shed light on what was revealed to them in terms of natural decay, wash out due to surface run off and mobilization away from site as a result of more than 25 years of elapsed time.

h) A detailed remediation plan along with the information gaps should have been included in the strategy section for the benefit of implementation agency. There is a room to improve Consortium (2010) final report in terms of organization of facts, information and communication of results of various tasks undertaken during the site assessment exercise. It is quite possible that many of the desirable data were collected by the Consortium team but neither were they presented in a logical and useful manner in the report; nor were they connected to the effort of strategy development. The results from several past studies were also not used gainfully.

Clearly, there is a lot to be included in the report in the present form before it will become useful to chart out further course of action for remediation of contamination at the UCIL site in Bhopal.

Following **three steps** are recommended in order to bring the report to a level so that it can be used for a meaningful articulation of strategy for remediation of site of UCIL, Bhopal and the adjoining areas:

Step 1: The Consortium report in the present form needs to be reorganized and rewritten to at least include and effectively communicate the results of work done by the Consortium. It should not be forgotten that there is a great need to compare the results from past studies with the learning from the investigation undertaken by the Consortium.

Step 2: The efforts should also be made to identify the gaps of knowledge and left-over tasks from the earlier studies including the investigation by Consortium. Those issues need to be identified and addressed under a separate study.

Step 3: A rigorous effort of connecting the findings of all the studies mentioned above will have to be undertaken so that the ground truth can be assessed in a more complete way (than what we know today based on the final report of Consortium). Based on the realistic understanding of the Bhopal site and educated techno-economic evaluation of candidate technologies, development of the credible strategy for remediation of the site will become possible.

3rd August, 2010
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Appendix A

Manufacture of a Carbamate Pesticide named Carbaryl (*i.e.* Sevin)

Raw Materials:

1. Phosgene - ($COCl_2$).
2. Monomethylamine (MMA) – (CH_3-NH_2).
3. Methyl Isocyanate (MIC)- ($CH_3N=C=O$)
4. Coke.
5. Chlorine gas (Cl_2).

Solvents:

6. Chloroform ($CHCl_3$).
7. Carbon tetrachloride (CCl_4).

Manufacturing Process

Phosgene also known as carbonyl chloride is manufactured by reacting chlorine with carbon monoxide. The chlorine for this reaction is brought to the plant in a tanker while carbon monoxide was produced from petroleum coke when it was made to react with oxygen. The UCIL had a facility to produce carbon monoxide.

The Monomethyl amine (MMA) was also brought in by a tanker, and was allowed to react with phosgene at around 30°C to 50°C in the presence of chloroform to produce methyl carbamoyl chloride (MCC) and hydrogen chloride gas. The process is called phosgenatation. The MMA and chlorine gas was brought in by tank truck from other parts of India and stored in tanks and used whenever MIC was needed to produce carbaryl (trade name: Sevin).

The methyl isocynate (MIC) is produced when Monomethylamine (MMA) is heated. The MIC was collected and stored in stainless steel tank while the remaining HCl, Chloroform were collected and recycled for use once again. This MIC is then reacted with 1-napthol in the presence of catalyst carbon tetra chloride (CCl_4) to

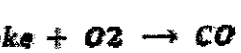
produce the main product Carbaryl/Sevin pesticide. Carbaryl was manufactured by the reaction of slight excess of α-naphthol with Methyl Isocyanate was gradually added upon stirring to an excess of alpha naphthol in carbon tetrachloride solvent at 60-80°C in presence of a catalyst. The reaction is exothermic. The yield of product was more than 95%. Data on the production of Sevin and MIC during 1977-84 are presented in **Table 1**.

Although Sevin was the major pesticide; smaller amounts of other carbamate pesticides were also manufactured using MIC. These were aldicarb (Temic) and butyl phenyl methylcarbamate and a formulation of Sevin-lindane was also made at UCIL.

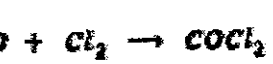
Production of Carbaryl/Sevin is a batch process. UCIL plant at Bhopal was actually designed to produce 5000 MTPA but they never came anywhere near this target. UCIL's production decreased from about 2500 MT in 1982 to approximately 1500 MT in 1983 and in 1984, even less than 1000 MT.

Reactions

1. Oxygen is allowed to pass over Coke bed, this results into limited oxidation of Coke to form Carbon monoxide gas (CO).



2. Carbon monoxide(CO) is allowed to reacts with Chlorine gas (Cl_2) to form Phosgene gas ($COCl_2$)

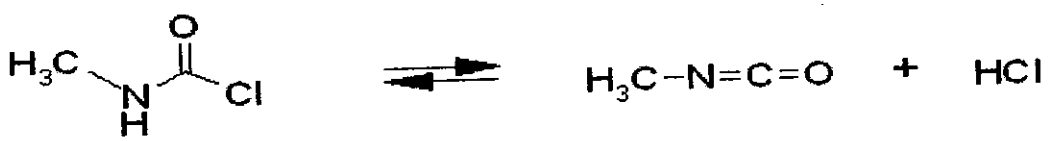


3. Monomethylamine (MMC) reacts with Phosgene to produce an intermediate Methyl carbamoyl chloride (MCC) and hydrochloric acid in the presence of Chloroform.($CHCl_3$). The reaction temperature is maintained 30°C to 50°C.

MCC

(Phosgene) (Monomethyl amine) (Methyl Carbamoyl Chloride)

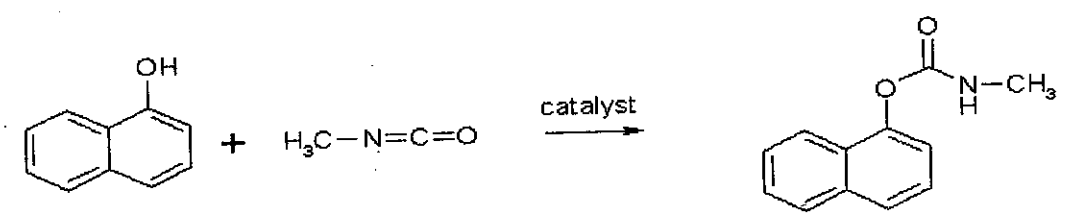
4. This MCC is then allowed to condensed to produce Methyl Isocynate (MIC)



MCC

(Methyl Isocynate)

5. This MIC is then heated in the presence of catalyst Carbon tetrachloride (CCl_4) with a-napthanol to give Carbaryl / Savin.



1-naphthol MIC carbaryl

(References: Cremlyn, 1980 and Kamrin, 1997)

Physical properties of materials involved

Table A1 Physical properties of carbaryl, MIC and intermediates manufactured at UCIL, Bhopal.

Properties	Units	Phosgene	Methyl Isocynate	Monomethylamine	Carbaryl
Physical State		Gaseous	Liquid	Gaseous	Solid
Molar mass	g/mol	98.92	57.1	31.06	201.22
Appearance		Colorless	Colorless	Colorless	Colorless Crystal
Density	g/cm^3	1.432 (at 0°C)	0.923 (at 23°C)	0.902 (at -15°C)	1.2 (at 25°C)
Melting Point	°C	-118 (at NTP)	-45 (at NTP)	-94 (at NTP)	142 (at NTP)
Boiling Point	°C	8.3	39.5	-6	Decomposes before boiling
Solubility	(Water)	Hydrolysis	Extremely Soluble	Slightly	Slightly
Solubility	(General)	Benzene, Toluene, Acetic acid	NA	Organic Solvents	Organic Solvents
Flash Point	°C	No	-7	8	193-202
Toxicity		High	High	slightly	High
TLV	ppm	0.1	0.02	NA	100 mg/kg
Auto ignation Temp	°C	NA	534	NA	NA

(References: Cremlyn, 1980 and Kamrin, 1997)

Appendix B

Manufacture of the Aldicarb Pesticide (*i.e.* Temik)

1. Aldicarb :

I. Introduction

Aldicarb is also called as aldicarbe with Trade names include Temik, ENT 27093, OMS 771. It is a pesticide of Carbamate class functional group. It is an extremely toxic, systemic enzyme, used to control mites, nematodes and aphids. It is directly applied to soil and widely used in India on Cotton, peanut and soyabean crops.

II. Manufacturing Process

When Chemicals containing Carbamate reacts with Oximes, aldicarbs produced. Aldicarb prepared from 2-methylpropene.

$$(CH_3)_2C = CH_2 + NOCl \longrightarrow ClC(CH_3)_2CH = NOH$$

(2-methylpropene)

$$ClC(CH_3)_2CH = NOH + CH_3SNa \longrightarrow CH_3SC(CH_3)_2CH = NOH$$

$$CH_3SC(CH_3)_2CH = NOH + COCl_2 \longrightarrow CH_3SC(CH_3)_2CH = NOCOCl$$

(phosgene)

$$CH_3SC(CH_3)_2CH = NOCOCl + CH_3NH_2 \longrightarrow CH_3C(CH_3)_2 - CH = NOCONHCH_3 + HCl$$

.....(aldicarb)

III. Physical Properties

Aldicarb is white crystalline solid. It is not compatible with alkaline materials and is noncorrosive to metals and plastics.

IUPAC Name – 2-methyl-2-(methylthio)propionaldehyde O-methylcarbamoyloxime.

Table B1 Physical properties of pesticide aldicarb

Properties	Units	aldicarb
CAS no.		116-06-3
Physical State		Crystalline solid
Molar mass	gm/mol	190.27
Melting Point	°C	100
Boiling Point	°C	Decomposes before boiling
Solubility	(Water) (mg/L)	6000 (at 25°C)
Solubility	(General)	Organic Solvents
Vapor Pressure	mPa	13 (at 20°C)
Adsorption Coef.		30
Appearance		White Crystals
Density	gm/cm^3	1.195 (at 25°C)

IV. Exposure Guidelines

Acceptable Daily Intake – 0.003 mg/kg/day

Max. Contaminant Level – 0.003 mg/L

Reference Dose – 0.001 mg/kg/day

Permissible Exposure Level – NA

(References: Cremlyn, 1980 and Kamrin, 1997)

Appendix C

Manufacture of the γ- hexachlorocyclohexane Pesticide (*i.e.* Lindane)

γ- hexachlorocyclohexane (γ-HCH)

I. Introduction

This hexachlorocyclohexane (HCH) or earlier also termed as Benzenehexachloride (BCH) was discovered in France in 1942. HCH was obtained in eight different forms of isomers of which five are actually found in crude product. Out of these eight isomers only γ-hexachlorocyclohexane (γ-HCH) or trade name is Lindane has powerful insecticide properties.

II. Manufacturing Process

It can be manufactured by treatment of benzene with chlorine under the influence of ultraviolet light without catalysts. In this reaction crude HCH is formed which contains five isomers out of which the most useful isomer is γ-HCH which contributes only 13% of the total crude formed. So this crude product is purified by extraction with a hot methanol solvent and it is followed by fractional re-crystallization to produce pure γ-HCH or lindane (99%).

$$C_6H_6 + 3\,Cl_2 \longrightarrow Isomers\ of\ HCH\ (70\%\ \alpha - HCH, 6\%\ \beta - HCH, 13\%\ \gamma - HCH, 6\%\ \delta - HCH\ and\ traces\ of\ \varepsilon - HCH)$$

$$Isomers\ of\ HCH + methanol \longrightarrow 99\%\ pure\ \gamma - HCH + mixture\ of\ other\ isomers$$

(Lindane)

III. Physical properties

IUPAC Name – gemma-1,2,3,4,5,6-hexachlorocyclohexane

Table C1 Physical properties of pesticide γ -hexachlorocyclohexane.

Properties	Units	γ -HCH
CAS no.		58-89-9
Physical State		Liquid
Molar mass	gm/mol	290.85
Melting Point	°C	113
Solubility	(Water) (mg/L)	7.3 (at 25°C)
Solubility	(General)	Organic solvents
Vapor Pressure	mPa	5.6 (at 20°C)
Adsorption Coef.		1100
Half life	hrs.	18

IV. Exposure Guidelines

Acceptable Daily Intake – 0.008 mg/kg/day

Max. Contaminant Level – 0.0002 mg/L

Reference Dose – 0.0003 mg/kg/day

Permissible Exposure Level – 0.5 mg/m3 (8-hour)

(References: Cremlyn, 1980 and Kamrin, 1997)

Director, IISE,
Bangalore.

Comments on the Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal, Final Report, NEERI 2010

1) Physico-chemical properties of soils

Soil organic matter (SOM) is often considered the dominant sorptive phase for organic contaminants and pesticides in soil–water systems (Sheng et al., 2001). Lafleur (1976) confirmed the overriding restraint imposed by organic matter content on cabaryl desorption and movement in soil columns. Sharom et al., (1980) and Jana and Das (1997) indicate that soil organic matter is a contributor to sequestering carbaryl in soils; these workers observed that a soil's resistance to water leaching of carbaryl and its sorption capacity for this pesticide increases with the soil organic content. Data reported in Table 28 (NEERI 2010) reports unusually large values of organic carbon content (3 to 12 %) for the surface and sub-surface (30 cm depth) black soil samples in UCIL plant premises. The soil in the UCIL campus is formed by in-situ weathering of basalt rock. Typically organic matter of < 2 % is obtained for such residually derived black soils (Bhattacharyya et al., 2007). Despite the high organic content, a poor correlation emerges between SOM and carbaryl content for the surface and sub-surface soil samples in UCIL premises (Figure 1, data extracted from Tables 20 and 28, NEERI 2010). Based on the earlier reported studies on soil organic matter and pesticide retention, the amount of pesticide (carbaryl) retention was expected to positively correlate with soil organic content in Figure 1.

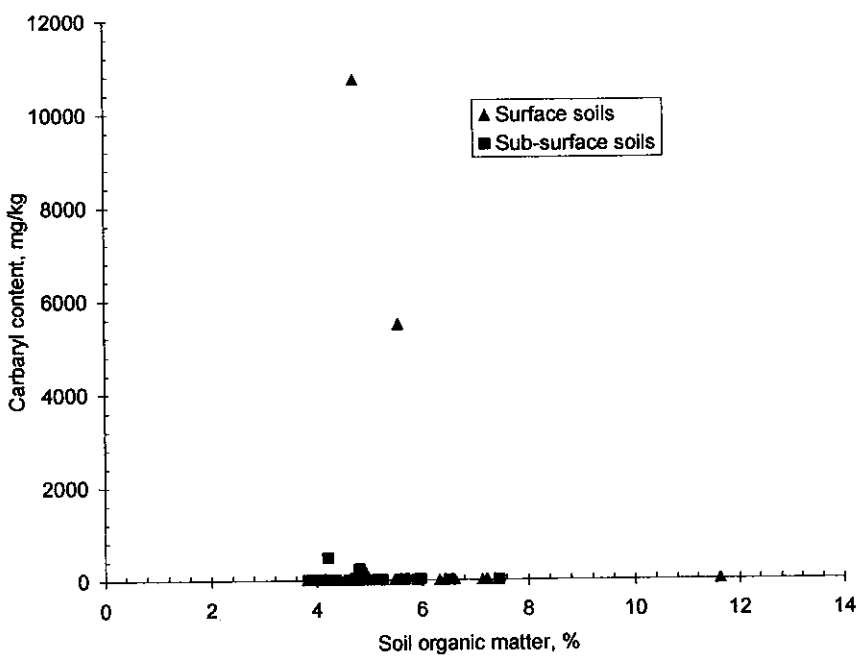


Figure 1: Variation of carbaryl content as function of soil organic content for soils in UCIL premises (data from Tables 20 and 28, NEERI 2010)

The unusually high range of SOM (3 to 12 %) cannot possibly be ascribed to soil contamination by organic chemicals as similar range of SOM (Table 17, NEERI 2010) is reported for the uncontaminated upstream and downstream soil samples (Tables 11 to 16, NEERI 2010).

Besides organic matter, the soil clay content also contributes to carbaryl sorption. Sheng et al. (2001) observed that potassium saturated smectite is a better sorbent for carbaryl than soil organic matter (SOM); the distribution coefficient (Kd) for carbaryl was five times greater in clay than for SOM rich soil. De Oliveira et al. (2005) observed that the amount of carbaryl sorbed was strongly dependent on the presence of exchangeable magnesium and sodium ions that interact strongly with the partial negative charge of the double-bonded oxygen atom of the insecticide. A positive correlation between carbaryl sorption with surface area, cation exchange capacity (CEC), and free Al_2O_3 (alumina) content in Ultisol (red clay soils) and Inceptisol (poorly weathered soils) soils was made by Jana and Das (1997). The residually derived black soils occurring in the UCIL premises are expected to dominate in smectite clay group (Rao and Venkatesh, 2010). Both clay and organic matter encountered in the top soil layer have strong affinity for semi-volatile/volatile organics resulting in the absence of these contaminants in the deeper soil stratum (> 2 m depth, Tables 29-33, NEERI 2010) and in the groundwater (Table 34, NEERI 2010) of the UCIL premises.

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a. Experimental procedures used to determine the organic carbon content of the contaminated surface and sub-surface soils in the UCIL premises.
b. Information on the chemical composition of the organic content of the surface and sub-surface soils.
c. Explanation for the unusually high organic content of the surface and sub-surface soil in UCIL premises.
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e. Clarification if the soil samples were dried by heating before extraction of organic chemicals (volatile and semi-volatile organics). If yes, would the drying temperature have affected the analyte amounts determined.
f. What organic solvents were used in the extraction of volatile organics, semi-volatile organics and pesticides from the soil and groundwater samples. Were Initial Demonstration of Efficiency as prescribed in US EPA 3500 C performed with the soil and groundwater samples
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3) References

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Sudhakar Rao
Department of Civil Engineering, IISc

Comments on NEERI report on Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/S Union Carbide India Ltd, Bhopal, June 2010

Centre for Science and Environment, New Delhi

1. **Study corroborates our analysis done in October-November, 2009 that the UCIL site is heavy contaminated with chlorinated benzene compounds, organochlorine pesticides, carbmate pesticides (Carbaryl and Aldicarb. It also confirms that this contamination has nothing to do with the gas accident, but is caused by UCC/UCIL dumping and disposing off waste indiscriminately on the site. All pesticides found in the soil and water samples were manufactured at the site and heavy metals, especially chromium and mercury were part of the process of manufacture.**
2. **Our study was done in conjunction with the Central Pollution Control Board (CPCB) and soil samples were jointly picked-up from the site. The CPCB analysis, though not yet made public, corroborates our analysis. Both the studies show very similar trends and pattern on the presence of various contaminants that were tested.**
3. **It is important to point that both CSE and CPCB study were limited in scale and we had recommended detailed investigation of the site before designing the decontamination plan.**
4. However, the investigation as reported by NEERI into the extent of contamination is still incomplete. The NEERI report accepts that large parts of the site are covered with thorny bushes, roads and concrete structures and water bodies. These sites have not been investigated through geophysical methods for identification of waste dumps or tested for contamination. The study, according to the report, was restricted to a relatively limited area.
5. NEERI has based its findings on the extent of contamination on 90 soil samples collected at different depths from the 5 boreholes. In addition 27 surface and subsurface soil samples were also checked from inside the plant and 24 samples from outside the plan and 30 samples from areas adjacent to the plant.

6. It finds:

   - Aldicarb not detected in any surface soil samples, but found in subsurface soil samples – shows either a dumpsite or contamination of soil.
   - Carbaryl detected in most of surface and subsurface soils, at varying concentration – from 0.038 mg/kg to as much as 10729 mg/kg.
   - 1-naphthol (alpha-naphthol) detected in most of the surface and subsurface soil samples throughout plant with a varying concentration from 0.511 to as much as 1460 mg/kg.

- Three isomers of HCH detected in soil samples.
- Dichlorobenzene was detected in few subsurface samples with concentration ranging up to 0.165 mg/kg. NEERI has not tested 1,3 dichlorobenzene, 1,4 dichlorobenzene and 1,2,3 trichlorobenzene all of which were found in our study.
- Mercury found in most surface and subsurface soil samples, up to 4.17 mg/kg

7. But in spite of finding such widespread contamination, the report concludes that "waste disposal area as reported by NEERI in its report of 1996 (done for UCIL as clients) was 7 ha." In addition to this, contamination has *spread to open areas* (emphasis ours) within the plant premises possibly due to surface runoff.
8. All this makes NEERI suggest that the area requiring containment is limited. "Moreover, the open areas in and around the abandoned manufacturing units, sheds, buildings are likely to be contaminated during the decontamination and decommissioning activities to be taken by BGTRRD through suitable contractor. The quantum of such areas is estimated to be 9 ha. Thus the total contaminated area within UCIL premises would require remediation is about 16 ha (9 ha+ 7 ha that NEERI had indentified for its clients UCIL in 1996)
9. This is when, earlier in the report, it has been made clear that the entire site could not be inspected because of lack of access. Furthermore, the samples collected from across the site, at random points, had high levels of toxins. It is therefore, clear that the entire site would need to be re-surveyed and samples collected to check the scale of contamination. Once this is done, the plan for decommissioning and decontamination can be finalized.
10. The report also clearly underestimates the extent of potential groundwater contamination and its spread in neighbouring areas.
11. It is important to recall that in its 1996 study NEERI had not found any groundwater contamination. However, all subsequent studies, done by government and non-government organistions, have found groundwater contamination. CPCB collected groundwater samples in October-November 2009 and found a-HCH, g-HCH and d-HCH at a number of places in varying concentrations. A large number of the above compounds along with volatile organic compounds were detected in the groundwater in Indira Nagar, which is situated at a distance of 2.4 km from the factory site.
12. CSE study had also found contamination of all groundwater samples with the same chemicals found in the soil within the UCIL premises. The groundwater sample collected from the hand pump near Chaurasia Samaj Mandir in Shiv Nagar was the most contaminated. It has highest concentration of carbaryl, lindane and mercury. This place is more than 3 km away from the UCIL factory.
13. According to the report, the National Geophysical Research Institute (NGRI)

re-visited its previous survey of 1996 to estimate the geophysical conditions on the site.

14. It's study showed that the subsurface in the area comprises the following: black soil, followed by silty soil, fractured sand stone and hard sandstone as bedrock. The combined thickness of black soil and silty soil was inferred to be 15.3 to 58.9m and hard sandstone to be 16.9. to 69.6 below ground level. In other words, as in most areas of the country, the soil profile is not uniform – it is well understood in naturally formed geophysical structures, there will be variations. In this case as well, the subsurface area spread over 35 ha areas, has silty soil and fractured layers at varying depths. It cannot be assumed that the entire area is impervious and will not result in any contamination.
15. The well inventory studied by NGRI confirms this pattern, found across the Vindhyan formations and valleys, occupied by alluvium and basalt. The borewells in the site have water at depth of as little as 9.5 metres. The study also finds that shallow groundwater exists in certain parts. The well hydrograph indicated a water level variation from 3.4 m to 23.37 m.
16. NGRI has based its conclusions that the aquifer is confined, only on the drilling of boreholes at just five sites and an exiting borewell near the main entrance. This is completely inadequate and in fact, this particularly finding is not confirmed by the reports analysis itself.
17. The HERT technology (high resolution electrical resistivity tomography) was used in the current study. This technology is used to identify possible dump areas, using resistivity profiling. This technology is not used to decide on the geophysical characteristics of the land or to determine if the entire area is impervious.
18. The use of HERT has only established what was earlier known that there are three dumpsites – Site I, North of the formulation plant, Site III, South of the Storage tank and police post and Site V, between the neutralization tank and the solar evaporation pond. This does not mean that it has been able to establish that the soil is contaminated or not at other sites.
19. The report finds that the groundwater flow direction is in the southeast direction. It also reports that aquifer conditions are variable and may change over time.
20. The sampling of soil and groundwater samples was found in three periods (April 2009, January 2010 and May 2010). It must be noted that these are not post-monsoon period and therefore, the study has not been able to study the runoff and changes in hydrology as well as possible contamination. In addition, the report admits that confirmatory sampling of boreholes was not possible. The well inventory was carried out by NGRI in November 2008 calling it as post-monsoon monsoon monitoring, but this certainly does not qualify as post-monsoon study.
21. In fact, just comparing table 7 with table 29, 30, 31, 33, it is evident that contamination with toxins like carbaryl and HCH isomers has been detected

at 3 metres depth. Therefore, the conclusion of the report, "the depth wise review of individual boreholes in terms of distribution of various contaminants within UCIL premises, indicate that maximum depth of contamination at present is restricted to 2 m."

22. The report contradicts its own findings that the subsurface area consists of black soil, with varying layers of silty soil, fractured layers and clay and hard sandstone. It also defies all knowledge about geology and hydrology to suggest that the entire area of just the factory premises has a unique geology, not found anywhere else, where there is just one clay and hard sandstone layer, which was built, so that the contamination would not permeate into the sub-soil and water level. In other words, UCC and UCIL, when they built the factory, chose this site, because they could dump hazardous material in the open, knowing that there was a clay layer, which would 'protect' them from any spread and seepage of contaminants.

23. The data on groundwater contamination in adjoining areas of the UCC/UCIL factory is in variance with tests done by CSE. While the study has confirmed and corroborated our study, which showed high levels of contamination in the factory compound – finding the same chemicals were had found at even higher levels in some cases – its suggests that this contamination has not spread. It is also interesting that the study has found one contaminant – chromium, which was used in UCC/UCIL, but not others. This requires more extensive research on the aquifer movements in and around the UCC/UCIL factory, so that the extent of contamination can be ascertained and the need for draining aquifers for remediation can be known.

24. Before designing groundwater remediation it is very important to prepare a aquifer profile which has not been done in the current study. Groundwater remediation is a very difficult exercise and can only be designed once the level of contamination in the entire area has been studied. Merely pumping out water, cleaning it and re-pumping it back into the aquifer will not work.

Remediation of Waste in UCIL, Bhopal
A comment on NEERI's report, 2010

1. The parameters tested by NEERI in soil and water are Aldicarb, Carbaryl, α-naphthol, HCH isomers, dichlorobenzene, and heavy metals. However, NEERI's earlier report of 1996 had identified Naphthalene as a major contaminant in the dumps, while the reports by GTZ and MPPCB have further identified aldrin, heptachlor, methoxychlor, endosulfan, dieldrin, endrin, tri-chlorobenzene isomers, and organic solvents. It is not clear why these parameters were not tested. Particularly in view of the fact that the investigation by CSE in 2009 had reported the presence of chlorinated benzene compounds in both soil and water.

2. The extent of soil contamination reported by NEERI in 1996 was three sites of 0.3 hectares (depth 60cm), 0.32 hectares (depth 30 cm), and 0.08 hectares (depth 30cm). At an assumed bulk density of 1.7 gm/cc this amounts to about 5,100 MT. But the later GTZ study estimated 25,000 MT of contaminated solid waste, with the University of Lueneburg study increasing that figure to 27,600 MT. And NEERI's 2010 study comes up with the much larger estimate of about 30 hectares contaminated up to a depth of 2 m and another small patch with >4 m depth, and a total quantity of 11,00,000 MT. It should be noted that M/s Ramkey under MPPCB had removed about 358 MT of waste before this study was carried out. Hence, there are no clear arguments presented about why the waste has spread both in volume as well as location.

3. Ground water contamination is reported to be insignificant within the UCIL premises by NEERI in 2010. Outside UCIL there are 3 wells contaminated with aldicarb and 4 with dichlorobenzene, with no presence of Mercury being reported. These are unacceptable results in view of the fact that, a year earlier, the CSE study had found that "Groundwater samples collected from colonies around the UCIL factory were contaminated with chlorinated benzene compounds and organochlorine pesticides". Even earlier a study by PSI, Dehradoon had found extensive Mercury contamination in wells outside the UCIL premises, particularly in the southern and south-eastern directions.

4. Consequently, the remediation measures proposed for the contaminated soil – ex-situ, on-site treatment (method not specified) and disposal through incineration and in secure landfills within the UCIL premises) – does not take into account the potential quantum of waste (there were no bores drilled into the third and deeper site) as well as the security of the landfill – the HDP liners of the earlier one are reported to be removed or damaged. Nor does it factor in the expense of securely covering the landfill and constantly monitoring the periphery and groundwater for leachates.

5. The proposed remediation for water (pump and treat with activated carbon) is also flawed because there is no precise estimate of the quantum of groundwater that has been contaminated as well as the degree to which the contamination has spread in linked aquifers. The proposal to incinerate the wastes at a TSDF is also contrary to international practice because it only contributes to a phase change in pollutants – especially the extremely toxic organochlorines.

Dunu Roy
Hazards Centre
August 2010

From: **virthagiri tv** <drtvgiri@rediffmail.com>
Date: Tue, Aug 10, 2010 at 6:18 PM
Subject:
To: jairam54@gmail.com
Cc: rameshdwarka@gmail.com

Dear Sir,

Ref: Your Letter dated 15th July 2010

Thank you for giving me an opportunity to go through the NEERI report on decontamination and remediation of Union Carbide plant site in Bhopal.
The report given is self explanatory and it is appreciated.
But the methods given for remediation are not clear. The correct treatment methods for each contaminant should be given. The estimated cost for soil remediation is found to be very high and is not justified. After specifying the appropriate treatment methods the cost analysis should be made and justified.
The cheaper and economical methods for soil remediation may be adopted. I will be very happy to offer more suggestions if required.
Thanking you

With Best Regards
Dr.T.VIRUTHAGIRI
Professor and Head
Department of Chemical Engineering
Annamalai University
Annamalai Nagar – 608002
Phone: 91-9443044503

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निदेशक

Prof. Surendra Prasad, F.N.A., F.A.Sc., F.N.A.E.,
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NO: IITD/D/L-1
Date: 4.8.2010

Hon'ble Shri Jairam Ramesh ji ,

This has reference to your letter No. 7(161)/2004-HSMD (Part-II) dated 13th July, 2010 inviting our comments on the Reports submitted by NEERI, NGRI and IICT on decontamination and remediation of the Union Carbide plant site in Bhopal. I had referred the report to a team of Professors who are experts in Environmental Science & Engineering. The comments of the team (led by Prof. T.R. Srikrishnan) are enclosed for your kind information. I hope these comments will be useful to you. We will be happy to provide any additional help that may be necessary.

With best regards,

Yours sincerely,

(Surendra Prasad)

Encl: a/a.

Shri Jairam Ramesh
Hon'ble Minister of State for
Environment & Forests
Govt. of India
New Delhi–110 003.

Office of the Minister of State For Environment & Forests

JS(RG)

DD (SM)

248

Comments on the report submitted by NEERI and NGRI titled "Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal.

NEERI, in association with NGRI has carried out an extensive evaluation of the UCIL premises at Bhopal in order to assess the extent of contamination of the soil and groundwater with the hazardous chemicals which were raw materials/intermediates/final products of the erstwhile UCIL, Bhopal.

The results of the hydro-geological investigations as well as soil and water analysis carried out are given in detail. The conclusions arrived at and the short term as well as long term remedial measures proposed appear to be sound and in tune with the field data generated. However, we have a few comments to make, which are as follows:

1. We agree with the comment on page 1 that '....contamination of the soil and groundwater in and around UCIL premises is solely due to dumping of abovementioned wastes during 1969 to 1984 and MIC gas tragedy has no relevance to it". But the gas tragedy had resulted in an abrupt shut-down of the entire facility and the inventory of chemical intermediates as well as final products needs to be accounted for. Especially, during the decommissioning of the plant and machinery as proposed in the report, the possibility of some of these chemicals being present at the site has to be made clear to those involved in the plant dismantling. Especially because some of the chemicals are extremely toxic.
2. Another possibility is to do a mass balance of the pollutants, accounting for the initial amount, estimated presence in the soil and groundwater, and escaped amount in order to understand possible fate of the unaccounted amount of the contaminants.
3. From the data presented, it is clear that the solar evaporation ponds outside the UCIL plant site as well as the defunct landfill are also contaminated. It is indeed a lucky break that the subsoil is clayey and the highly toxic chemicals have not penetrated beyond 2 meters, with the groundwater table located at a comfortable 25 meters. However, this potentially dangerous situation should not be allowed to continue. While the soil penetration may be prevented by the clayey subsoil, surface run-off is a very real possibility. The ex-situ on-site

remediation recommended in the report should be initiated at the earliest. Since this will be a long-drawn exercise, measures should be put in place to prevent any surface run-off from these contaminated sites joining nearby surface waters.

4. The exact treatment technique for the contaminated soil has not been mentioned in the report. It is mentioned that after appropriate treatment, the soil may be dumped in a secured landfill.

   Perhaps it may be worth thinking about constructing a modern incineration facility some where near by, burn off the waste at the highest possible Destruction and Removal Efficiency (DRE) as per the standards for Hazardous waste treatment. Say, a DRE > 99.9999%. Then it is possible to put back the waste to the excavated site itself. Or, dump it in a secured landfill made at the excavated site itself if the DRE achieved is less than that.

5. The study has reported that there is no contamination of groundwater beyond the UCIL premises. This observation could be supported with the transport properties (using laboratory tests) of the pollutants in the soil media, as a confirmatory measure.

6. A confirmatory test must be performed for level of contamination in the ground water. Even if the bore wells are damaged/ broken, a new bore in a representative location could have been made in order to confirm the observations. It is important to understand the change in concentrations with respect to time, for establishing the direction and the rate of migration of pollutants.

7. The data presented shows that the groundwater table has not been affected by the toxic chemicals. In such a scenario, we fail to understand the recommendation for 'pump and treat system' for the groundwater. What will you treat the water for and which water will you treat? Rather, no more boring should be allowed at the contaminated site since these are potential entry points for those contaminants which are otherwise kept away by the non-porous natural soil layer. The damage caused to the sampling bore wells as detailed in the report, highlights this point.

Comments on the Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal, Final Report, NEERI 2010

1) Physico-chemical properties of soils

Soil organic matter (SOM) is often considered the dominant sorptive phase for organic contaminants and pesticides in soil–water systems (Sheng et al., 2001). Lafleur (1976) confirmed the overriding restraint imposed by organic matter content on cabaryl desorption and movement in soil columns. Sharom et al., (1980) and Jana and Das (1997) indicate that soil organic matter is a contributor to sequestering carbaryl in soils; these workers observed that a soil's resistance to water leaching of carbaryl and its sorption capacity for this pesticide increases with the soil organic content. Data reported in Table 28 (NEERI 2010) reports unusually large values of organic carbon content (3 to 12 %) for the surface and sub-surface (30 cm depth) black soil samples in UCIL plant premises. The soil in the UCIL campus is formed by in-situ weathering of basalt rock. Typically organic matter of < 2 % is obtained for such residually derived black soils (Bhattacharyya et al., 2007). Despite the high organic content, a poor correlation emerges between SOM and carbaryl content for the surface and sub-surface soil samples in UCIL premises (Figure 1, data extracted from Tables 20 and 28, NEERI 2010). Based on the earlier reported studies on soil organic matter and pesticide retention, the amount of pesticide (carbaryl) retention was expected to positively correlate with soil organic content in Figure 1.

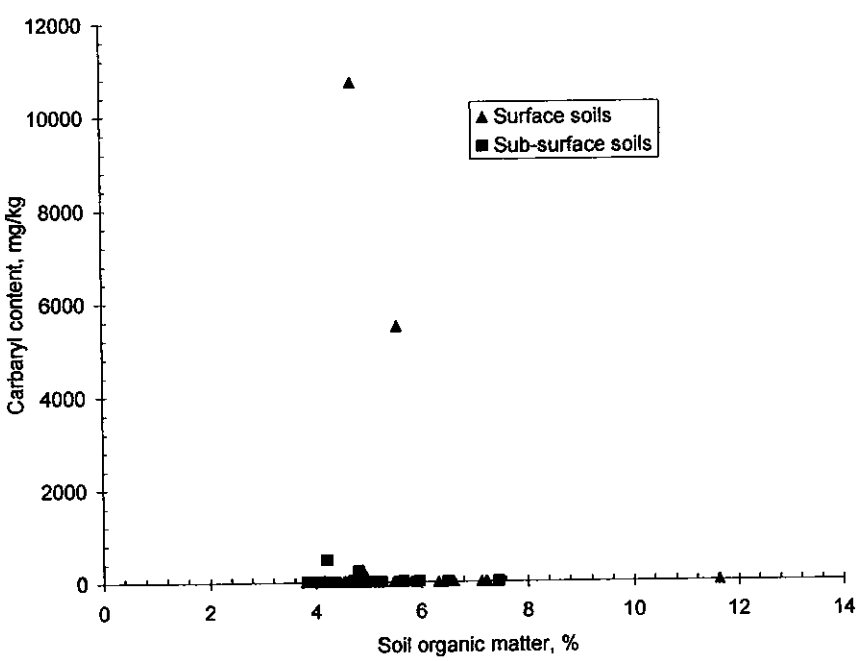

Figure 1: Variation of carbaryl content as function of soil organic content for soils in UCIL premises (data from Tables 20 and 28, NEERI 2010)

The unusually high range of SOM (3 to 12 %) cannot possibly be ascribed to soil contamination by organic chemicals as similar range of SOM (Table 17, NEERI 2010) is reported for the uncontaminated upstream and downstream soil samples (Tables 11 to 16, NEERI 2010).

Besides organic matter, the soil clay content also contributes to carbaryl sorption. Sheng et al. (2001) observed that potassium saturated smectite is a better sorbent for carbaryl than soil organic matter (SOM); the distribution coefficient (Kd) for carbaryl was five times greater in clay than for SOM rich soil. De Oliveira et al. (2005) observed that the amount of carbaryl sorbed was strongly dependent on the presence of exchangeable magnesium and sodium ions that interact strongly with the partial negative charge of the double-bonded oxygen atom of the insecticide. A positive correlation between carbaryl sorption with surface area, cation exchange capacity (CEC), and free Al_2O_3 (alumina) content in Ultisol (red clay soils) and Inceptisol (poorly weathered soils) soils was made by Jana and Das (1997). The residually derived black soils occurring in the UCIL premises are expected to dominate in smectite clay group (Rao and Venkatesh, 2010). Both clay and organic matter encountered in the top soil layer have strong affinity for semi-volatile/volatile organics resulting in the absence of these contaminants in the deeper soil stratum (> 2 m depth, Tables 29-33, NEERI 2010) and in the groundwater (Table 34, NEERI 2010) of the UCIL premises.

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e. Clarification if the soil samples were dried by heating before extraction of organic chemicals (volatile and semi-volatile organics). If yes, would the drying temperature have affected the analyte amounts determined.
f. What organic solvents were used in the extraction of volatile organics, semi-volatile organics and pesticides from the soil and groundwater samples. Were Initial Demonstration of Efficiency as prescribed in US EPA 3500 C performed with the soil and groundwater samples
g. Suggest that appropriate leachability and modeling studies be performed with contaminated surface and sub-surface soils from UCIL premises to aid in predicting the time-scales for eventual migration of the contaminants into the aquifer for a scenario where fraction of contaminated top soil layer escapes being securely disposed or remediated.

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Sudhakar Rao
Department of Civil Engineering, IISc

Dear Sir

This is in response to your letter to our Director, Prof.Balaram my comments regarding the report - Assessment and Remediation of Hazardous...
Please find below the comments for your information and consideration:

1. Bioremediation could be an effective approach to remove the contaminants from soil and water. For example studies have shown certain species of algae have the tendency to uptake hazardous contaminants and convert them to inert substance. Similarly proven fungi species can be used to decontaminate the soil. Creating landfill of contaminated soil is not a viable approach.

2. Decontaminating well water through bioremediation than sealing the contaminated well. Sealing will not sove the problem unless measures are taken to reduce the effectiveness of the carcinogens in the system.

3. Barricading the entire area and planting of select species of flora (tree sapling and shrubs) would also help in decontamination process.

4. Pollutants resident in the surroundings (outside the factory premises) need to be addressed - especially accumulation of Carcinogenic compounds in the surroundings.

thankyou

sincerely

Dr.T.V.Ramachandra
Centre for Ecological Sciences
Indian Institute of Science
Bangalore.

The report appears to be a comprehensive account of what has caused the contamination, to what extent the contamination has damaged the soil and ground water within the UCIL area, and what steps need to be taken to clean up. It is good to know from the data that the contamination is more or less contained within the UCIL premises. It is also appropriate that the report highlights on page 1 that the contamination has nothing to do with the MIC leak. I hope that the recommendations for the cleanup of the contaminated site and groundwater would be taken up in the neare future.

I have a few observations which are listed below:

Executive summary (penultimate para), and penultimate para on page 80: these two paragraphs should clearly state that the capital cost for pump and treat unit and operating costs refer to the treatment of groundwater at UCIL premises.

page 5: the maximum sevin content in dump was recorded as high as 520003 mg/kg. Why is it so high?

page 40: I find it surprising that while carrying out such a sensitive study these borewells were not secured!. As a result, they "were found to be broken, tampered and filled with unknown materials."

page 52 (and later): It would be better to specify which isomer of dichlorobenzene is referred to.

page 56 :why surface organic carbon in S-15 is more than double compared to other samples? There is no contaminant listed in the earlier tables.

Prof. Uday Maitra
Dept. of Organic Chemistry
IISE, Bangalore

Observations on NEERI/NGRI reports

1. NEERI report shows that the contaminants are limited to 2m of soil and that the aquifer within the UCIL plant premises is not contaminated. This is observed in the borehole data. As natural recharge in the area is about 40-170 mm/yr, it is understandable, unless there are deep fractures in the premises. Total area contaminated soil within plant premises is found as 16 hectors.

2. Outside plant area, near solar evaporation ponds and secured landfill areas, area of soil contamination is assessed as 14 hectors. The contaminants are assumed to be limited to the depth of 2m. The depth of contaminated soil has been assumed, it has not been investigated by boreholes/ geophysical surveys, as was done within the plant premises for estimating soil and aquifer contaminations.

3. Waste dump sites have been located using geophysical surveys. Under a dump site, (III in NGRI report where dumps were located upto depth of 8m), leachates have been suspected up to depths of 14m. Generation of leachates and their movement in unsaturated zone is not investigated.

4. Groundwater samples in 5 sites outside the plant show contaminations, three sites being near the boundary of the plant premises. It is stated that in these three sites aquifer contamination occurs due to surface runoff as surface waters are collected near wells in rainy seasons. It is suggested in the NEERI report that the groundwater should be pumped and treated. The volume of contaminated groundwater is not estimated.

5. Issues pointed out in items (2), (3) and (4) need to be investigated and quantified. This can be done using boreholes and geophysical surveys and geochemical modeling in unsaturated/saturated zones.

6. The parts of wastes lying in the plant premises by now would have been transformed and transported in various environmental compartments, which needs to be investigated and modeled to have confidence that all environmental complexity associated with fate and transport of all wastes has been understood and addressed in remediation program.

7. Above mentioned investigations (item 6) will also provide knowledge about how the natural attenuation of different contaminants, if any, has taken place till now. This would further help in designing remediation strategy.

R N Singh
INSA Senior Scientist
August 12, 2010

Comments on the NEERI Report "Assessment and Remediation of Hazardous waste contaminated areas in and around MIS Union Carbide India Ltd., Bhopal"

Present status of soil contamination at UCIL premises and around

The report on ', based is based on the geophysical and the hydro geological studies conducted by NGRI and NEERI. It has come to the conclusion that 7 hectares of soil within UCIL premises is contaminated with Aldicarb, Carboryl, α naphthol, HCH isomers, dichlorobenzene. Inorganic metal pollution is practically nil, except for Mercury, which also is not alarming (compare metal concentrations in soil samples upstream and downstream of UCIL (Table 18) and within UCIL premises (Table 27). Apart from this, the solar evaporator ponds and the secured landfill outside UCIL premises covering an area of 14 hectares need also to be remedied. In addition, the site of the plants, buildings, tanks etc. spread over 9 hectares has also to be decontaminated. Taking the average depth of 2 meters to which depth the contaminants have penetrated the total volume of contaminated soil works out to 6,00,000m^3. The depth of penetration of one of the dumpsites has been found to be as high as 8m. Taking all this into account, the total volume of soil to be decontaminated is of the order of 6,50,000m^3.

Method of Soil decontamination suggested by NEERI

The NEERI report rules out in situ remediation as thermal de-sorption, permeable reactive barriers, bioremediation etc. due to the clayey nature of the soil. In view of the high cost involved in transportation of the excavated soil for any off site remediation, a via media has been recommended for an

on site secured landfill system, for the material after treatment (if necessary). The details of the proposed treatment have to be still worked out. Apart from this, the cost of excavation and making the secured landfill, ranges from 78 to 117 crores.

Ground water contamination

Regarding the ground water, it has been assessed that there is no significant presence of contaminants in the downstream samples as also within UCIL premises. Out of 30 ground water samples, two of them indicated the presence of Dichlorobenzene and three of them of Dichlorobenzene and Aldicarb. These can be attributed to surface run off as their locations are in low-lying areas. It is proposed to treat the contaminated ground water at the five bore well locations by pump and treat system. It is gratifying to note that there has been no major contamination of ground water.

My Suggestions: -

In view of the high cost involved in excavation and creating a secured landfill, 'Phytoremediation' is suggested. Phytoremediation involves a number of processes, including the stimulation of microbial activity in the soil. These activities lead to the metabolisation of the organic pollutants present in the soil and to their degradation. This method is cheap, and is accepted well by the general public, compared to chemical methods.

Phtoremediation using some of the plant varieties, preferably with fibrous roots, which normally grow in the area should be considered seriously. In this context, 'Vetiveria Zizanirdes' (commonly known as Khas Khas) is suggested. One can also look at the possibility of growing Lemon grass. These plants are of commercial value and as such the locals in the area could be encouraged to take part in this activity. The economic benefits accruing

from it can go to them. One thing to remember is that none of the edible plants should be grown there, for the present. In this context, one can also study the plants, which have naturally grown in the UCIL premises as, which are seen around the dilapidated plant and machinery (see plate 2, Page 17). It may also be worthwhile to take a few samples in the area for the pollutants – Aldicarb, Carbaryl, α Naphthol, HCH isomers, Dichlorobenzene and compare it with data for soil samples collected in the other locations of the UCIL premises. This will give an idea whether there has been any phyto remediation in this area. Groundwater available in the five contaminated wells can be used for irrigation. This way, the water can also be decontaminated.

During the period, when Phytoremediation is being organized, investigated, the immediate remedial measures mentioned in page 69 - proper fencing of the area, sealing of the five contaminated wells, excavation and recovery of dump materials and their decontamination, decontamination and decommissioning of the plant should be taken up.

It would be worthwhile to spend a year in the above activities in an area of 10 hectares, assess the results before taking a decision on excavation; transportation and making a suitable land fill for the excavated soil.

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(A Govt. of India Undertaking)

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A. K. PURWAHA
CHAIRMAN & MANAGING DIRECTOR

13 August 2010

Sub: Assessment and recommendation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal

Hon'ble Sir,

This has reference to your DO Letter No.1.58 (MOS(I/C)E&F/10 dated 15 July 2010 regarding Assessment and Recommendation of Hazardous Waste Contaminated areas in and around M/s Union Carbide India Ltd., Bhopal.

We have reviewed the reports generated by NEERI, NGRI and IICT. These reports are quite exhaustive and the analysis drawn/recommendations made seem to be in order.

With warm regards,

Yours sincerely,

(A.K. Purwaha)

1349 dt 23/8/10

Shri Jairam Ramesh,
Hon'ble Minister of State
(Independent Charge),
Environment & Forests,
Government of India,
New Delhi 110003.

DD (SR)

→ JS (RH)

MOS (I/C) E & F
Dy. No....1339.....
Date....20.8.10.....

Dr. T. Ramasami

August 19, 2010

Dear Hon'ble Minister,

Subject: Comments on the Report of NEERI-NGRI on Assessment and Remediation on Hazardous Waste – Bhopal Gas Leak Disaster.

--XX--

I enclose my comments on the reports written in my personal capacity as someone who had received training in Chemistry and participated in providing technical solutions to environmental problems in my previous assignments. These comments are personal and do not reflect the views and position of the Department of Science and Technology.

As advised by you, I am sharing these comments also with the Peer Review Committee.

Kindest regards,

Yours sincerely,

(T. Ramasami)

Encl: As above.

Sh. Jairam Ramesh,
Hon'ble Minister of State (I/C) for Environment & Forests,
Ministry of Environment and Forests,
'Paryavaran Bhavan'
CGO Complex, Lodhi Road,
New Delhi – 110 003.

MOS (I/C) E & F
Dy. No. 3161
Date 24.8.10

COMMENTS ON THE FINAL REPORT SUBMITTED BY NATIONAL ENVIRONMENTAL ENGINEERING RESEARCH INSTITUTE (NEERI) AND NATIONAL GEOPHYSICAL RESEARCH INSTITUTE (NGRI).

TO

BHOPAL GAS TRAGEDY, RELIEF AND REHABILITATION DEPARTMENT, GOVERNMENT OF MADHYA PRADESH, BHOPAL.

BY

Dr. T. RAMASAMI*
IN PERSONAL CAPACITY
AS A CHEMIST

SUBMITTED TO
THE MINISTRY OF ENVIRONMENT & FORESTS
GOVERNMENT OF INDIA

*Present Address:

Secretary to the Government of India,
Department of Science and Technology,
Technology Bhavan,
New Mehrauli Road,
New Delhi – 110 016.

1. Assessment of Current Status of Contamination

The two institutions have adopted scientific methodologies and tools to assess the type, level and extent of contamination of the tragedy site. Data presented in the reports seem credible and the study has been made professionally. Conclusions and inferences drawn from the data presented seem logical.

- The contamination of soil and ground water in and around the premises, is due to disposal practices deployed by M/s Union Carbide India Limited (UCIL) during 1969-1984 even preceding MIC leakage
- Appearance of contamination of the disused facilities in the plant is reported but no scientific assessment is included
- Various studies seem to reveal that the ground water below a depth of 2.2-2.5 m is not contaminated.
- On account of poor permeability, the contamination depth may be limited generally to 2 m and only in limited cases to 4-8 m.
- An assessment has been made that the total volume of contaminated soil may be about 6,50,000 m^3 and weight of 11,00,000 MT.
- Contamination of ground water within the premises is attributed to surface run off and feasibility of pump and treat methodologies examined.

On the whole, the assessment of the scope of the challenge appears to be fair and sound.

2. Remediation Measures suggested

Management option for remediation seem to be the focus of the report of NEERI. Some practical suggestions and recommendations have been made. They seem pragmatic. However, there are some important gaps in remedial plans proposed. Remedial plan suggested primarily involves a four - step process, viz.,

- Decommissioning of the dis-used plant.
- Decontamination of tragedy site and remediation of contaminated soil and ground water.
- Incineration of decommissioned plant
- Safe disposal of decontaminated soil through secured land fill system.

These are technically sound suggestions, in my opinion.

3. Perceived gaps in Remedial Action Plans

Various technical options for:

- Decommissioning
- Decontamination
- Securitization of decontaminated soil
- On-site and off-site opportunities

have not been assessed and technical merits and demerits of each proposed option have not been included in the Report.

A scientific assessment of various technical options and an analysis of risk factors including the social viability of remedial technology options would have been beneficial.

As a decision support system, a technical report based on risk-minimized least social cost option would have been valuable.

The Reports merit a Peer Review along the areas of gaps with respect to their potentials in Decision Support System.

While the reports are sound in technical assessment of the type and extent of contamination, the Peer Review Committee may like to address gap areas relating to support to decision making and selection of risk minimized least social cost option based on merits of technical alternatives. Off-site and On-site opportunities may merit review.

4. General Remarks

There are a few typographical and other errors, some of which could limit the value of the report, if left uncorrected. The respective institutions may be advised to revise the report to avoid such errors, which do limit the technical merit, however.

--xx--

August 24, 2010

To,

Shri Jairam Ramesh
Minister of State (Independent Charge)
Ministry of Environment & Forests
Paryavaran Bhawan
CGO Complex
Lodhi Road
New Delhi – 110 003

Dear Minister Ramesh,

We would like to acknowledge the initiative of the Ministry of Environment and Forest in seeking feedback on the report conducted by the National Environmental Engineering Research Institute (NEERI), supported by the National Geophysical research Institute (NGRI), which assesses the contamination in and around the Union Carbide India Limited (UCIL) site in Bhopal, and proposes strategies for the remediation of contaminated areas in and around the UCIL site.

While we are conscious of the fact that the technical workshop as proposed by the Ministry pertaining to this issue has been undertaken, we hope our feedback will be taken into consideration, in the follow-up, towards arriving at strategies for the remediation of contaminated areas, in and around the UCIL site.

Inspite of the UCIL – Dow Chemical factory being shut down since 1984, the site and surrounding areas pose an ongoing toxic threat to the local inhabitants as well as being a source from which toxic contaminants can spread into the groundwater and environmental compartments.

While the NEERI report confirms the contamination of the site and of groundwater, it suggests and recommends totally inadequate and ineffective remedies.

There are significant gaps and flaws in the report and not all of its findings or recommendations can be supported. For instance

a. The soil sampling outside the site was ill judged and provided no useful information.
b. The geophysical and chemical survey within UCIL walls was hampered by water logging and failure to clear vegetation; even where these problems did not pertain, the survey was patchy, so the dumpsites and soil contamination are not as well defined as they need to be before cleanup can begin.
c. The recommendations to either incinerate or landfill the wastes are also unacceptable. Landfill will not solve the problems and incineration will inevitably release dioxins, furans and mercury to the environment.

Please find enclosed the document ***'Comments on the June 2010 NEERI Report entitled Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal'*** which details Greenpeace's position and feedback to the NEERI report.

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For the cleanup of the UCIL site to be conducted, on an urgent basis, a number of recommendations are made (refer to the enclosed document), which we strongly believe, should be followed.

Finally, Greenpeace continues to believe that the matter of liability of Dow Chemicals in this case must not be underestimated or brushed aside. This toxic waste and resultant contamination relates to the factory when it was in operation.

Dow Chemicals, which bought over the assets of Union Carbide, cannot deny liability now. It is also important to consider that the remediation of the site will be expensive and that the company responsible for the problem must be required to pay full costs of clean-up and health impacts.

Look forward to your response.

Thanking You

Yours Sincerely

Sanjiv Gopal
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Comments on the June 2010 NEERI Report entitled

Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal

and sponsored by the

Bhopal Gas Tragedy Relief and Rehabilitation Department
Govt. of Madhya Pradesh, Bhopal

GREENPEACE

Greenpeace International
August 2010

Executive summary

The Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTRRD), Govt. of Madhya Pradesh, commissioned the National Environmental Engineering Research Institute (NEERI), supported by National Geophysical Research Institute (NGRI), to assess the contamination in and around the Union Carbide India Limited (UCIL) site in Bhopal, which has been closed since the gas disaster in December 1984 but which is still severely polluted and poses an ongoing toxic threat to local inhabitants as well as being a source from which toxic contaminants can spread into the groundwater and environmental compartments.

The NEERI report confirms the seriousness of the soil pollution, and estimates that 1.1 million tonnes of soil and other wastes need to be dealt with. It also recognises that groundwater pollution is emanating from the site and will need to be remediated. It makes a number of short and longer term recommendations for action, including the immediate fencing off of the site, closure of contaminated wells and the engaging of a competent professional company to carry out the cleanup.

However, there are significant gaps and flaws in the report and not all of its findings or recommendations can be supported. The soil sampling outside the site was ill judged and provided no useful information. The geophysical and chemical survey within UCIL walls was hampered by water logging and failure to clear vegetation; even where these problems did not pertain, the survey was patchy, so the dumpsites and soil contamination are not as well defined as they need to be before cleanup can begin. The recommendations to either incinerate or landfill the wastes are also unacceptable. Landfill will not solve the problems and incineration will inevitably release dioxins, furans and mercury to the Indian environment.

For the cleanup of the UCIL site to be conducted, a number of recommendations are made, which we believe, should be followed:

To immediately reduce the ongoing risk to the health of the community:

- The site and SEPs should be properly fenced off immediately
- All wells identified as contaminated in this and previous research should be sealed
- Safe and clean water to be provided free of charge wherever water sources are closed off
- Measures should be taken to ensure that contaminated milk and other animal products cannot enter the food chain.

For longer term cleanup of the site:

- Consultation and transparency:
  - that the community and other stakeholders be consulted at all stages in the development of the cleanup plan
  - independent experts should monitor the process throughout.
  - that all monitoring and other data be made freely available.
- Protection of local environment and population:
  - all possible measures be taken to protect the local community from adverse chemical and other impacts of the cleanup process;
  - the community should be appropriately compensated, without delay, for any that damages that occur.
- Standards and monitoring:
  - all procedures should be carried out to the highest international standards;
  - soils should be cleaned up to residential standards;
  - water should be cleaned up to drinking water standards.

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- Appropriate disposal technologies:
  - incineration and landfill should be rejected in favour of closed loop technologies;
  - that whichever technology is selected, it will not result in the release of further pollution to the Indian environment;
  - if cleanup cannot be carried out to the required standards in India, wastes should be shipped to the USA or other OECD country for treatment.
- Responsibility and financing:
  - that the responsibility for the contamination remains with the polluter, Union Carbide, now owned by Dow Chemical, and that they should therefore shoulder all costs associated with cleaning up the UCIL site and its environs.

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Introduction:
This review discusses the report "Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal" commissioned by the Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTRRD), Govt. of Madhya Pradesh and carried out by the National Environmental Engineering Research Institute (NEERI) at Nagpur with the assistance of the National Geophysical Research Institute (NGRI), Hyderabad.

The purpose of the NEERI report is "for assessment of contamination and delineation of suitable strategies for the remediation of contaminated areas in and around the UCIL site."

Unfortunately, this review finds that this purpose has not been fulfilled. This review will explain some of the lacunae in the report, discuss previous research about the contamination in and around the UCIL site and suggest an alternative strategy for survey and remediation.

Soil contamination within the UCIL site:
It has long been known that there are both a number of dumpsites within the site and other areas where the soil was contaminated, such as near the Temik (aldicarb) pesticide plant. NEERI refer to their previous report from 1996 that there were some 7 hectares of dumps at UCIL, with three main dumping zones. Maximum concentrations in different places of of 52% Union Carbide's main product, Sevin (carbaryl), 33% naphthalene and almost 8000 mg/kg (0.8% aldicarb), as well as other toxic chemicals.

The value of a survey of soil contamination within the site prior to decontamination would therefore be to delineate the borders of these known dumps and clearly locate hotspots so that cleanup contractors would be able to work precisely. Greater knowledge of the nature and concentrations of contaminants would also have made it possible to select the best treatment methods for different contaminant profiles.

The analysis of the surface and subsurface soil samples certainly indicates extensive soil contamination with the main contaminants being BHC (a mixture of hexachlorocyclohexane isomers including gamma-HCH, sold as the insecticide lindane), aldicarb, carbaryl (Sevin), alpha-naphthol, and dichlorobenzene and mercury. As a result of this, NEERI states that "*the open areas in and around the abandoned manufacturing units, sheds, buildings are likely to be contaminated ...the quantum of such areas is estimated to be 9 hectares. Thus the total contaminated area within UCIL premises that would require remediation is about 16 hectares.*"

However, the distance between the samples on such a large site means that it is possible that some small hotspots have been missed.

This problem is far more serious with respect to the geophysical surveys. These were conducted on accessible areas of the site and reported the likely presence of dumps in three specific locations; north of the formulation plant; south of the storage tank and police post; and between the neutralization tank and the SEP.

This geophysical survey was not completed to the satisfaction of the NEERI scientists. They point out that they were hampered by standing water and vegetation which had not been cleared; the map of surveyed regions shows that only a minor proportion of the site was covered. Given that NEERI have had over a year in which to produce the report, it should have been perfectly possible to arrange for the necessary vegetation clearance and return to

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the site to sample waterlogged areas during the drier months of the year, when no standing water remains.

Whatever the reasons, only a fraction of the site has been subjected to geophysical survey and the although this section of the report provides useful new information, it is still not sufficient to guide any future cleanup and further surveying will still need to be done.

Soil contamination outside the UCIL site
The NEERI report includes the analysis of soil samples "*from eight different locations outside the UCIL plant premises considering the ground water flow direction, which is generally towards the north-east or east direction as reported in previous studies. The soil samples at these locations were collected at three different depths (surface, 30 cm deep and 60 cm deep).*"

Given that NGRI's geological survey locates the groundwater at around 8-25m below the surface, it is a logical impossibility that the groundwater would deposit contaminants either at the surface or a depth of 30-60cm. Surface water runoff during the monsoon is equally unlikely to have carried contaminants as far away as the above-mentioned sampling sites; the closest was at the SEPs, a couple of hundred metres from the site and the furthest was of the order of 1km from the site. Hence the likelihood of obtaining useful information from these samples is obviously extremely limited. Indeed this was reflected in the results of these samples; 8 locations, organic contaminants or mercury were only found at three sites.

First, traces of aldicarb were in sample DS3, near the railway line. The absence of other chemicals associated with UCIL mean there it could be from an unrelated source. Second, beta-HCH and mercury were identified in sample DS2, at the western side of the landfill and third, aldicarb, carbaryl, aplpha naphthol, beta-HCH and mercury were all identified in samples DS1 taken from the SEPs. Since the SEP was a waste disposal site during UCIL operating years, finding contaminants there is to be expected. There is no reason to believe that it was a result of the [SENTENCE LEFT HANGING] Similarly, contamination at the landfill site is most likely to be the result of [SOMETHING MISSING] have been dumped there. Consequently, the analyses of the samples outside the UCIL plant add nothing to the sum of knowledge about the site.

Groundwater survey and contaminant analysis
NGRI drilled a number of borewells in the UCIL site to give a better understanding of the geology of the site and the depth of the groundwater. They then collected some 30 groundwater samples from inside and outside the site, which were analysed for various inorganic salts, metals, pesticides and semivolatile organochlorines. The inorganic salts and most of the metals are of little use in understanding the contamination emanating from the site and the pesticides have physicochemical characteristics that would incline them to bind to soil rather than be transported in groundwater.

Nevertheless, NEERI found aldicarb (Temik) in the groundwater near where it was manufactured- the Temik plant in the northernmost corner of the facility.

The only solvent reported by NEERI was dichlorobenzene (isomer unspecified), which was found in 4 samples. Two were close to the area where extreme contamination was identified previously, close to the north-east perimeter (Labunska *et al.* 1999), and two were located to the north of the factory.

On the basis of this, NEERI recommend the closure of the contaminated wells and pump and treat technologies to decontaminate the groundwater. This is certainly necessary, but these measures do not go nearly far enough because the report does not address the problem of groundwater contamination with chlorinated solvents.

In 1999, Greenpeace published a technical note on the groundwater contamination around UCIL (Labunska *et al.* 1999); this is cited by NEERI in their report. Greenpeace found 12 different chlorinated volatile and semivolatile pollutants in 5 of the 12 samples collected. The contaminants that were present in the highest concentrations were chloroform (aka trichloromethane), carbon tetrachloride (aka tetrachloromethane) and 1,2-dichlorobenzene (also known as o-dichlorobenzene or o-DCB). A later technical note also reported that water from a domestic well located to the south of UCIL, and that had not been analysed previously, contained high concentrations of carbon tetrachloride and lower concentrations of a number of other organochlorines, including chlorinated benzenes (Labunska & Santillo 2004). Both these studies found contamination levels hundreds of times higher than internationally accepted drinking water standards; the worst single result (Labunska *et al.* 1999) was 1700 times the WHO drinking water standard

NEERI also cites a report by Delhi-based NGO Shristi, which reproduced court testimonies of estimated quantities of chemicals dumped during UCIL operations. According to this, 500 tonnes of carbon tetrachloride, 300 tonnes of carbon tetrachloride and 500 tonnes of 12-dichlorobenzene, which had been used as solvents, were dumped during the time that UCIL was in operation (Srishti 2002). This explains the source of the contamination found by Greenpeace and indicates the potential severity of the problem.

Finally, NEERI cite Birke and Burmeier, who regarded dumped solvents as a major threat. They believed that they were likely to be present as DNAPL (dense non-aqueous phase liquids) with the potential to cause large scale contamination of the groundwater.

Despite clearly being aware of the concern about the solvent contamination of the groundwater, NEERI did not report a single analysis result for chlorinated solvents.

This should be recitified as a matter of urgency. All the wells should be retested for the presence of volatile pollutants, particularly chloroform and carbon tetrachloride. All contaminated wells, as identified in the NEERI report and Greenpeace research should be closed and affected residents provided, free of charge, with an adequate supply of safe, unpolluted water.

Contamination of the buildings and manufacturing plant

Many of the buildings, particularly the manufacturing, formulation and storage areas, were either contaminated as a result of the routine activities of the plant during its operational phase and through having toxic waste stored in them at a later date. As well as the buildings themselves, many of the drains will have to be excavated as they too contain pollutants (Labunska *et al.* 1999, Stringer *et al.* 2002).

If any elements of the built environment are to be removed, they will need to be surveyed properly to establish which parts buildings need to be treated as hazardous; the particular contaminants relevant to each structure; and to estimate the volume of material that need to be treated. The NEERI report does not include any such information.

In any case, it would be advisable to keep in mind the sentiments of the survivors of the gas tragedy, and evolve a dismantling, decontamination plan for key structures, including manufacturing plant, that would enable easy re-assembly or reconstruction of the same as part of the memorial that is to come up on site. Such preservation of "industrial heritage" would be in line with the practice of memorialising location-specific disasters of this nature.

Costs:

NEERI has estimated the cost of the proposed landfill as 78-117 crore INR (approx 17.5-26 million USD), but has provided no information on the engineering, so it is hard to validate the estimate.

This is true also of the recommendation of 25 to 30 lakhs (approx 55,000 – 67000 USD) capital costs and 10 to 15 lakhs per annum (approx 22,000- 33,000 USD) for operating costs.

No estimate is given for: the proposed incineration; waste transportation; for the proper fencing around the site; decontamination/demolition of buildings; any further survey work that will be necessary; ongoing monitoring of contaminant levels; clean drinking water to replace the contaminated sources; measures to protect the local inhabitants from any emissions during the remediation or compensate then for any damages occurring.

In the absence of these data, the economic analysis is wholly incomplete, though the costs of a well executed cleanup will be far higher than is estimated.

Cleanup recommendations:

Following on from the survey, the purpose of the NEERI report was the "delineation of suitable strategies for the remediation of contaminated areas in and around the UCIL site".

Within this section, a number of recommendations are given. NEERI's short term recommendations include:

"Proper fencing and security to UCIL premises and SEP area for preventing unauthorized access and use of these areas by public."

"Immediate sealing of five contaminated wells so as to prevent use of water from these wells for any purpose by the residents."

Both of these are recommendations should be acted upon without delay, with some additions. The 2002 Greenpeace report assessing the stockpiles of toxic wastes in the UCIL site noted the fact that locals accessed the site regularly, and that toxics such as HCH could be passed on to people via the milk of cattle grazing there (Stringer *et al.* 2002). The exposure was described as "unacceptable" at the time and remains so now.

Once the site, SEPs and any other contaminated areas are properly fenced off, measures should be taken to ensure that any existing contamination is not passed into the food chain. Any animals that have been grazing on contaminated areas should be purchased at the current market price by the authorities so that their owners can buy un-contaminated livestock. The authorities would guarantee that no milk, eggs or meat from these contaminated animals is allowed to enter the food chain elsewhere after their purchase.

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In the same way that it is necessary to protect the local inhabitants from contamination residing in the soil, so it is essential to ensure that they have a clean source of water. As Some of the contaminated wells were indeed sealed in the wake of Greenpeace's research revealing the extent of the groundwater pollution. Since then, some drinking water has been supplied in tankers and new mains installed. More than half of the population now has piped supply of drinking water of superior quality. However, some of the contaminated hand pumps are known to be back in use and the NEERI report, even with the gaps in the data for chlorinated solvents, confirms that borewells used for domestic purposes are contaminated.

Hence, the recommendation that contaminated well be sealed is to be supported, but with additions. First, safe, clean water must be supplied free of charge to replace the supply from any sealed sources, so that there is no incentive to reopen the contaminated wells, as has happened in the past. Second, that the wells be sealed in such a way that they can still be opened when necessary to collect samples to monitor the contamination of the groundwater.

The next recommendation from NEERI is:

"Excavation and recovery of dumps materials. The incinerable wastes should be disposed off in TSDF at Pithanpur. The non-incinerable wastes to be disposed off in on-site secured landfill facility".

This is not acceptable. Greenpeace has already laid out a number of principles and guidelines for the proper cleanup of the UCIL site (Stringer & Johnston 2002). These reject both incineration and landfill.

There are a number of reasons for this. It is essential that the cleanup be carried out to the highest possible standards and that it be done without adding further contamination to the Indian environment. Any incinerator is an open-ended process and will inevitably release pollution to the atmosphere, as well as producing toxic ash that should be classified and landfilled as hazardous waste. Hence it fails this test of not increasing the contamination of the Indian environment. Moreover, the TSDF facility is unlikely to meet international standards. The Stockholm Convention, which India ratified in 2006, has a guideline of 0.1ng/ITEQ dioxins and furans per m^3 in flue gas (www.pops.int), the same limit as applies in the European Union (EU 2000).

Landfill must be rejected as a solution to the contamination in and around UCIL first and foremost because it is not a solution. All that is proposed is digging up buried contamination and reburying it. It is also difficult to see how it will be possible to carry this out on a site where almost all the open ground is acknowledged to be contaminated. NEERI have not suggested the location for the landfill, set standards for the engineering or explained how it should be carried out safely and in this respect the report has failed to achieve its goal to properly delineate cleanup strategies.

If it is not done to the highest standards, excavating contaminated soil will also result in mobilization of pollutants in dust, which is likely to increase the local contamination rather than decrease it. This is no trivial or theoretic risk in the light of the poor standards of the operations carried out to date. The NEERI report itself notes that the excavation of contaminated soil from hotspots that were contracted out to M/s Ramkey Ltd have not been completed as required.

Instead of incineration and landfill, Greenpeace recommends closed loop technologies to extract and destroy the contaminants in the soil and groundwater. Should the expertise

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and/or equipment to do so not be available in India, then the waste and other contaminated materials should be sent for disposal to the USA or other OECD country with the appropriate facilities.

NEERI also recommends the "*decontamination and decommissioning of plant, machineries and buildings prior to remediation of contaminated soil and groundwater*". However, they do not provide any guidance as to how this should be done, again failing to delineate the decontamination strategy.

NEERI further recommends a pump-and-treat system for the contaminated groundwater. Greenpeace also recommended pump-and-treat in 2002 (Stringer & Johnston 2002), but with one significant difference from what is proposed in the NEERI report.

NEERI recommend that activated carbon filtration to remove the contaminants from the groundwater, followed by incineration. Greenpeace recommends air stripping, reverse osmosis or other technique which does not produce such a large quantity of contaminated residue for disposal; and all entrained pollutants and other residues should be disposed of by closed-loop non-incineration technologies, in the OECD if it is not possible to do so in India. (the names of, if not brief descriptions of such technologies would be good)

The final recommendation of the NEERI report is that "*BGTRRD should engage competent professional contractors for detailed engineering, and execution of various remedial measures suggested by NEERI*"

Certainly any contractors appointed to clean up the Union Carbide India Limited site and surrounding areas should be competent, but given the numerous flaws in the survey and cleanup strategy contained in the NEERI report, they should not be constrained to consider only the disposal methods suggested by NEERI.

Instead, a further survey should be carried out by independent researchers prior to the commissioning of any cleanup. A full review of the pros and cons of each of the possible technologies, including contaminant extraction from soil and closed loop non-incineration technologies should also be carried out.

On the basis of this, a request for proposals should be issued to competent professional contractors and the best chosen for execution.

At all times the process should also adhere to basic principles such as those laid out already by Greenpeace in 2002 (Stringer & Johnston 2002).

- Consultation and transparency:
  - that the community and other stakeholders be consulted at all stages in the development of the cleanup plan
  - independent experts should monitor the process throughout.
  - that all monitoring and other data be made freely available.
- Protection of local environment and population:
  - all possible measures be taken to protect the local community from adverse chemical and other impacts of the cleanup process;
  - the community should be appropriately compensated, without delay, for any damages that occur.
- Standards and monitoring:
  - all procedures should be carried out to the highest international standards;

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- soils should be cleaned up to residential standards;
- water should be cleaned up to drinking water standards.

- Appropriate disposal technologies:
  - incineration and landfill should be rejected in favour of closed loop technologies;
  - that whichever technology is selected, it will not result in the release of further pollution to the environment;
  - if cleanup cannot be carried out to the required standards in India, wastes should be shipped to the USA or other OECD country for treatment.
- Responsibility and financing:
  - that the responsibility for the contamination remains with the polluter, Union Carbide, now owned by Dow Chemical, and that they should therefore shoulder all costs associated with cleaning up the UCIL site and its environs.

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No.DIR/IITR/
18th August, 2010

Hon'ble Shri Ramesh Ji,

This is with reference to your D.O. No-7(161)/2004-HSMD (Part-II) asking for the comments on the reports submitted by NEERI , NGRI and IICT on decontamination and remediation of the Union Carbide plant site in Bhopal.

A committee consisting of the following Professors of IIT Roorkee was constituted to look into the reports and submit their comments:

Prof. I.M.Mishra, Deptt. of Chemical Engineering, IIT Roorkee	Convener
Prof. Deepak Kashyap, Deptt. of Civil Engineering, IIT Roorkee	Member
Prof. D.C.Singhal, Deptt. of Hydrology, IIT Roorkee	Member

The comments of the Committee are enclosed for your kind perusal.

Thanking you and with deep regards,

Yours sincerely,

(S.C. Saxena)
Director, IIT Roorkee

Hon'ble Shri Jairam Ramesh Ji
Minister of State(Independent Charge)
Environment & Forests
Government of India
Paryavaran Bhawan
CGO Complex
Lodhi Estate
New Delhi- 110003

Encl: As above.

MOEF (RG) R & F
Dy. No. 3456
Date 27/8/10

Indian Institute of Technology, Roorkee
Roorkee-247667

Comments on the Reports of NEERI, Nagpur and NGRI, Hyderabad on Decontamination and Remediation of the Union Carbide Plant Site in Bhopal.

As a follow up of the D.O.letter from Shri Jairam Ramesh, Minister of State (Independent Charge), Environment & Forests, Government of India, to Prof. S.C.Saxena, Director, IIT Roorkee, the Director constituted a Committee consisting of the following to study the reports of NEERI and NGRI, and to give their Comments thereon:

Prof. I.M.Mishra, Deptt. of Chemical Engineering, IIT Roorkee	Convener
Prof. Deepak Kashyap, Deptt. of Civil Engineering, IIT Roorkee	Member
Prof. D.C.Singhal, Deptt. of Hydrology, IIT Roorkee	Member

The Committee carefully went through the reports and deliberated upon the issues involved on the assessment of contamination of soil and groundwater in and around UCIL Plant from dumping of wastes, solar evaporation ponds and landfills, and measures to be adopted for the decontamination and remediation thereof. The comments of the Committee are given below:

(a) Geophysical/ Hydrogeological Investigations

The NGRI studies comprise detailed hydrogeological /geophysical studies followed by flow modeling. This report is appended to and the extracts included in the NEERI Report. The NGRI Report provides detailed geophysical / hydrogeological investigations on the contamination of soil and aquifers in and around UCIL Plant. It was noted that that the BGTRRD was required to complete "the decontamination and safe disposal of the plant, machinery, buildings and materials from the abandoned manufacturing units as well as clearing of dense bushes from the UCIL premises" before the investigation and sampling and analysis of soil and ground water was to be undertaken by the NEERI and NGRI. Since this work was not done, the NEERI-NGRI investigations did not cover these areas (see pages 16-17). Therefore, the NGRI and NEERI Reports are incomplete to that extent. As and when the decontamination and dismantling of the manufacturing units will be carried out, these and adjacent areas are expected to be contaminated further. Therefore, it is necessary to carry out investigations to assess the extent and level of contamination of the soil strata and the underneath groundwater.

1. The NGRI investigated nine sites within the UCIL premises during the HERT survey to know the extent and thickness of the contaminated soil from the solid waste dumped in these areas. The depth of the contaminated soil has been estimated by the vertical electrical sounding and 2D-3D resistivity imaging. It is

mentioned that wherever high resistivity areas are indicated on the surface, these have been taken to indicate the presence of substantial thickness of the contaminated soil. It is not indicated clearly as to what is the scientific basis of taking a high resistivity (100-300 ohm-m) as an indication of contaminated soil. Normally, from a geophysical logic, these waste dumps (if saturated by percolating rain water/surface runoff) should show low resistivity. Of course, at some places, the presence of leachate generated by percolating rain water/ surface runoff has been indicated as manifested in the low resistivity layers directly beneath the high resistivity areas. This ambiguity, however, needs a detailed clarification so that the presence of waste dumps at the 3 designated sites (site I, III and V) is established.
Dimensions (unit) of electrical conductivity (EC) as given in the report seem to be erroneous and should be corrected to micro-mho/cm (or micro Siemens/cm).

2. Though a geological fence diagram has been provided both in the reports of NEERI and NGRI (downloaded from MOEF websites), the information/text given therein is vague / illegible, except at a few places in the NEERI report. The colored figures given in the NGRI report are especially illegible and can not be deciphered properly. Further, geological map of the area has not been provided in any of the reports, although it is available in the Central Ground Water Board (CGWB) archives. From the details of lithologs of newly drilled 5 bore wells in the UCIL premises, some idea of the lithological distribution in the UCIL area can be made out. Wide-spread occurrence of a thick silty clay layer is indicated beneath the top black cotton soil in the study area.

3. Page 28 (last para) of NEERI report: Large variation in monsoonal water table fluctuation among borewells and dugwells is observed. This variation appears to be due to variation in specific yield of the shallow sandy aquifer (in dug well) and the deeper aquifer (in bore well).

4. Page 29 (last para) NEERI report: The reported occurrence of a layer of "sandy alluvium" with pebble beneath the basalt is doubtful because the alluvium is of "Recent Age" and will not be usually encountered beneath "basalt" which is of "Palaeocene" age, unless these geological beds are structurally disturbed. Thus, the reported "sandy alluvium with pebbles" may in fact be the upper weathered part of "Vindhyan sand stone" which is of Algonkian age. This fact also seems to be corroborated from the NGRI report. A confined aquifer appears to be present beneath a layer of yellow silty clay (aquitard) of about 3 m thickness (occurring at depth between 22 m to 25 m bgl) in all the newly drilled borewells. This confined aquifer seems to have a lower specific yield as compared to the upper shallow (localized) aquifer present in an open shallow dug well. (Sl. No. 2 in table 4, page 28, of NEERI report).

5. Locations of three reported Disposal areas (I, II & III) are not clear in the report. However, in Table 6 (page 36) of NEERI report, it is indicated that Disposal area II is located near eastern side of the UCIL plant (near borehole C)

6. A detailed saturated flow modeling is conducted on the aquifer to estimate the travel times and the capture zones. However, these features are relevant only if the aquifer receives contaminating leachate from the top. Thus, there seems to be some contradiction among different components of the study. The pathway and fate of toxics such as mercury, heavy metals and semi- volatiles have not been delineated

7. Vertical recharge has been considered while conducting the flow modeling. This is contradictory to the basic inference. A vertical recharge, if occurring, would inevitably bring in the contaminant leachate also.

(b) Monitoring of Soil and Ground Water

1. NEERI conducted three rounds of sampling of soil and groundwater during April 2009, January 2010 and May 2010 and followed EPA /BIS protocols for sampling and analysis. However, the results of the analysis shown in Tables 11-37 do not show the results of all the three rounds of sampling and analysis.

2. It is noted that NGRI did not drill boreholes in the SEP and Landfill areas outside UCIL premises, which are spread over an area of 14 hectares. Therefore, no assessment has been made about the mass / volume of contaminated soil and groundwater and the depth of soil contamination. Since water was stored for a long duration in SEP, and concentration of contaminated water took place due to solar evaporation of water, it is expected that the contamination of soil (and may be groundwater) in this area by water borne (dissolved and suspended) chemicals may be higher than that in other areas. Soil and water sampling and analysis, therefore, need to be done in these areas. The assumption of 2 m depth of contaminated soil (page 62, para 1 of NEERI Report) needs to be verified through bore hole log analysis. The conclusion that the " Absence of these contaminants in the downstream soil samples, in general, shows the downstream soils were not contaminated with the compounds present in UCIL premises" (Page 62, para 2, last sentence) may not hold.

3. The general inferences and conclusions drawn from the analysis reports seem to be correct subject to any corrections in the volume/mass and level of contaminated soil and groundwater in the SEP and Landfill areas as well as the areas covered by the manufacturing plant units, and contamination of the area and adjoining space from detoxification and dismantling of the plant, machinery etc. as the assessment of contamination has not been done in these areas.

(c) Strategy for Remediation

1. The remedial measures as suggested in the NEERI Report may be followed. However, the dismantling/detoxification of the contaminated plant/machineries, transport lines, storage tanks, etc. is a very specialized job, and can not be handled by ordinary contractors, even under the supervision of IICT, Hyderabad. The materials/chemicals to be handled are toxic, volatile and some may be flammable. Therefore, only a knowledgeable and experienced engineering company having expertise in diverse areas of chemical plant design, erection, commissioning, trouble shooting, environmental engineering, and industrial hazards management may be entrusted with this job.

2. The detoxification and dismantling and disposal of plant machineries, etc. must be completed before the work of decontamination and disposal of soil and groundwater is undertaken.

3. The characterized waste is a mixture of several semi-volatiles, pesticides and heavy metals. These compounds are also toxic and hazardous in nature. In case of landfilling, these persistent and harmful substances can affect the soil conditions affecting the resistance to seepage and movement of leachate over a period.

4. Using the same amount of binder as the contaminated soil waste in a 1:1 ratio will substantially increase the volume/mass to be handled. The binder must be such as to chemically fix the matrix with substantial reduction in leachate formation and gas evolution. Suitable measures should be taken to collect and treat the leachate and the gas before they are allowed to be discharged. The engineering design of landfill needs to be checked and verified.

5. The cost estimates as provided by NEERI are only approximate. The updated cost can be available only after the assessment of contamination in the left out areas is completed.

6. The decontamination and disposal of the soil and ground water should be done by a well-versed and experienced engineering company, having experience in detailed engineering, design, erection, commissioning, wastewater treatment, solid waste treatment and disposal and hazards management.

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Deptt. of Hydrology.
I.I.T. Roorkee

(D. Kashyap)
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प्रोफेसर डी. आचार्य, एफ एन ए ई, एफ एन ए एस सी
निदेशक
Prof. D. Acharya, FNAE, FNASc
Director

No. D/M-7/288
August 17, 2010

→ JS (RG)

Shri Jairam Ramesh
Hon'ble Minister of State (Independent Charge)
Ministry of Environment & Forests
Government of India
New Delhi 110 003

MOS (I/C) E & F
Dy. No. 3475
Date 30/8/10

Dear Sir,

This has reference to the D.O. letter No. 7(161)/2004-HSMD (Part-II) dated 13th July 2010 on the subject of reviewing the reports submitted by NEERI, NGRI.

The reports have been reviewed by some of our expert faculty members and the same is enclosed herewith for your kind consideration.

1684 (AS (R&D)) 30/8/10

With warm regards,

DD (R)

Yours sincerely,

DAcharya

(D. Acharya)

Encl : As stated

Dy. No. 506.
Date 1/9/10.

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Comments on NEERI report on Assessment and Remediation of Hazardous Waste Contaminated Areas in-and-around M/S UCIL, Bhopal

The report provides a background of the study conducted by NEERI. They have conducted a site reconnaissance and investigated the contamination levels by carrying out soil, hydrological and ground water monitoring studies, and developed a strategy for remediation and forwarded recommendations for short term and long term measures. The assessment study presented in the report is found to be systematic and the methodology followed is reasonable. However, there are some points not clearly mentioned and hence, the following suggestions are provided.

It has been mentioned that prior to the study conducted by NEERI, BGTRRD was supposed to carry out the cleaning and decontaminating work in the area. As this was not done NGRI-NEERI has not studied certain area (page 76), however, how much area has not been studied and the criticality of that portion has not been explicitly mentioned. Similarly, the report has not shown the detailed plan of the excavation and waste recovery carried out by M/S Ramkey Ltd. It has been mentioned that this work is incomplete. This work will have to be critically evaluated as the waste excavation may release toxic materials, if exist.

From the results, it is clear that many locations were identified as contaminated sites, for example the down-stream site (DS1), upstream sites (UST1 (high OC) and USI4 (heavy metals, Cd and Cr), etc. Also the sites S2, S3, S7 and S8 contains excess concentration of Aldicarb, α-Naphthol and α-HCH, β-HCH and carbaryl in surface or sub-surface soil (single or multiple), which are exceeding the EPA prescribed limits for the industrial soils. In many locations, the presence of the above contaminants were found to be within the EPA tolerance limits under the industrial soil category, however, the available concentration is well above the admissible limit for the natural water. This point should be considered before excavation of landfill or re-dumping the soil to any another location. The ground water samples collected in UCIL area (say GW-27, GW-28 and GW-29) were also found to have trace level of pesticide and contaminations. In this report, it is mentioned that the δ-HCH was not identified in any of the sampling sites. The methodology of the extraction and the analysis are to be re-visited before starting the remediation. Also the lowest detection limits of contaminants in the studied method are not mentioned in this report (only ND = Not Detected is provided).

It has been concluded that most of the remains of plants, machinery, buildings and sheds within UCIL "appeared to be contaminated". The statement should be supported by measured parameters. It should be highlighted which parameters are being assessed to ascertain the contamination levels. BGTRRD is executing decontamination and safe disposal of machinery. The risk associated with this may be highlighted. The methodology followed by BGTRRD needs to be evaluated.

It has been mentioned that UCIL premises are being used by children as play ground. A survey should be initiated to find if there exist any health hazards that can be attributed to possible effects of exposure to the contaminants.

The total volume of contaminated soil is estimated as 0.6 Mm^3. The remediation of this amount will require excavation and re-handling of excavated soil. The extent of handling will be

determined by the methodology for treatment of the contaminated soil. The cost of remediation is estimated in the range of Rs. 78-117 crore. However, this estimation should be re-examined after determining the treatment process and its cost. No strong justification in favour of this strategy or against other strategies has been presented. The cost will depend on the systems designed for the excavating and bulk material handling. Recovery of metals and minerals may be a better option on financial and technical grounds for remediating the contaminated soil. As this will be a quarrying activity, compliance of mining and environmental regulations may escalate the price. Perhaps, feasibility studies with small portions can be done to demonstrate that. Phytoremediation or bioremediation are also cheaper remediation strategies, and hence, the best possible strategy should be examined in detail.

For remediation of contaminated groundwater pump and treat system has been recommended (page 74). Proper ground water contamination model must be prepared prior to such actions. While pumping the uncontaminated water there may be a risk that it could mix with the contaminated water. The pumping well network will have to be properly designed to avoid the mixing.

As an immediate action the five contaminated wells are asked to be sealed. However, it should be ascertained if the wells have contributed to reduction of contamination levels by evaporation of volatile pollutants. The wells should be properly barricaded so that people cannot use it.

Not only the above studied chemicals are the contaminants, but also their degraded products can cause toxicity. Hence the concentrations of possible degradation products of the above chemicals in soil and water bodies of the UCIL area may need to be studied for effective remediation.

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Comments on the Geophysical survey conducted by NGRI, Hyderabad in UCIL Campus Bhopal

Electrical method of geophysical prospecting is the most suitable technique for mapping near surface lithological variation. This approach is widely used for versatile applications such as groundwater exploration, mineral exploration, subsurface pollution study and monitoring, saline water incursion in coastal area and various applications related with civil engineering constructions.

The problem in the campus of Union Carbide plant Bhopal is related with subsurface pollution study. NGRI has selected the appropriate geophysical technique to delineate the conditions of subsurface structures. The systematic study is carried out by a standard and well established approach.

Analysis of the data is the most significant part of any geophysical work. In the report, data interpretation is shown in terms of 2-dimensional resistivity cross-sections of subsurface in figures 12 to 35. These figures depict the actual subsurface conditions and constitute the main geophysical study.

In the PDF file of the report, above mentioned figures have very poor resolution and the resistivity values cannot be read. It will be meaningful to analyze the result if geophysical report is available in proper resolution for figures 12 to 35.

Resistivity measurement carried out by the NGRI delineates the location of hazardous waste materials. It concludes that thickness of hazardous waste is not very large. Visual analysis of color codes in various figures suggests the presence of low resistive zones below the high resistive hazardous dumps. These low resistive zones are fractures. There is leaching from dumps and the leachate will easily contaminate subsurface groundwater. This can easily be seen from various figures. Geophysical study together with geochemical analysis of groundwater will be helpful to avoid the adverse effect of the subsurface pollution. Direction of low resistive zones which depicts either lateral or vertical percolation of contaminated leachate from toxic waste can easily be detected from resistivity data interpretations presented in various figures 12 to 35.

In the NGRI report it is mentioned that the depth of the contaminants in the three sites (Site I, Site III and Site V) are restricted to only 2 m depth (except Site III upto 4-8M). Also the hydrological studies reveal that the UCIL premises is occupied by a thick layer of black silty clay and yellow silty clay up to a depth of 22-25 m below the ground level. The assumption made is that in the UCIL area the contaminants are only around 2 m depth in an average. However, there is no soil-geochemical and clay property analyses carried out to delineate the level of the penetration of contaminants.

Further, the delineation of the bio-available portion of each contaminant, if determined, could have given more precise information towards the soil and water quality.

Conclusions are not been presented in the report. The report should summaries the main findings and highlights suggestions in the conclusions.

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Devang V. Khakhar, Director
देवांग वि. खख्खर, निदेशक

No.D-III/D-4/C-3/2010
August 26, 2010

Dear Shri Ramesh,

This has reference to your letter D.O. No.7(161)/2004-HSMD(Part-II) dated 13.7.2010 asking us to have the report on decontamination and remediation of the Union Carbide plant site in Bhopal reviewed by our faculty.

I had forwarded this request to five of my faculty colleagues (list enclosed). I am enclosing the review comments from four of my faculty colleagues. I believe Prof. Shyam Asolekar from the Centre for Environmental Science & Engineering has separately sent the review comments.

I hope the reviews are useful to you. Please let me know if you need any further inputs.

With warm regards,

Yours sincerely,

(Devang Khakhar)

Encl: as above

Shri Jairam Ramesh
Hon. Minister of State (Independent Charge)
Environment & Forests
Government of India
NEW DELHI – 110 003

Copy to: Dean (R&D)

MOS (I/C) E & F
Dy. No. 35-86
Date 8/9/10

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LIST OF FACULTY WHO REVIEWED THE REPORT:

1. Prof. S.R. Asolekar, Centre for Environmental Science & Engg.
2. Prof. N. Rangaraj, Industrial Engineering & Operations Research
3. Prof. S. Roy, Dept. of Chemical Engg.
4. Prof. V. Sethi, Centre for Environmental Science & Engg.
5. Prof.(Ms.) Chandra Venkataraman, Dept. of Chemical Engg.

******

REVIEWER 1:

1. **Introduction:**

Based on the directives of the Task Force constituted by Hon'ble High Court of Madhya Pradesh, the Bhopal Gas Tragedy Relief and Rehabilitation Department (BGTRRD), Govt. of Madhya Pradesh requested National Environmental Engineering Research Institute (NEERI), Nagpur, and National Geophysical Research Institute (NGRI), Hyderabad, to undertake a fresh assessment of the extent of contamination and delineate suitable strategies for the remediation of contaminated areas in and around the UCIL site. The study was awarded by Bhopal Gas Tragedy Relief and Rehabilitation Department Govt. of Madhya Pradesh, Bhopal (BGTRRD) in March 2009. NEERI's report entitled *Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd. (UCIL), Bhopal* was made available around June 2010.

NEERI had earlier submitted a report in November 1996, on *Assessment of Contaminated Areas due to Past Waste Disposal Practices at EIIL (erstwhile UCIL), Bhopal*. The report had documented that UCIL had dumped their solid/hazardous wastes in open areas within the plant premises, and that it could be a potential source for contamination of groundwater. Based on the risk-based quality criteria for soil and ground water delineated by USEPA, the 1996 report concluded that there were two main disposal areas (I and II), and that the entire Disposal Area I (0.3 ha to a depth of 60 cm) and a few identified contaminated zone in Disposal Area II (0.32 ha to a depth of 30 cm) and at two sites in rest of area (0.08 ha to a depth of 30 cm) were contaminated and required remediation.

The latest joint study by NEERI and NGRI and the report thereof was prompted by continued apprehensions raised by various agencies/organizations on the level of contamination of soil and groundwater within and in the vicinity of the erstwhile UCIL premises. The field studies for assessment of contamination comprised of detailed hydrogeological investigations (geophysical investigations, borehole drilling, development of monitoring wells etc.), followed by collection and analysis of existing field samples (dumpsite, subsurface soil and groundwater). The hydrogeological investigations were carried out by NGRI whereas sampling and characterization of soil and groundwater were carried out by NEERI. The goal of the study was to carry out quantitative assessment of the concentration levels of a large group of possible contaminants in the soil and groundwater in the areas adjoining and inside the UCIL site. These include semi volatiles/pesticides (Carbaryl, aldicarb, α-naphthol, hexachlorocychlohexane isomers and naphthalene), volatile organics (carbon tetrachloride, chloroform, methylene chloride, 1,2- dichlorobenzene, chlorotoluene and toluene), and heavy metals (mercury, cadmium, nickel, chromium, cobalt, lead, zinc, and copper).

2. Principal Findings of the NEERI/NGRI Report:

The report under present review represents a reasonably comprehensive effort towards determining the existent degree of local environmental contamination in a quantitative manner. It also suggests both *immediate* and *long-term* strategies for decontamination and the necessary financial resources. The principal findings of the report may briefly be surmised as follows:

- During its production operations which involved manufacture of carbamate pesticides and the associated intermediate chemicals, UCIL had resorted to considerable dumping of solid, liquid and tarry wastes within their premises in an unplanned and "unscientific" manner, resulting in contamination of soil and groundwater within and, to some extent, outside the premises.

- The soil in UCIL premises is contaminated with a number of hazardous compounds which include aldicarb, carbaryl, α -naphthol, three HCH isomers, dichlorobenzene and mercury. The percolation of these contaminants into the soils is restricted up to about two meters, below which none of the contaminants have been detected. However, the areas upstream and downstream of the UCIL premises do not appear to have been subject to any measurable degree of contamination from the afore-mentioned compounds.

- The total volume of contaminated soil (within and outside UCIL premises) is estimated to be about 6,50,000 m^3. This corresponds to about 11,00,000 MT of soil, which appear to be in need of decontamination.

- The analysis of groundwater samples collected from the borewells constructed by NGRI and one existing borewell near the main entrance of UCIL indicates isolated contamination of groundwater in five of the wells. The contamination of these wells is possibly due to surface runoff from the chemical dumping sites. However, the quantum of contaminated groundwater could not be estimated due to the isolated nature of contamination.

- The cost of soil remediation through secured landfill is estimated to be in the range of Rs. 100 crore. For decontamination of the ground water, the capital cost for pump and treat unit is expected to be Rs. 25-30 lakhs, while its operating and maintenance would be Rs. 10-15 lakhs per annum, including cost of activated carbon and its disposal.

3. Remediation Strategies Suggested in NEERI/NGRI Report:

The report identifies a series of short and long-term remediation measures to reverse the damage caused by the UCIL waste disposal activities.

Select short-term measures include: (i) isolation of the site against any unauthorized access; (ii) sealing of all contaminated wells; (iii) decontamination and decommissioning of plant, machineries and buildings; (iv) soil excavation for recovering materials dumped at the disposal areas, and ex-situ (on-site) treatment for relieving the hazardous potential of chemicals.

For long-term measures, it is recommended that (BGTRRD) engages professional contractors for detailed engineering, and execution of various curative measures which include (i) remediation of contaminated soil by an on-site secured landfill facility; (ii) decontamination of groundwater using pump-and treat system.

4. Comments and Suggestions on NEERI/NGRI Study:

The NEERI/NGRI study constitutes a fairly broad attempt to assess the degree of contamination of soils and groundwater sources within and in the nearby locality of the UCIL facility in quantitative terms. It also suggests remedial measures that need to be undertaken in order to control and reverse the adverse environmental impact of the dumping practices of UCIL. As such the report should serve as an effective guide for further decision-making and action. However, in the opinion of the present reviewer a few more points of further assessment preferably by NEERI/NGRI team may help improve the utility of the present report. They are as follows:

(i) The report records several previous studies and impact assessments on the UCIL site carried out by other agencies, including expert teams, governmental agencies and NGOs. A comparative, critical evaluation of the findings of such earlier studies and the present one would help delineate points of convergence or otherwise. This would help consolidate the conclusions of the present NEERI/NGRI study and/or point to issues that need further study for unambiguous resolution and action.

(ii) The NEERI/NGRI study purports to have evolved remedial measures based on the assessment of the risk posed by the present state of contamination of the soil and groundwater sources. As the report states: "The contaminated soil and groundwater needs to be remediated to a risk based levels". Since at the present clean-up standards for hazardous waste contaminated sites are yet to be formulated in India, the latest standards/screening levels published by USEPA *("Regional Screening Level (RSL) Summary Table", USEPA, December 2009)* have been employed for the present study. The report enlists the relevant screening standards in section 4.3.1 on "Risk based remediation levels". However, it may be necessary to make explicit how the analytical results of the NEERI/NGRI study on the contamination levels of soil and groundwater sources at the UCIL site compare with these standards. This would help clarify the risk levels posed at present. In addition, some observations on the nature of risks posed would also aid decision-makers.

(iii) If more exact quantitative measure of the current risk levels is difficult to evolve at present, even a qualitative appraisal (low, medium, high, etc) would serve the purpose of underscoring the level of immediacy or urgency of the situation, which in turn would aid demarcation of timelines for implementation of the remedial measures suggested in the report.

(iv) The report observes that "the quantum of contaminated groundwater could not be estimated due to the isolated nature of contamination". This being the case it is not evident if the risk due to groundwater pollution has been adequately assessed in the present study. Thus, the report may need a documented observation from the NEERI/NGRI team on any attendant uncertainties and any future human consequence thereof; and whether the subject needs further study and evaluation.

(v) The report indicates certain financial resources needed to carry out the decontamination of the soil and groundwater at the UCIL site. This amounts to slightly over Rs 100cr as fixed cost and Rs. 10-15 lakhs per annum as operational cost. Provision of the basis of these costs in the report may provide a guide to prompt implementation of the suggested decontamination measures.

REVIEWER 2:

The subject of investigation of the report is to establish the extent of soil and groundwater contamination by the improper dumping of pesticides and chemicals manufactured in the Union Carbide facility between 1969 and 1984. Suitable remediation action is recommended.

The report summarizes findings on the basis of geophysical monitoring by NGRI and soil and groundwater monitoring by NEERI. The main findings are:

1. Significant soil contamination has occurred, for which remediation in terms of excavation, treatment and secure land-filling on-site is identified as the more feasible method. This analysis is tenable.
2. Groundwater contamination has not occurred except in a few isolated wells. This reviewer was concerned that groundwater sampling was carried out only during 3 months of the year (as the bore-wells were later tampered with and filled). No groundwater sampling was carried out during the monsoon. While this reviewer is not an expert on groundwater contamination, the certainty of conclusion that groundwater is not contaminated must be supported by longer term monitoring.
3. Previous studies in the area are summarized, which found NAPLs, high persistent organic compounds, and DDT contamination in the soil. It is important to determine beyond doubt that such persistent pollutants are not present in the contaminated soils. It is not clear to this reviewer whether the current monitoring ruled out completely the presence of NAPL and DDT contamination. Some clarification on this is needed. If these are present, remediation measures, including bioremediation may need to be considered.

REVIEWER3:

Locational aspect of sampling of soil samples

The flow of groundwater is reported as

- *"towards east"* In the abstract [page 4 of the report] ,
- *"in the southeast direction} which could change with time}}*, on page 31 and
- *"generally towards the northeast or east direction} as reported in previous studies}}* on page 38 [in section b) of 3.4 of the of the report].

This may be clarified.

The location of the downstream soil samples outside the UCIL campus (figure 14) are to the northwest, north and to the northeast of the campus. This should be finally reconciled with the groundwater flow direction (see para above).

Reviewer 4:

(I am not an expert in this area. My comments may therefore kindly be viewed in the broader view of some concerns as a researcher in the area of Environmental Science and Engineering – Thank you).

1. The report relies on base data from a report previous prepared by NEERI in 1996.

2. Other studies have been reported, and it would be useful to study whether these present similar/dissimilar results for assessment. The credibility of the report would be enhanced if the assessment results by NEERI were also supported by the other independent reports. Further, in cases where the results are dissimilar, it would be educative to reassess or justify the differences.

3. Based on the soil core samples and ground water samples, the problem for remediation is well defined in the report. In all tables, baseline risk threshold of the measured contaminant needs to be stated, or simply as acceptable/not-acceptable based on standards for hazardous wastes.

4. Were the sampling locations (hot spots) identified from the results of the NGRI study as the "most likely points for "leakage" into the groundwater ? Any groundwater modeling work carried out ?

5. A graphical link between the results of NGRI and the contaminant contours is suggested for better communication to decision makers. Figure 12 is useful, however it is suggested that it be integrated with the contours for contaminants.

6. The report does not provide a list of references.

7. A materials flow chart that includes scale of operation, raw materials, products and wastes, solubility, and the-then-intended fate of wastes could helpful. It has been a long time, but would there be records of any studies / clearances of on-site storage and risk study for ground water contamination ? Or probably these considerations are only more recent.

8. Is there any cross reference for Table 2 (Srishti report) ? Would be needed if there are any material flow studies to be carried out.

9. Section 1.4 , line 4 : What does the reference "industry officials" mean ?

10. Plant layout and all figures require a scale bar.

11. If the soil is impermeable, where did the run-off water transport the contaminants ?

12. I do not have any comments on the mode of remediation. However, USEPA has gone through intense exercise of remediation and clean-up under the Superfund programme [http://www.epa.gov/superfund/].

13. Are there any international expert opinions in this case? If yes, they should be included as references.

14. I do not have access to Annexures I and II listed in the Table of Contents.

15. 30-60 cm depth contamination in 1996 (page 6, section 1.2.1(vi), now is reported as 2 m depth – based on the time period between (1969-84) to 1996 and now 1996 to 2010, is this explainable ?

CONCLUDING SUGGESTION

The NEERI report needs to take the "other" studies and evaluate them critically vis-à-vis their own finding with NGRI. The report seems to lead to quantification of remediation task as the end point. Attention to cross referencing and bringing together findings in a scientific manner is strongly suggested to take the effort to the next level.

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R K Pachauri *Ph.D.*
Director-General

September 14, 2010

Mr. Jairam Ramesh
Hon'ble Minister of State (I/C) for Environment and Forests
Ministry of Environment and Forests
Paryavaran Bhawan
CGO Complex, Lodi Road
New Delhi 110 510

Dear Shri Ramesh,

I am sorry I forgot to hand over to you the Peer Review carried out by a couple of my colleagues on "Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal" prepared by the National Environmental Engineering Research Institute (NEERI). I had brought this write-up with me to hand over to you this morning. I am enclosing it now for your perusal.

With warm personal regards,

Yours sincerely,

R.K. Pachauri

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Date 16/9/10

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PEER REVIEW CARRIED OUT BY TERI

Assessment and Remediation of Hazardous Waste Contaminated Areas in and around M/s Union Carbide India Ltd., Bhopal
By
National Environmental Engineering Research Institute (NEERI)

The conclusions and recommendations made in this report clearly highlight the need for remediation. However, the report lacks clarity on the quality of background information used, the basis for creating a sound sampling plan, and the lack of a conceptual framework used to assess the need for remediation. This report doesn't highlight what use the Government of India foresees for this piece of land and as such the appropriate economically and technologically feasible level of remediation required is assessed without a significant endpoint. The level of cleanup required would be different were this area to be used for agricultural purposes, were that feasible at all, as compared to the level of cleanup required were this to be used as a manufacturing unit. To determine if a remedial response action is necessary at disposal sites and to identify target cleanup levels in the event that such action is required, the remedial agencies should document that a level of no significant risk of harm to public health, safety, and welfare and ecological damage has been achieved in terms of the articulated end points. The tools used for such assessments need to be protective of both public at large and the environment. The risk assessment process should describe quantitatively the risks associated with contamination at a particular site.

A more detailed analysis of specific sections and sub-sections of the report along with suggestions for improvement are below. While conducting a study of such immense scientific, social and humanitarian importance one must be sure that the report has addressed significant issues from many different angles and the study is truly exhaustive.

1. **BACKGROUND STUDIES**

While this report deals effectively with delineating the extent of contamination through an inventory of contaminants found at varying depths, it lacks a fundamental clarity **on current and foreseeable use** for the designated land and also lacks a conceptual framework within which the study is designed rendering the risk assessment incomplete. The risk assessment should address all possible activity and land use scenarios which could result in exposure to oil and/or hazardous material by human or environmental receptors if any significant concentration of toxic contaminant remains. The fundamental elements of a **conceptual model** include the source, the pathway and the receptors. While the source studies should ascertain the contaminants, concentrations, times, and location of contamination and test if they can be contained/removed and disposed/treated, the pathways need to assess the media, rates of migration, time, and loss and gain functions. This study also needs to assess if the pathway of contamination can be interrupted or eliminated. The receptors evaluation is perhaps the most crucial part and has been given very little significance in this study. The types of receptors and respective sensitivities (human and ecological), the concentration of people with respect to time and locations needs to be assessed through the prism of the following hypotheses:

a) receptor can be relocated	b) receptor can be protected
c) institutional controls can be applied	d) complete remediation is economically and technologically feasible

Table 1. Receptor Sensitivity Hypotheses

An example of a conceptual framework used by the United States Environmental Protection Agency (USEPA) as per the tenets of its Superfund Program is attached for your reference.

3. SAMPLING PLANS

Using this framework, groundwater samples are not collected solely on the basis of geological and hydro geological perspectives but also keeping in mind

a) Drinking water use
b) Surface water use
c) Source of indoor contamination by presence of Volatile Organic Compounds (VOCs) etc

Soil contamination is assessed keeping in mind

a) The type of receptor
b) Frequency of use
c) Intensity of use
d) Accessibility of soil

Environmental Risk Characterization specifies that risk assessments should focus on receptors that are most susceptible to the contamination in question. Thus, the risk assessment report should document that the combination of effects evaluated in the assessment represent potential effects from all pathways of concern and are relatively sensitive indicators of risk.

The spatial scale of an Environmental Risk Characterization should be consistent with the site-specific exposures, receptors and impacts of concern. Portions of sites being evaluated separate from the rest of the site are not likely to lend themselves to a valid or meaningful environmental risk characterization.

More specifically,

1. Page 70, first bullet, second last line should read "the incinerable material from such dumps shall be combusted and residue disposed at an authorised TSDF at Pithampur in Madhya Pradesh"

2. Page 73, last paragraph: the options for solidification/ stabilisation needs to be specified as conventionally used option of cement/lime/fly ash etc would not be very effective because pollutants which need to be immobilised are essentially organic in nature. Vitrification of contaminated soil can be option but would be much more expensive.

3. The capex and recurring cost of the pump and treatment system seem to be on lower end of the spectrum.