

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule-9 of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules – 2016

Utilization of Spent Methyl Chloride gas/ liquid (generated during manufacturing of Monocrotophos Pesticide products) in production of Glufosinate (Technical Grade Pesticide)



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**Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change,
Government of India)
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Procedure for grant of authorization by State Pollution Control Board (SPCBs)/Pollution Control Committee (PCCs) for utilization of Hazardous waste

- 1) While granting authorization for utilization of hazardous wastes, SPCBs/PCCs shall ensure that authorization is given only to those wastes for which Standard Operating Procedures (SOPs) for utilisation have been circulated by Central Pollution Control Board (CPCB) ensuring the following:
 - a. The waste (intended for utilization) belongs to similar source of generation as specified in SOP.
 - b. The utilization shall be same as described in SOP.
 - c. End-use/ product produced from the waste shall be same as specified in SOP.
 - d. Authorization shall be granted only after verification of details and minimum requisite facilities as given in SOP.
 - e. Issuance of passbooks (similar to passbooks issued for recycling of used oil, non-ferrous scrap, etc.) for maintaining records of receipt of hazardous waste for utilization.
 - f. Monitor closely the quantity of Spent Methyl Chloride being sent by generators and the quantity being utilized by industries who may be authorized in the State as per this SoP.
- 2) After issuance of authorization, SPCBs/PCCs shall verify the compliance of checklist and SOP on quarterly basis for initial 1 years; followed by random checks during subsequent period for atleast once a year. The compliance reports may be submitted to CPCB.
- 3) In-case of lack of requisite infrastructures with the SPCBs/PCCs, they may engage 3rd party institutions or laboratories having EPA, 1986/NABL/ISO17025 accreditation/ recognition for monitoring and analysis of prescribed parameters in SOPs for verification purpose.
- 4) SPCBs/PCCs shall provide half yearly updated list of units permitted under Rule 9 of Hazardous & Other Wastes (Management & Transboundary Movement) Rules, 2016 (HOWM Rules, 2016) to CPCB and also upload the same on SPCB/PCC website, periodically. Such updated list shall be sent to CPCB.
- 5) Authorization for utilisation shall not be given to the units located in the State/Union Territory where there is no Common TSDF, unless the unit ensures authorised captive disposal of the hazardous waste (generated during utilisation) or its complete utilisation or arrangement of sharing with any other authorised disposal facility.
- 6) In case of the utilization proposal is not similar with respect to source of generation or utilization process or end-use as outlined in this SOP, the same may be referred to CPCB for clarification /conducting trial utilization studies and developing SOPs thereof.
- 7) The source and work zone standards suggested in the SOP are based on E(P)A notified and OSHA/NAAQ standards, respectively. However, SPCBs/PCCs may impose more stringent standards based on the location or process specific conditions.
- 8) SPCBs/PCCs shall ensure that the utilizer of spent methyl chloride shall maintain daily records in National Hazardous Waste Tracking System (NHWTS).



114.0 Utilization of hazardous waste (H.W.):

Type of HW	Source of generation	Recovery/ Product
Spent Methyl Chloride (CH ₃ Cl) gas / liquid Category 29.1 of Schedule I and C-1 of Schedule-II of HOWM Rules – 2016	During manufacturing of 'Monocrotophos' Pesticide products.	To produce Glufosinate Ammonium (Technical Grade Pesticide) for use as herbicide.

114.1 Source of Waste:

Spent Methyl Chloride (MeCl) gas (liquid at lower room temperature) generated during manufacturing of 'Monocrotophos' Pesticide product is categorized as hazardous waste listed at Category 29.1 of Schedule-I and C-1 of Schedule-II of HOWM Rules – 2016. Purity of Spent MeCl gas shall be more than 99 %.

Table 1. Typical Characteristics of Spent Methyl Chloride gas

Sr. No.	Test Parameter	Unit (SI)	Spent Methyl chloride gas
1.	Purity	%	> 99.98
2.	Residue of Evaporation	ppm	36
3.	Acidity as Hydrochloric Acid	ppm	8
4.	Monocrotophos	ppm	BDL (<0.001)
5.	Ethlyne Dichloride (EDC)	ppm	BDL (<0.001)

Note: Note: SPCBs/PCCs to check the characteristics of MeCl gas prior to issuance of authorization, any significant deviation with respect to typical values mentioned in the table above may be examined with respect to the source or may be referred to CPCB.

114.2 Utilization Process:

Spent methyl chloride (99.98% purity) is utilized in the production of Glufosinate, a technical pesticide, through a systematic series of chemical processes. The manufacturing begins with the synthesis of Methyl Magnesium Chloride, a crucial intermediate, followed by the preparation of Diethyl Chloro Phosphite (DECP) and Diethyl Methyl Phosphite (DEMP), both essential for subsequent reactions. The process is divided into several stages: the preparation of DECP establishes the first key intermediate, followed by the refinement of DEMP, which is then converted into Glufosinate Acid through multiple sub-steps ensuring quality and precision. Finally, Glufosinate Acid is processed into Glufocinate Ammonium, the ammonium salt form of Glufosinate, for use as herbicide.

Utilization of Spent Methyl Chloride gas/ liquid (generated during manufacturing of Monocrotophos Pesticide products) in production of Glufosinate (Technical Grade Pesticide)

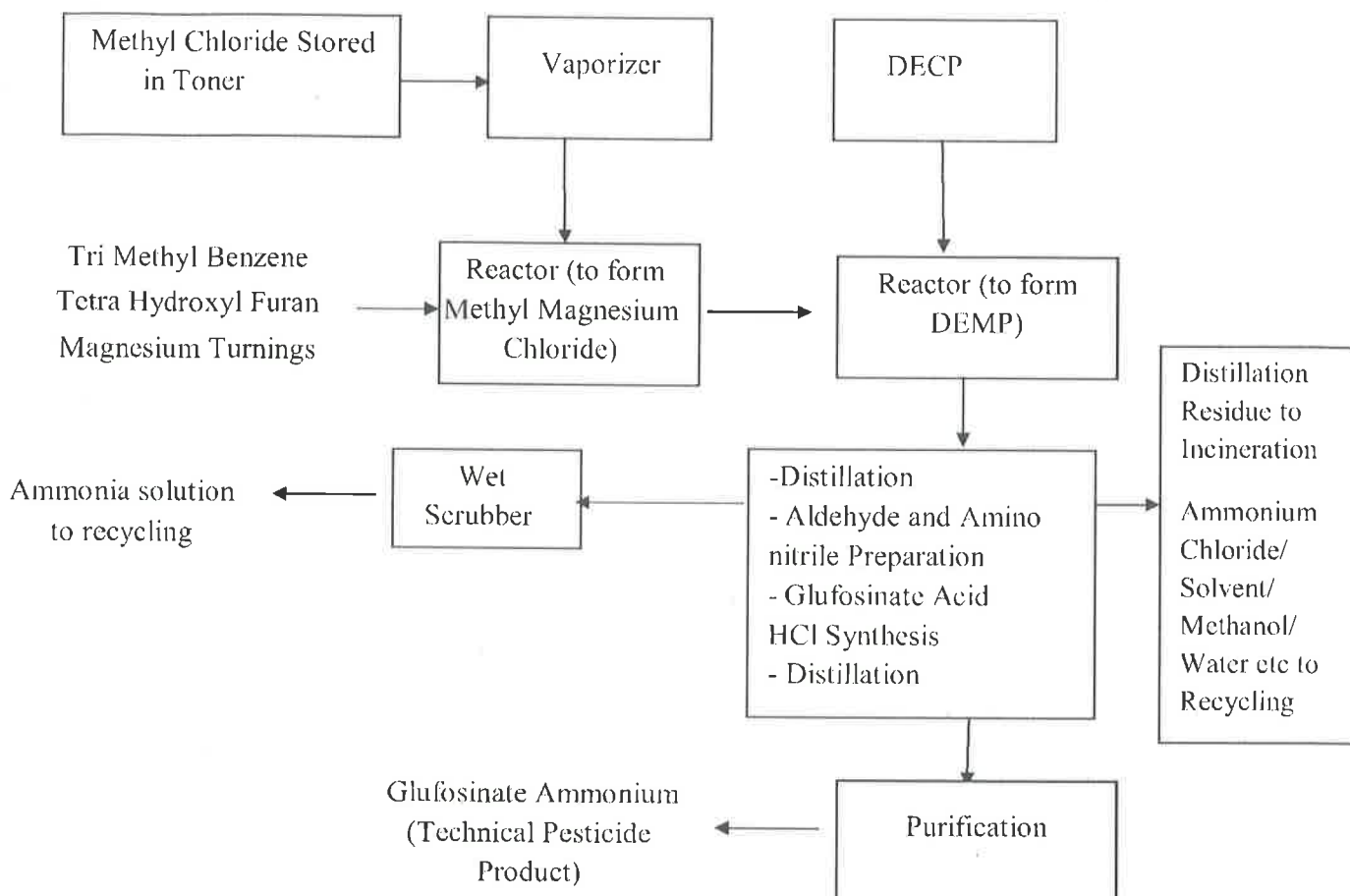


Figure: Process flow diagram for manufacturing of Glufosinate (Technical Pesticide Product).

114.3 Standard Operating Procedure for utilization:

This SOP is applicable only for Utilization of Spent Methyl Chloride (generated during manufacturing of Monocrotophos Pesticide products) in manufacturing of Methyl Magnesium Chloride i.e. Grignard reagent which is suitable in production of Glufosinate- pesticide technical finished product.

- 1) Spent Methyl Chloride shall be procured only in gas cylinders / tonner mounted over vehicles compliant to Motor Vehicles Act for transport of hazardous waste/substances, fitted with requisite safeguards to manage leakage of gas and other emergencies.
- 2) The spent methyl chloride shall be brought in tonner and stored in designated closed storage shed. The shed for storage of spent methyl chloride shall be provided with safety measures like Continuous automatic sensors / detectors for methyl chloride with alarm / hooter, fire alarm system, firefighting system and self-contained breathing apparatus (SCBA) and and gas venting arrangement.
- 3) Transfer of Spent Methyl Chloride from storage cylinder shall be carried out through dedicated fixed pipeline and leak proof pump.

- 4) Material transfer / handling in entire utilization process shall be done in closed system. Manual handling shall be strictly prevented.
- 5) The unit shall provide separate tanks for storage of chemicals and the storage tanks should be at designated place with proper cover, impervious floors and gas venting arrangement.
- 6) Unit shall obtain necessary permission from Petroleum & Explosives Safety Organization (PESO) for storage of methyl chloride.
- 7) As required in normal process (with or without using spent MC), the intermediate compound, methyl magnesium chloride is water-sensitive product that emits flammable gases upon contact with water or moisture, potentially igniting immediately. It is imperative to have necessary provisions to prevent any contact with water or moisture to mitigate the risk of fire.
- 8) As required in normal process (with or without using spent MC), nitrogen blanketing should be maintained in reaction vessel during manufacturing process of methyl magnesium chloride to eliminate the presence of oxygen.
- 9) The manufacturing Reaction vessel of methyl magnesium chloride shall be completely closed system and maintained under vacuum.
- 10) Adequate water scrubber to be installed to scrub ammonia fumes liberated during the utilization process.
- 11) The treated gases shall comply with emission norms prior to dispersion into atmosphere through stack. The stack height shall be a minimum of 30 m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 12) The unit shall maintain proper ventilation in the work zone and process areas. All personnel involved in the plant operation shall wear proper personal protective equipment (PPE) specific to the process operations involved and type of chemicals handled as per Material Safety Data Sheet (MSDS). The safety precautions of the worker shall be in accordance with the Factory Act, 1948, as amended from time to time.
- 13) Treatment and disposal of wastewater:
Wastewater generated from floor-washings, spillages, equipment washing, scrubber bleed shall be treated Physico-Chemically in an ETP or may be sent to CETP for final disposal or be treated further in a captive facility to comply with discharge standards as prescribed by SPCB/PCC. In case of zero discharge condition by SPCB / PCC, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB / PCC. The treated effluent shall be discharged in accordance with the conditions stipulated in the Consent to Operate issued by concerned SPCB / PCC under the Water (Prevention and Control of Pollution) Act, 1974.
- 14) The hazardous wastes namely the distillation residue generated shall be collected and temporarily stored in non-reactive drums / bags under a dedicated hazardous waste storage area and be sent to authorized common TSDF or Common Hazardous Waste

- Incineration Facility (CHWIF) for landfill / incineration as per pre-defined disposal pathway or Co-processing or other authorized facility within 90 days from generation of the waste in accordance with the authorization issued by the concerned SPCB / PCC. Such storage area shall be covered with proper ventilation.
- 15) It shall be ensured that the Spent Methyl Chloride is procured from authorized industries as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
 - 16) Transportation of Spent Methyl Chloride shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorization from the concerned SPCB under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.
 - 17) Prior to utilization of Spent Methyl Chloride, the unit shall obtain authorization for collection, storage and utilization of Spent Methyl Chloride from the concerned State Pollution Control Board under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
 - 18) In case of environmental damages arising due to improper handling of hazardous wastes including accidental spillage during generation, storage, processing, transportation and disposal, the occupier (sender or receiver, as the case may be) shall be liable to implement immediate response measures, environmental site assessment and remediation of contaminated soil / groundwater / sediment etc. as per the "Guidelines on Implementing Liabilities for Environmental Damages due to Handling & Disposal of Hazardous Wastes and Penalty" published by CPCB.
 - 19) During the process of utilization and handling of hazardous waste the unit shall comply with requirement in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable. The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
 - 20) The unit shall take requisite safety measures with respect to storage and handling of raw material, process intermediates, operation of reactors, etc. as per standard industry operations with requisite safety approvals from concerned agencies. This SOP is limited to utilization of spent CH_3Cl in place of raw CH_3Cl with the specified purity to produce Glufosinate pesticide (herbicide) without exceeding environmental norms in such process of utilization. The unit shall be responsible for ensuring product quality.

114.4 Product Usage / Utilization

- 1) The Glufosinate (Technical Grade Pesticide) produced by utilizing Spent Methyl Chloride shall only be used in Pesticide sector. The final product shall not be used in Food/Pharma/and Fertilizer products.
- 2) The Final product i.e. Glufosinate Ammonium soluble liquid shall comply with Bureau of Indian Standards (IS 15233), for further respective utilization.
- 3) The unit shall label its product i.e. Glufosinate (Technical Grade Pesticide) manufactured by utilizing Spent Methyl Chloride (generated during manufacturing of Monocrotophos Pesticide products) as "Produced utilizing Spent Methyl Chloride (generated during

manufacturing of Monocrotophos Pesticide products)".

114.5 Record>Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of spent Methyl chloride as mentioned below:
 - Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of Receipt in the premises
- 2) A log book within formation on source and date of procurement of Spent Methyl chloride, date wise utilization of the same, hazardous waste generation and its disposal, etc. shall be maintained including analysis report of fugitive emission monitoring & effluent discharged as applicable.
- 3) The unit shall maintain record of hazardous waste generated, utilized and disposed as per Form-3 & also file annual return in Form-4 as per Rule 20(1) and (2) of HOWM Rules, 2016, to concerned SPCB/PCC.
- 4) The unit shall submit quarterly and annual information on hazardous wastes consumed, its source, products generated or resources conserved (specifying the details like, type and quantity of resources conserved) to the concerned SPCB/PCC.
- 5) Each procurement, production and transportation details (alongwith quantity of hazardous waste generated, utilized & disposed) shall be maintained on the National Hazardous Waste Tracking System/ Vehicle Location Tracking System (VLTS).

114.6 Standards

- 1) The source emissions from stack connected to reaction vessel/ process unit shall comply with the following emission standards or as prescribed by concerned SPCB/PCC, whichever is stringent;

Parameters	Standards
PM	150 mg/Nm ³
Methyl chloride	20 mg/Nm ³
NH ₃	30 mg/Nm ³

- 2) Work zone emission in the work zone area shall comply with the following standards:

Parameters	Standards
PM ₁₀	5 mg/m ³ *(PEL)
Methyl chloride	100 ppm TWA
Acid Mist (as H ₂ SO ₄)	1 mg/m ³ , #

*PEL - Permissible Exposure Limit.

*Time-weighted average (TWA)- measured over a period of 8 hours of operation of process.

- A ceiling limit is one that may not be exceeded for any period of time, and is applied to irritants and other materials that have immediate effects.

- 3) Monitoring of the above specified parameters for source emission shall be carried out quarterly for first year followed by at least annually in the subsequent year of utilization. Fugitive emission for specified parameters shall be carried out quarterly. The monitoring shall be carried out by ISO 17025 accredited or EPA, 1986 approved laboratories and the results shall be submitted to the concerned SPCB/PCC on a quarterly basis.
- 4) Standard for wastewater discharge: Treated effluent shall be discharged in accordance with the conditions stipulated in Consent to Operate issued by concerned SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974. In case of (i) zero discharge as per consent or (ii) non-availability of the common Effluent Treatment Plant (CETP), the unit should achieve zero discharge by setting up adequate captive treatment facility.

114.7 Siting of Industry

Facilities for utilization of Spent Methyl chloride shall be preferably located in a notified industrial area or industrial park/estate/cluster and in accordance with Consent to Establish issued by the concerned SPCB/PCC.

114.8 Size of Plant and Efficiency of Utilisation

1 MT of Glufosinate (Pesticide technical Grade) is produced by using approximately 0.475 MT Methyl Chloride (purity around 99.98%).

Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

114.9 Online detectors/ Alarms/ Analysers

In case of continuous operations, online emission analyzers for PM in the stack shall be installed and the online data be connected to the server of concerned SPCB/PCC.

114.10 Safety measures for handling, storage and transportation:

I. Spent Methyl Chloride (Hazardous Waste):

a) For gas carrying vessel (toner)

1. Upon parking the truck in the unloading area, truck tyre shall be blocked with "wheel chock" to immobilize the vehicle and prevent any inadvertent movement during unloading.
2. Unloading of toner from truck shall be carried out by crane. Filled tonner should be labelled as 'filled' and stored in designated storage area.
3. Inspect the tag on tonner for Hydrostatic test due date, condition of tonner and functionality of valve.
4. Based on requirement, shift the tonner on load cell for further connection and transfer of Methyl Chloride to Reactor. Upon completion of the transferring activity, shift the tonner to the designated empty tonner area and label it as 'Empty'. Load 'Empty' marked tonner in truck (immobilized using "wheel chock") by crane.

b) Leakage



1. Evacuate the area, provide adequate ventilation and consider the risk of potentially explosive atmosphere.
2. Eliminate all ignition sources, if safe to do so and monitor the concentration of the released product.
3. Prevent the spilled material from entering sewers, basements and work pits, or any place where its accumulation can be dangerous.
4. Prevent further leakage/spillage if safe to do so.

c) Fire Safety

1. On catching fire, the toxic and/or corrosive fumes (Phosgene, Hydrogen Chloride, Carbon Monoxide) may be produced on thermal decomposition.
2. Stop the leakages, if safe to do so.
3. Do not extinguish flames at the leakage due to possibility of uncontrolled explosion/ re-ignition.
4. Carry out the continuous water spray from protected position until tonner stays cool.
5. Use extinguishers to contain the fire, isolate the source of the fire or let it burn out.

d) Personal Protective Equipment

1. Eyes – Face shield, goggles
2. Skin – PVC apron, fireproof suit
3. Lungs – Acid gas canister, gas mask, airline respirator, self-contained breathing apparatus

The unit shall have suitable First Aid arrangements such as water showers, removal of contaminated clothing and shoes, moving to fresh air area, oxygen kit, etc. along with contact of physician after first aid. Further, material Safety Data Sheet shall also be referred for hazards of methyl chloride

II. Methyl Magnesium Chloride (Intermediate Compound):

Unit shall take proper safety practices in process operations, as required in standard industrial process irrespective of utilizing spent MC or not. The following care should be taken in production of intermediate chemical compound MMC.

1. Methyl Magnesium Chloride (MMC) is a water sensitive product and emits flammable gases/catches fire when comes in contact with water / moisture.
2. Nitrogen blanketing should be maintained in reaction vessel during manufacturing process of methyl magnesium chloride to eliminate presence of oxygen.
3. Sampling of methyl magnesium chloride should be carried out in closed sampling system with nitrogen inertization.
4. Sample of MMC should be collected in glass bottle only.

5. Never allow MMC to get in contact with water.
6. Bottle should be tightly closed and stored away from heat and source of ignition.
7. PPEs like hand gloves, organic vapour mask, goggles, PVC apron should be used during handling of methyl magnesium chloride solution.
8. Dry residue of methyl magnesium chloride is explosive, never allow sample to get dry. MMC is highly reactive and can form explosive peroxides upon exposure to air. Regularly test for peroxide formation, especially before distillation, to mitigate the risk of explosion from its dry residue
9. Analysis of the material should be done by experienced person under supervision of competent supervisor.

114.11 Checklist of Minimal Requisite Facilities:

Sl. No	Particulars
1.	Dedicated storage area for storage of Spent Methyl chloride in tonner/ cylinder, with adequate leak evacuation and ventilation system.
2.	Mechanical transfer pumps with fixed pipeline for transportation and handling of Spent Methyl chloride.
3.	Analytical facilities so as to ensure the progress of the reaction and quality of the raw materials and product.
4.	Material transfer / handling in entire utilization process shall be done in closed system. Manual handling shall be strictly prevented.
5.	Gas leak detectors shall with alarm system should be installed in storage and process area.
6.	Closed system reactor, Distillation columns and with nitrogen blanket for Methyl Magnesium Chloride reactor
7.	Vaporizer with chilling system and steam supply followed by knockout pot with pressure, temperature transmitter and level switch.
8.	Distillation units for glufosinate acid synthesis purification.
9.	Wet Scrubber to scrub ammonia fumes liberated in the process (with or without utilizing spent MC).
10.	Stack of proper height as prescribed by SPCB with sampling port, platform, access to the platform etc. as per the guidelines on methodologies for source emission monitoring published by CPCB under Laboratory Analysis Techniques LAT5/80/2013-14.
11.	ETP for treatment of scrub liquor recovered process waste water to meet standards prescribed by SPCB or linkage with CETP.
12.	In case of continuous operations, online emission analyzers for PM in the stack shall be installed and the online data be connected to the server of concerned SPCB/PCC. Install OCEMS for treated wastewater as may be stipulated by SPCBs/PCCs

