

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 Hydrochloric Acid [generated during manufacturing of Cypermethric Acid Chloride (pesticide) & Chlorobenzene (synthetic organic chemical)] as a supplementary resource in production of Dicamba (pesticide/herbicide)



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Procedure for grant of authorization by State Pollution Control Boards (SPCBs)/Pollution Control Committees (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 utilization 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 similar to 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, waste oil, non-ferrous scraps, etc.) for maintaining records of receipt of hazardous waste for utilization.
 - f) Monitor closely the quantity of hazardous waste (spent HCl) being sent by generators and the quantity being utilized by authorized facilities in production of Dicamba.
- 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 at least 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 utilization 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 (if any generated during utilization) or its complete utilization or arrangement for transfer to 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 standard respectively, however, SPCBs/PCCs may impose more stringent standards based on the location or process specific conditions.
- 8) This SOP shall not be applicable for spent HCl generated from banned pesticides or in production of banned pesticides.
- 9) SPCBs/PCCs shall ensure that the utilizer of spent HCl shall maintain daily records in National Hazardous Waste Tracking System (NHWTS).

95.0 Utilization of Spent HCl:

Type of HW	Source of generation	Recovery/Product
Spent Hydrochloric Acid (HCl) 29.6 of Schedule-I & B-15 (Inorganic Acids) at Note 7 of Schedule II of HOWM Rules, 2016	During manufacturing of Cypermethric Acid Chloride (pesticide) & Chlorobenzene (synthetic organic chemical)	As a supplementary resource in production of Dicamba (Pesticide)

95.1 Source of Waste:

Spent HCl is generated during manufacturing of Cypermethric Acid Chloride (i.e. pesticide sector) is listed as hazardous waste at 29.6 of Schedule-I & Chlorobenzene (i.e. synthetic organic chemical sector) is categorized as hazardous waste at Category B-15 (Inorganic Acids) at Note 7 of Schedule II, HOWM Rules – 2016.

Table 1. Criteria Characteristics of Spent HCl are given below:

Sr. No.	Parameter	Unit	Value
1.	Free Chlorine	mg/L	0.05 – 6.06
2.	pH	-	<1
3.	TOC	%	0.06 – 0.07
4.	Purity of HCl	%	>30%
5.	Cadmium (Cd)	mg/L	0.023 – 0.033
6.	Chromium (Cr)	mg/L	0.065 – 0.072
7.	Copper (Cu)	mg/L	0.051 – 0.062
8.	Lead (Pb)	mg/L	0.156 – 0.205
9.	Manganese (Mn)	mg/L	0.028 – 0.096
10.	Mercury (Hg)	mg/L	< 0.08
11.	Zinc (Zn)	mg/L	0.024 – 0.253

95.2 Utilization Process

The production of Dicamba involves several stages such as preparation of (i) Dichlorophenol, (ii) Dipotassium Salt of 3,6-Dichlorosalicylic Acid (DCSA K₂ Salt), (iii) Methyl chloride preparation and (iv) Dicamba ester preparation. As per trial studies, the stages where spent HCl can be utilized in preparation stages of Methyl Chloride and Dicamba.

Spent HCl and Methanol is reacted to generate Methyl Chloride. Methyl Chloride is condensed and collected. Unreacted spent HCl is used for acidification in subsequent step of Dicamba preparation.

For preparation of Dicamba Methyl Ester, Di potassium salt is methylated by Methyl Chloride. KCl is generated during the reaction is filtered out and washed with Methanol followed by drying to sell as product. Methyl Ester and Methanol Solution is taken for Methanol recovery followed by Dicamba Methyl Ester recovery. Dicamba Methyl Ester thus obtained is further taken for Dicamba Preparation.

Dicamba Preparation: Dicamba Methyl Ester is hydrolysed with NaOH in aqueous medium to get Na- Dicamba, which is further acidified with spent HCl to get Dicamba. Aqueous layer is separated and molten Dicamba layer is washed with water to get rid of chlorides. Washed molten Dicamba layer is dehydrated to remove the trapped water. Dehydrated Dicamba is flaked and packed.

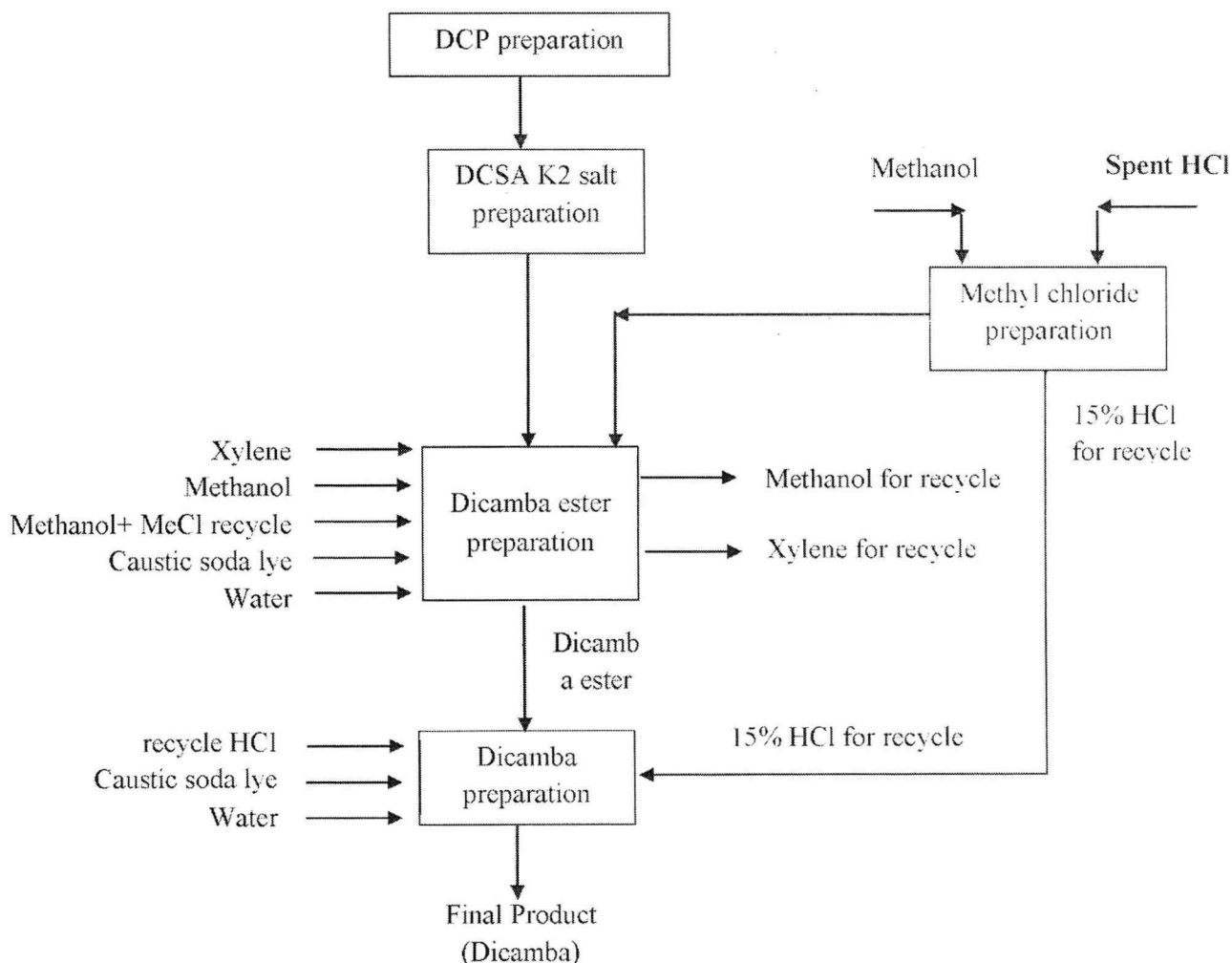


Figure: 1-Process flow diagram for utilization of spent HCl in production of Dicamba.

95.3 Product Usage / Utilization

1. Spent Hydrochloric acid (HCl) shall be used as supplementary resource in place of fresh acid in production of Dicamba (3, 6-Dichloro-2-methoxy benzoic acid), a herbicide.
2. The unit shall label its product i.e. Dicamba manufactured by utilizing afore said Spent HCl as "This Dicamba has been manufactured by utilizing Spent HCl (generated during manufacturing of pesticide & synthetic organic chemical)".

95.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of Spent Hydrochloric Acid (generated during manufacturing of Cypermethric Acid Chloride (pesticide) & Chlorobenzene (synthetic organic chemical) for manufacturing of Dicamba.

- 1) The Spent HCl shall be procured only in SPCB/PCC authorized barrels/closed tanks mounted over vehicles fitted with requisite safeguards ensuring no spillage of the acid.
- 2) Spent HCl shall be stored in HDPE/FRP or mild steel tank and kept in acid proof brick lined dyke under shed above the ground. The unit shall provide slope and collection pit in storage area. The unit shall install storage tanks under cool, dry, well ventilated covered storage

shed(s) within premises, as authorized by the concerned SPCB/PCC under HOWM Rules, 2016.

Further, the storage area of Spent HCl acid shall have leak-proof floor tiles with adequate slope to collect spillage, if any, into a collection pit. The spillage from collection pit shall be transferred to ETP, as the cases may be, through chemical process pump.

- 3) There shall be no manual handling of the Spent Hydrochloric acid. The feeding of Spent HCl shall be done through closed loop pipelines using dedicated transfer pump.
- 4) The unit shall provide pre-treatment facility for spent HCl to reduce the TOC <100mg/l.
- 5) Alkali/Wet scrubber shall be provided to the process vent (where Spent HCl acid is utilized) to treat the emissions liberated from the reactors. Also, the vent of Spent Hydrochloric Acid storage tanks shall be connected to the alkali scrubber through a common header.
- 6) The treated gases/fumes shall comply with emission norms prior to dispersion into atmosphere through stack. The stack height shall be minimum of 30m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 7) Treatment and disposal of wastewater:

Wastewater generated from floor-washings, spillages, reactor washing, scrubber bleed shall be treated Physico-Chemically in an ETP to comply with surface water discharge standards or may be sent to CETP for final disposal.

In case of zero discharge, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB/PCC.

- 8) 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.
- 9) The hazardous wastes generated (namely the chemical sludge, MEE residue, etc.) 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 other authorized facility within 90 days from its generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC. Such storage area shall be covered with proper ventilation.
- 10) It shall be ensured that the Spent HCl is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 11) Transportation of Spent Hydrochloric Acid shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorization from the concerned SPCB/PCC under HOWM Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.
- 12) Prior to utilization of Spent Hydrochloric Acid, the unit shall obtain authorization for storage, utilization and disposal of Spent Hydrochloric Acid from the concerned SPCB/PCC under HOWM Rules, 2016.
- 13) 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.

- 14) 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.
- 15) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 16) 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.

95.5 Record/Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of spent acid 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 logbook with information on source and date of procurement of Spent HCl, 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 an 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) The unit shall use NHWTS to manage the manifest, enter daily records of quantity generated, disposed, etc.

95.6 Standards

- 1) Source emissions from the stack connected to reactors/process unit shall comply with the following Emission standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

Particulate matter	50 mg/Nm ³
HCl mist	20 mg/Nm ³
Methyl Chloride	20 mg/Nm ³



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

PM ₁₀	5 mg/m ³ TWA
HCl mist	7 mg/m ³ #
Benzene	10 ppm TWA

*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 shall achieve zero discharge by setting up adequate captive treatment facility.

95.7 Siting of Industry

New facilities for utilization of Spent Hydrochloric Acid 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. This may not apply to the facilities already engaged in production of Dicamba and have obtained CTE/CTO.

95.8 Size of Plant and Efficiency of Utilization

1 MT of Dicamba is produced by using approximately 0.5 MT of spent Hydrochloric Acid (of purity around 30-34%).

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

95.9 On-line Detectors / Alarms / Analyzers

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

95.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1.	Storage tanks of adequate capacity to store Spent Hydrochloric Acid. Such storage tanks shall be placed above the ground and contained with low rise parapet/bund wall and acid proof floor with slope to collect spillages, if any, in to collection pit.
2.	Cool, drywell-ventilated covered sheds for Spent Hydrochloric Acid storage tanks, product storage tanks and process activities within premises and dedicated hazardous storage area for temporary storage of hazardous waste generated during utilization process.

3.	Mechanized system for transfer of Spent Hydrochloric Acid from storage tanks to process unit.
4.	Pumps, pipes, feeder and equipment for mechanical handling of Spent Hydrochloric Acid.
5.	Pre-treatment facility for spent HCl to reduce the TOC <100mg/l.
6.	Suction ducting with hoods, connected to alkali/wet scrubbing system for safe venting of process / fugitive emissions.
7.	pH sensor for scrubbing media with hooter/alarm system
8.	Dryer/ Granulator with adequate APCM preferably bag filters shall be provided, if the product is required to be converted in powder form.
9.	Stack to have 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 LATS/80/2013-14.

