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/Distillation of Dilute Acetic Acid (generated from Pharmaceutical/ Pesticide/Chemical Sector) as resource material for manufacturing of Acetic Anhydride or Glacial Acetic Acid

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Central Pollution Control Board
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Procedure for grant of authorization by SPCBs/PCCs for utilization of Hazardous waste

1) While granting authorisation for utilization of hazardous wastes, SPCBs/PCCs shall ensure that authorisation is given only to those wastes for which SoPs for utilisation have been circulated by 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. Authorisation 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.

2) After issuance of authorization, SPCB shall verify the compliance of checklist and SoP on quarterly basis for initial 2 years; followed by random checks in the subsequent period for atleast once a year.

   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.

3) SPCBs 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 website, periodically. Such updated list shall be sent to CPCB on a half yearly basis i.e., by July and January respectively.

4) Authorisation for utilisation shall not be given to the units located in the State/UT 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.

5) 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.

6) The source and work zone standards suggested in the SoP are based on the E(P)A notified and OSHA standard respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions.

63.0 Utilization of Dilute Acetic Acid:

Type of HW/OW	Source of generation	Recovery/Product
Dilute Acetic Acid (Schedule-I, Cat-26.3/ 29.6/Schedule-II Class B 15 Inorganic acids (of HOWM Rules, 2016)	Generated from Manufacturing of Pharmaceutical/Pesticide/Chemical Industry	Dilute Acetic Acid is used along with Fresh Acetic Acid for manufacturing of Acetic Anhydride to reduce quantity of fresh acetic acid required for manufacturing of Acetic Anhydride/ Preparation of Glacial Acetic acid

Utilization/Distillation of Dilute Acetic Acid (generated from Pharmaceutical/ Pesticide/Chemical Sector) as resource material for manufacturing of Acetic Anhydride or Glacial Acetic Acid

63.1 Source of Waste

Dilute Acetic Acid (25-30% acidity) generated from manufacturing process of Pharmaceutical/Pesticide/Chemical Industry are categorized as hazardous waste at Cat-26.3/ 29.6 of Schedule-I, / Class B 15 Inorganic acids of Schedule-II of HOWM Rules, 2016, that can be utilised as resource.

Typical characteristics of Dilute Acetic Acid (25-30% acidity) are presented at as below:

Table 1- Characteristics of Dilute Acetic Acid (25-30% acidity)

Sr. No.	Parameter	Unit	Pharmaceutical
1	Appearance		Light Brown
2	pH		<1
3	Purity	%	38.19
4	TOC	%	20.8
5	Chloride as Cl	ppm	146
6	Copper as Cu	mg/Kg	0.08
7	Zinc as Zn	mg/Kg	0.082
8	Iron as Fe	mg/Kg	0.18
9	Nickel as Ni	mg/Kg	0.098
10	Lead as Pb	mg/Kg	0.012
11	Moisture content by KF	%	18.39
12	Ethyl Acetate	%	0.02

63.2 Utilization Processes

Hazardous waste Dilute Acetic Acid (25-30% acidity) and dilute acetic acid generated internally from furnace during anhydride manufacturing process is mixed and diluted to 20 % acidity and then extracted with ethyl acetate in extraction column. Extract phase (Ethyl Acetate + Acetic Acid) is separated out using atmospheric distillation. Acetic acid is recovered from extract phase in recovery column and recovered dilute acetic acid (20 % acidity) is sent to furnace followed by absorption column and distillation column for recovery of product i.e. Acetic Anhydride. Acetic acid recovered from this section is further used as raw material for anhydride generation section.

The Product Acetic Anhydride is manufactured from Acetic Acid in three stages.

In first stage, Acetic Acid is cracked at high temperature under vacuum in a furnace in presence of catalyst Tri Ethyl Phosphate (TEP) and ammonia (inhibitor) producing Ketene gas and water.

$$\underset{\text{(Acetic Acid)}}{CH_3COOH} \longrightarrow \underset{\text{(Ketene)}}{CH_2=CO} + H_2O$$

In Second stage, Ketene is absorbed in glacial acid in absorption section, producing crude Acetic Anhydride.

$$\underset{\text{(Ketene)}}{CH_2=CO} + \underset{\text{(Acetic Acid)}}{CH_3COOH} \longrightarrow \underset{\text{(Crude Acetic Anhydride)}}{(CH_3CO)_2O}$$

In third stage, Crude Anhydride is distilled out in Distillation section under vacuum to get pure Anhydride (99.5 %).

63.3 Product Usage / Utilization

Hazardous waste i.e. Dilute Acetic Acid shall be used along with fresh acetic acid for manufacturing of Acetic Anhydride. Final product i.e. Acetic Anhydride is widely use as acetylating agent or in chemical synthesis.

63.4 Standard Operating Procedure for utilization

This SoP is applicable only for Utilization/Distillation of Dilute Acetic Acid (generated from (Acetylation Process from Pharmaceutical Sector) as resource material for manufacturing of Acetic Anhydride.

1) The Dilute Acetic Acid shall be procured only in SPCB/PCC authorised barrels/closed tanks mounted over vehicles fitted with requisite safeguards ensuring no spillage of the same.

   Hazardous waste i.e. Dilute Acetic Acid (DAA) from generator shall be transported in dedicated tanker and stored in tank. DAA is pumped from this tank to DAA feed tank for extraction, Extraction Column (adding Ethyl Acetate), Furnace, Absorption, Distillation, Acetic Anhydride as Product.

2) Dilute Acetic Acid shall be stored in either HDPE or rubber lined steel tank and kept in acid proof brick lined dyke under shed. Unit shall provide slope and collection pit in storage area.

   Hazardous waste i.e. Dilute Acetic Acid (DAA) shall be transported from the external unit through dedicated tankers and after checking the require documentation and quality parameter this was allowed to unload in dedicated storage tank in the tank unloading area. DAA was unloaded from closed tanker to the closed storage tank directly through hose pipe

3) There shall be no manual handling of the Dilute Acetic Acid. Diluted Acetic Acid shall be unloaded from the closed tanker to the storage tank by using nitrogen gas pressurization technique and using dedicated transfer pump. Spill containment arrangement shall be provided around the Dilute Acetic Acid storage tanks.

4) The storage and handling of Dilute Acetic Acid shall be done under a shed of proper vertical height and over imperviously lined flooring.

5) 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 Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016, .

   Further, the storage area of Dilute Acetic 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.

6) The unit shall provide separate storage tanks for storage of chemicals and the storage tanks should be at designated place with proper cover and with acid brick lining floors.

7) The treated gases shall comply with emission norms and prior to dispersion into atmosphere through stack. The height of stack shall be a minimum of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.

8) 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.

9) Treatment and disposal of wastewater:

   Wastewater generated from floor-washings, spillages, reactor washing, scrubber bleed including the wastewater from filtration 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 surface water discharge standards.

   Wastewater Standard for treated effluent from ETP shall be prescribed in Consent to Operate issued 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.

10) 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.

11) The hazardous wastes generated (namely the Process residue, ETP Sludge, Corrosive waste , waste insulation material , Contaminated aqueous waste phase, Spent Solvent , Distillation 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 MEE 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.

12) It shall be ensured that the Dilute Acetic Acid are procured from the industries, which have valid authorization from the concerned State Pollution Control Board as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.

13) Transportation of Dilute Acetic Acid shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorisation 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.

14) Prior to utilization of Spent Dilute Acetic Acid, the unit shall obtain authorisation for generation, storage and utilization of Dilute Acetic Acid from the concerned State Pollution Control Board under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.

15) 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.

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

17) 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.

63.5 Record/Returns Filing

1) The unit shall maintain a passbook issued by concern SPCB wherein the following details of each procurement of Dilute Acetic Acid shall be entered:
   - 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 with information on source and date of procurement of Dilute Acetic Acid, date wise utilisation 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 utilised, hazardous waste generated and disposed as per Form 3 & shall file annual returns in Form 4 as per Rule 20 (1) and (2) of the Hazardous and Other Wastes (Management and Transboundary Movement) 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.

63.6 Standards

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

Parameters	Standard
PM	50 mg/Nm^3
SO_2	100 ppm
NO_x	50 ppm
Acid Mist (CH_3COOH)	50 mg/Nm^3

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

Parameter	Standards
PM_{10}	5 mg/m^3 TWA* (PEL)
Acid Mist (CH_3COOH)	25 mg/Nm^3

 # PEL. Permissible Exposure Limit

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

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 NABL or EPA 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 respective SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974. In case of zero discharge or no discharge condition stipulated in the said consent or non-availability of the Common Effluent Treatment Plant (CETP), zero discharge shall be met.

63.7 Siting of Industry

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

63.8 On-line detectors / Alarms / Analysers

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

63.9 Checklist of Minimal Requisite Facilities

S.No.	Particulars
1.	Storage tanks of adequate capacity to store Dilute Acetic 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. Alternately, the storage tanks may be below the ground provided it has HDPE liner system beneath the tank and leachate collection system below HDPE liner.
2.	Cool, dry well-ventilated covered sheds for Dilute Acetic Acid storage tanks, product storage tanks and process activities within premises and dedicated hazardous storage area for temporary storage ofhazardous waste generated during utilization process.
3.	Mechanized system for transfer of Dilute Acetic Acid from storage tanks to Distillation Column or Extractor.
4.	The process units shall have suction hood. (The suction hood shall be connected with alkali scrubber and stack of adequate height)
5.	Spare vessel to transfer the reaction mass, if any, in case of leakage or damage to the Distillation Column or Extractor.
6.	Pumps, pipes, feeders and other equipment for mechanical handling ofDilute Acetic Acid.
7.	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.
8.	Furnace, Absorption Column, Distillation Column, External Column, Condenser, Recovery Column, Chiller.
9.	ETP Plant
10.	Connection of vent of all the dilute acetic acid storage tanks be connected to condenser.
11.	VOC absorption media connected to vent of condenser

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