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 sulphuric acid generated during manufacturing of Hydrobromic acid (HBr) as resource material for manufacturing of Bromine (liquid) through bittern route

June, 2021

Central Pollution Control Board

(Ministry of Environment, Forest & Climate Change, Government of India)

Parivesh Bhawan, East Arjun Nagar,

Shahdara, Delhi – 110032

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 on 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 spent acid 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/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 & Trans-boundary 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.

65.0 Utilization of Spent Sulphuric Acid

Type of Hazardous Waste	Source of Generation	Recovery/ Product
Spent Sulphuric acid (Schedule – II Class B 15 Inorganic acids of HOWM Rules, 2016)	Manufacturing of Hydro bromic acid (HBr)	For the production of liquid Bromine through bittern route

65.1 Source of Waste

Spent Sulphuric acid is generated during manufacturing process of Hydro Bromic Acid (HBr) is categorized as Hazardous waste as per Schedule – II Class B 15 Inorganic acids of HOWM Rules, 2016 which are required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource material. The said waste can be utilized as resource material for the production of liquid Bromine through bittern route.

Table 1: Characteristics of Spent Sulphuric acid

S. No.	Parameters	Unit	Typical characteristics
1	pH	--	Around 0.86
2	Appearance	--	Clear Liquid
3	% Purity	%	48
4	TOC	%	ND
5	Fluoride	%	ND
6	Heavy Metals	%	ND

65.2 Utilization Process

The utilization of process involves Bromine rich bittern & sulphuric acid, which are pumped into acidification reactor where acidification takes place. The acidified bittern is chlorinated thereby bromine is liberated which is continuously stripped out using stripper in which steam is used. Bromine is recovered through condensation & separation followed by purification. The entire production process takes place in closed system.

The de-brominated hot effluent generated from the stripping process is utilized to preheat acidified bittern in the process and then sent to ETP. Generated vapours during condensation and separation stage are vented through caustic scrubber followed by vent.

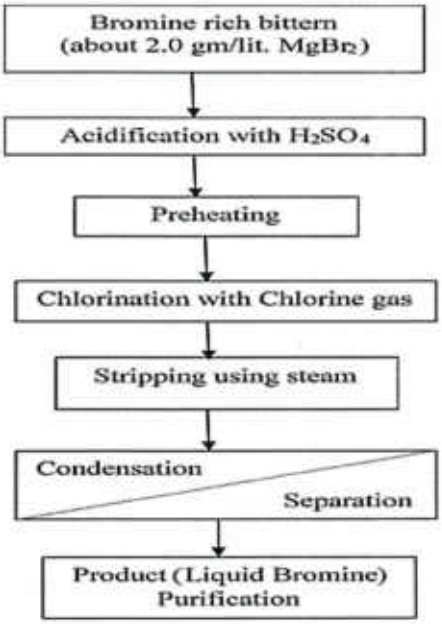

Fig-1: Utilization process of spent sulphuric acid

65.3 Product Usage/Utilization

The liquid bromine shall be utilized in pesticides and other chemical industries only. It should not be utilized in Pharmaceuticals and food industries.

The product i.e. liquid bromine shall comply with Bureau of Indian Standards IS : 2142 (1992) for use as technical grade chemical except pharma/food grade.

The unit shall label its product (i.e. Liquid bromine) manufactured by utilizing aforesaid hazardous waste as "This liquid bromine has been manufactured by utilizing spent sulphuric acid generated during manufacturing of Hydrobromic acid".

65.4 Standard Operating Procedure for Utilization

This SoP is applicable only for utilization of spent sulphuric acid (Generated from Hydrobromic acid-HBr) in acidification process of manufacturing of bromine through bittern route.

1) The spent sulphuric acid shall be transported in SPCB/PCC authorized tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the same.
2) There shall be a designated space for unloading of spent sulphuric acid into the acid proof storage tank. The receiving storage tank shall be placed above the ground and contained with low raise parapet/bund wall with slope to collect spillages, if any, into collection pit. Alternatively, storage tanks for spent sulphuric acid may be kept below the ground provided it has HDPE liner system beneath the tank and leachate collection system below HDPE liner. In the event of leachate detection in the leachate collection system, corrective measures shall be taken immediately.
3) The unit shall install storage tank under cool, dry, well ventilated covered storage shed(s) within premises, as authorized by the concerned SPCB / PCC under Hazardous and Other Wastes (Management & Trans-boundary Movement) Rules, 2016, so as to eliminate rain water intrusion.
   Further, the storage area shall have leak-proof, acid resistant floor tiles with adequate slope to collect spillage, if any, into a collection pit. The spillage from collection pit shall be transferred to reaction tanker or ETP, as the cases may be, through chemical process pump.
4) There shall be no manual handling of the spent sulphuric acid. Acid Proof pump shall be used for transfer of spent sulphuric acid through pipelines to acidification process vessel/reactor.
5) TOC of spent sulphuric acid shall be less than 100 ppm for utilization.
6) The vent of spent sulphuric acid storage tanks shall be connected to scrubber for treatment using alkaline medium.
7) 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 proof brick lining floors.
8) Sulphuric acid mist and vapours are expected to be liberated from the reactors, where the spent sulphuric acid is added. Thus, the said reactors shall be connected with hood over it to

suck acid fume/vapour. The hood shall be maintained under suction followed by treatment in scrubber using alkaline medium.

9) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within the unit.
10) 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 Factories Act, 1948, as amended from time to time.
11) In case of environmental damages arising due to improper handling of hazardous wastes including accidental spillage during generation, storage, processing, transportation and disposal, the unit 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.
12) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
13) During the process of utilization and handling of hazardous waste, the unit shall comply with the requirements in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable.
14) SPCBs/PCCs shall ensure synchronization of generation and utilization of spent sulphuric acid and the same shall be reflected in respective authorization specifying name and quantity.
15) The treated effluent shall be discharged in accordance with the conditions stipulated in the Consent to Operate (CTO) issued by respective SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974.

65.5 Record/Returns Filing

1) The unit shall maintain a passbook issued by concern SPCB wherein the following details of each procurement of spent sulphuric 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 spent sulphuric acid quantity, 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 utilized, 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 Trans-boundary Movement) Rules, 2016, to concerned SPCB/PCC.

4) The unit shall submit quarterly and annual information on hazardous wastes utilized, its source, products generated or resources conserved (specifying the details such as, type and quantity of resources conserved) to the concerned SPCB.

65.6 Standards

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

Sulphuric acid Mist & vapours (H_2SO_4)	1.0 mg/m^3 TWA* 3 mg/m^3 STEL#
Chlorine (Cl_2)	1 ppm
Bromine (Br_2)	0.1 ppm

**time-weighted average (TWA): measured over a period of 8 hours of operation of process.*
 # Short Term Exposure Limits
(Reference: Occupational Safety and Health Standards 1910: 1000);

2) Source emission monitoring stack attached to Condensation / separation Process vented through alkali scrubber shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

Particulate Matter	150 mg/Nm^3
NOx	50 ppm
SOx	100 ppm
Sulphuric Acid / vapour Mist (H_2SO_4)	50 mg/Nm^3

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 accredited or ISO17025 / EPA approved laboratories and the results shall be submitted to the concerned SPCB/PCC on a quarterly basis.

65.7 Siting of Industry

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

65.8 Size of Plant and Efficiency of Utilization

1 MT of spent sulphuric acid (conc. 48 %) would be required to produce 1.01 MT of liquid bromine. Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

65.9 On-line detectors / Alarms / Analysers

Online emission monitoring system shall be installed with the data transmission to CPCB and SPCB server in case of continuous process operations for PM and H_2SO_4 vapour and mist.

65.10 Check List of Minimal Requisite Facilities

Sr. No.	Particulars
1.	Storage tank(s) of adequate capacity to store spent sulphuric acid of at least two weeks requirement. Such storage tank(s) shall be placed above the ground and contained with low raise parapet/bund wall and acid proof floor with slope to collect spillages, if any, into collection pit. Alternately, the storage tank(s) 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 storage shed(s) for spent sulphuric acid storage tanks within premises.
3.	Mechanized system for transfer of Spent Sulphuric Acid from tankers to storage tanks to reactor vessels.
4.	The process shall have proper ventilation (preferably with ventilation ducts above the process units).
5.	Acidification Reactors with suction hood connected via duct to scrubber and stack of adequate height as prescribed by concerned SPCB/PCC.
6.	Preheaters
7.	Stripping Column
8.	Distillation Column
9.	Adequate Effluent treatment plant so as to comply with standards/conditions prescribed by the concerned SPCB/PCC. Reverse Osmosis & Forced Evaporator (in case of zero discharge condition by SPCB/PCC)
10.	Stack of height as prescribed by SPCB/PCC with easy access to port hole, for conducting stack monitoring
11.	On-site Emergency plan as approved from Industrial Health & Safety Department
12.	On-line analyzers for PM & H_2SO_4 vapour and mist emission monitoring in stack

*****