

**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 Alkali Bromide and Spent Acidic Bromide generated
during manufacturing of various pesticides, pharmaceuticals and organic
chemicals for recovery of liquid Bromine
(Revised)**



December, 2019

Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change, Government of India)
Parivesh Bhawan, East Arjun Nagar,
Shahdara, Delhi – 110032

A handwritten signature in blue ink, located in the bottom right corner of the page.

Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

Procedure for grant of authorisation 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) should have similar source of generation as specified in SoPs.
 - b. The utilization process should be similar to the process of utilization described in SoPs.
 - c. End-use / product produced from the waste shall be same as specified in SoPs.
 - d. Authorisation shall be granted only after verification of utilization process and minimum requisite facilities installed as given in SoPs.
 - e. Issuance of passbooks (similar to the passbooks issued for recycling of used oils, waste oil, non-ferrous scraps, etc.) for maintaining records of receipt of hazardous wastes for utilization.
- 2) After issuance of authorization, SPCB shall verify the utilization process, checklist and SOPs on quarterly basis for during the initial 02 years; followed by random checks in subsequent period for at least once in every 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) SPCB/PCCs shall provide half yearly updated list of units permitted under Rule 9 of Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 (HOWM Rules) 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 SoPs are based on the E(P)A notified and OSHA standards respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions

48.0 Utilization of Spent Ammonium Chloride:

Type of HW	Source of generation	Recovery/Product
Spent Alkali Bromide and Spent Acidic Bromide (Category no. C2, C4 of Schedule II and 29.1 & 28.1 of Schedule I of HOWM Rules, 2016)	During manufacturing of pesticides, pharmaceuticals and organic chemicals	Liquid Bromine

Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

48.1 Source of Waste

The Spent Alkali bromine (KBr, NaBr and NH₄Br) and Spent Acidic bromide (HBr) are generated during the manufacturing of pharmaceuticals, pesticides and organic chemicals. Typical Characteristics of the waste (NaBr, KBr, NH₄Br & HBr) is given below:

S No	Characteristics	NaBr	K Br	NH ₄ Br	HBr
1.	Physical State	Liquid	Liquid	Liquid	Gas
2.	Color	Colorless	Colorless	Colorless	Colorless
3.	pH	6.5-8.5	6.5-8.5	6.5-8.5	< 2
4.	Odor	Odorless	Odorless	Pungent	Odorless
5.	Chemical Composition	NaBr – 25 %, Water – 73 %, Inorganic impurities like NaCl, NaNO ₃ , CaCl ₂ & Organic impurities – 2%	KBr – 25 % Water – 73 % Inorganic impurities like NaCl, NaNO ₃ , CaCl ₂ & Organic impurities – 2 %	NH ₄ Br – 20 % Water – 78 % Inorganic impurities like NaCl, NaNO ₃ , CaCl ₂ & Organic impurities–2%	HBr – 30 % Water – 68 % Inorganic impurities like NaCl, NaNO ₃ , CaCl ₂ & Organic impurities–2%

The aforesaid Spent Alkali Bromide and Spent Acidic Bromide is categorised as Hazardous waste at S. No. C2, C4 of Schedule II and 29.1 & 28.1 of Schedule I of HOWM Rules, 2016 which are required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

48.2 Utilization Process

Spent Alkali Bromide is mixed with water to reduce specific gravity and make it 50% concentration, so as to avoid choking of the reactor. The diluted spent alkali bromide is transferred to Reactor, where it is acidified with HCl (30%) to de-emulsify the organic impurities present in the waste. The organic impurities/residues from the bottom of the reactor is collected in drums and stored for disposal in TSDF.

Acidified alkali bromide solution is fed to stripping column (packed column) over the top of the column, whereas chlorine gas and steam (65 °C) is passed from beneath the column. During the above process chlorine reacts with alkali and liberates Bromine as vapours by using steam. Vaporised bromine passes through condensers to get crude bromine liquid. The acidic effluent generated from the reaction column is sent to ETP for further treatment.

Crude bromine is further subjected to distillation to remove traces of organic impurities and chlorine. Organic impurities generated from the distillation column is collected and stored for disposal in TSDF. Chlorine recovered from the distillation column is reused in the stripping column. Bromine is again passed through Sulphuric acid (98 %) and is re-boiled for drying (moisture removal). The pure bromine is bottled in small amber colour bottles or collected in tanks. The flow diagram of utilization process of spent alkali bromine is shown in Figure 1.

Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

In case of recovery of liquid bromine from Spent Acidic Bromide, the utilization process includes pretreatment, bromine recovery and post treatment stages, however acidification process in the pretreatment stage may not be applicable.

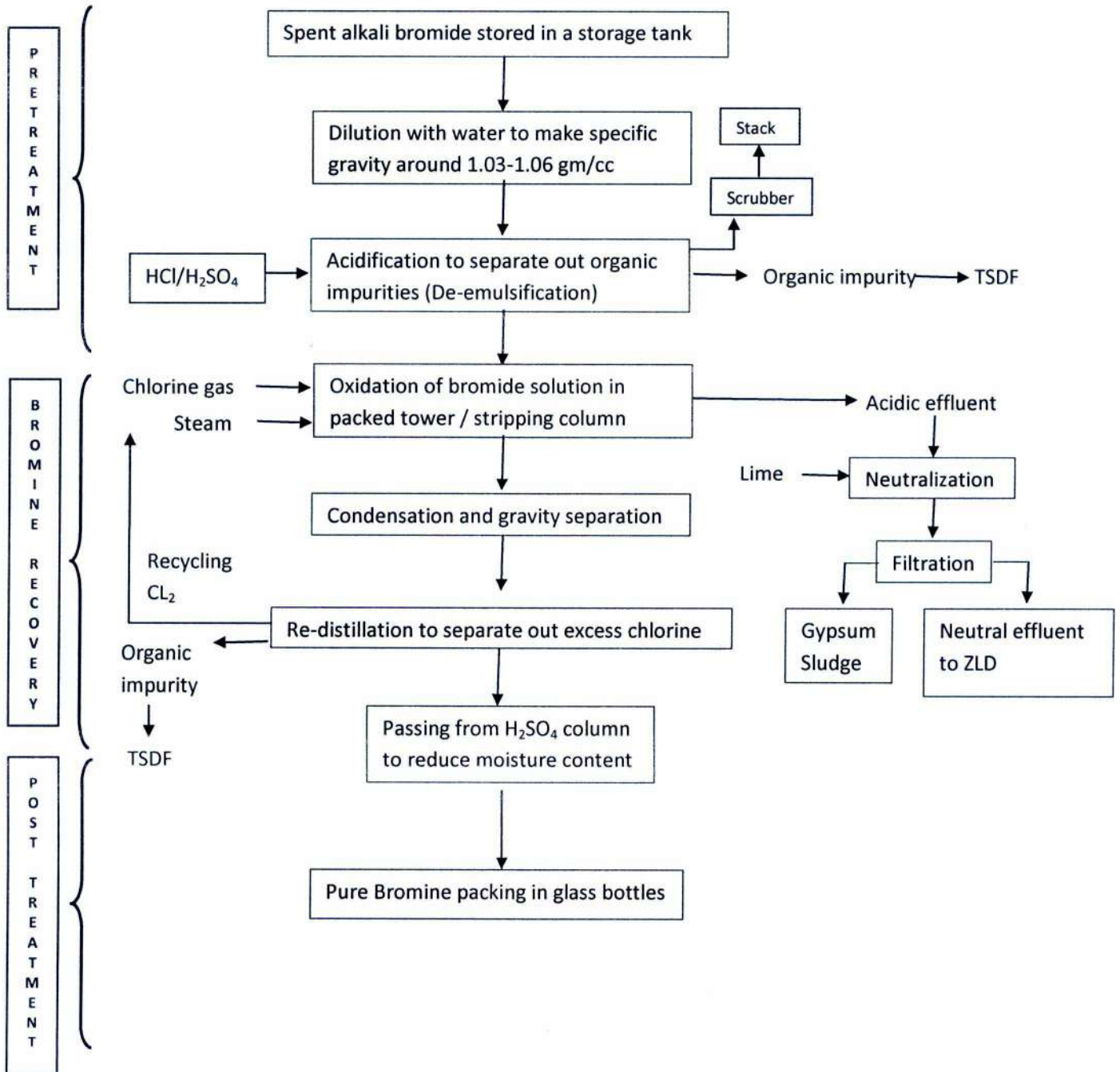


Figure 1: Flow diagram of Utilization of Spent Alkali Bromide for manufacturing of Liquid Bromine



Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

48.3 Product Usage / Utilization

The liquid bromine shall be utilised in pesticides and other organic chemical industries.

The product i.e. liquid bromine shall comply with the Bureau of Indian Standard: BIS for use as a 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 Alkali Bromide and Spent Acidic Bromide, generated from pharmaceuticals, pesticides and organic chemicals manufacturing process."

48.4 Standard Operating Procedure for utilization

This SoP is applicable only for the utilization of Spent Alkali bromine and Spent Acidic Bromide generated during manufacturing of pharmaceuticals, pesticides and organic speciality chemicals.

- 1) The Spent Alkali bromine and Spent Acidic Bromide shall be transported in SPCB/PCC authorized anti-corrosive tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the same.
- 2) There shall be a designed space for unloading of Spent Alkali bromine and Spent Acidic Bromide in to the 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. The storage area shall have 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 & Transboundary Movement) Rules, 2016 so as to eliminate rain water intrusion.
- 4) There shall be no manual handling of the hazardous wastes (Spent Alkali bromide and Spent Acidic Bromide) chemical process pump shall be used for transfer of Spent Alkali bromide and Spent Acidic Bromide through pipelines to the acidification reactor, stripping column etc.
- 5) The entire process area 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 or reaction tank, as the cases may be, through chemical process pump.
- 6) The acidification reactor shall be a closed system to avoid release of acid mist to the atmosphere. Vent ducts of the acidification reactor be connected to caustic scrubbing system followed by dispersion through stack.
- 7) Vent of all storage tanks shall be connected to scrubber for treatment using appropriate medium.



Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

- 8) 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.
- 9) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within the unit.
- 10) The wood/ briquette fired boiler shall be connected to stack of height 30 meters above the roof top or at height prescribed by SPCB/PCC, whichever is higher.
- 11) Spent Alkali bromide and Spent Acidic Bromide shall be transferred to all the process units like stripping column followed by multi-distillation column through closed loop system to avoid escape of chlorine gas and Bromine to the atmosphere. The vents connected to stripping column shall be attached to caustic scrubbing system followed by dispersion through stack.
- 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 MSDS. The safety precautions of the worker shall be in accordance with the Factories Act, 1948, as amended from time to time.
- 13) It shall be ensured that the aforesaid hazardous waste is procured from the industries, which have valid authorization for the same from the concerned State Pollution Control Board as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
- 14) SPCBs/PCCs shall ensure synchronization of generation and utilization of Spent Alkali bromide and Spent Acidic Bromide and the same shall be reflected in respective authorization specifying name and quantity.
- 15) Transportation of Spent Alkali bromine and Spent Acidic Bromide shall be carried out by sender or receiver (utilizer) only after obtaining authorisation from the concerned SPCB under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- 16) Prior to utilization of Spent Alkali Bromide and Spent Acidic Bromide, the unit shall obtain authorization for generation, storage, and utilization of spent Alkali bromide and Spent Acidic Bromide solution from the concerned State Pollution Control Board under the Hazardous and Other Wastes (Management and Transboundary Movement) Rules 2016.
- 17) Treatment and disposal of wastewater:
Wastewater generated from stripping column, floor washing, spillages, reactor washing, scrubber bleed, boiler blow down, etc. shall be treated physio-chemically in ETP followed by suitable treatment so as to meet inlet norms of CETP, through technologies like Advance Oxidation Process (AOP) or Reverse Osmosis (RO) or Multi Effect Evaporator (MEE). In case, CETP is not available, condition of Zero Liquid Discharge (ZLD) be enforced by SPCB/PCC.

Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

- 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 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.
- 19) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 20) The hazardous wastes generated (namely the organic residue from acidification reactor, organic residue from distillation column, residue from the acidic effluent storage tanks, gypsum/filter cake from the filter press after neutralisation of the effluent, salt from the forced evaporation process, scrubber residue, process 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 generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC. Such storage area shall be covered with proper ventilation.
- 21) 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.

48.5 Record>Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB wherein the following details of each procurement of Spent Alkali bromine and Spent Acidic Bromide 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 Alkali bromide and Spent Acidic Bromide, quantity, date wise utilisation of the same, quantity of Liquid bromine manufactured, hazardous waste generation and its disposal, etc. shall be maintained including analysis report of 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.



Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

48.6 Standards

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

HCl	7.0 mg/m ³ Ceiling limit
Cl ₂	1 ppm Ceiling limit
Br ₂	0.1 ppm Ceiling limit

Reference: Occupational Safety and Health Standard 1910:1000

TWA: time-weighted average*

The permissible Exposure Limit is 8-hours TWA

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.

2) Source emission monitoring from the stack attached to the Acidification reactor and forced evaporators shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

HCl vapour & Mist	35.0 mg/Nm ³
HBr	5.0 mg/Nm ³
NH ₃	30.0 mg/Nm ³
TOC	20.0 mg/Nm ³
Chlorine	15.0 mg/Nm ³

3) Monitoring of the specified parameters for source emission shall be carried out quarterly for the 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.

4) Standards for wastewater discharge: The condensate shall be discharged to CETP in accordance with the conditions/norms stipulated in the 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.

48.7 Siting of Industry

Facilities for utilization of Spent Alkali bromide and Spent Acidic Bromide 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.

48.8 Size of Plant & Efficiency of utilisation

12.5 MT of Spent Alkali bromide would be required to produce 1 MT of liquid bromine. Therefore, requisite facilities of adequate size of storage shed and other plants & machineries as given in para 48.10 below shall be installed accordingly.

Utilization of Spent Alkali Bromide and Spent Acidic Bromide generated during production of pharmaceuticals, pesticides & Organic chemicals for production of liquid Bromine

48.9 On-line detectors / Alarms / Analysers

Online emission monitoring systems shall be installed with data transmission to CPCB and SPCBs server in case of continuous process operations for HCl vapour and mist and ammonia mist.

48.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1	Storage tank(s) of adequate capacity to store spent alkali bromide of at least two weeks requirement. Storage tank(s) 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 may be provided with HDPE liner system beneath the tank and leachate collection system below HDPE liner.
2	Cool, dry, well-ventilated covered storage shed(s) for Spent Alkali bromide and Spent Acidic Bromide storage tanks within premises.
3	Mechanized system for transfer of Spent Alkali bromide and Spent Acidic Bromide from tanker to storage tank and storage tank to the each unit operation.
4	The process units shall have proper ventilation (preferably with ventilation ducts above the process units connected to ID fan with exhaust above roof level)
5	Acidification Reactor
6	Stripping column
7	Distillation column
8	Filter Press
9	Cooling tower
10	Boiler operated electrically or by fuel as permitted by the concerned SPCB/PCC. Depending upon type of fuel, suitable air pollution control device(s) shall be installed with the boiler followed by stack of height as prescribed by the concerned SPCB/PCC.
11	Suction arrangement to suck vapours from suction hood system provided over acidification reactor, stripping column, bromine bottling section and for channelizing the fumes to the vent followed by stack.
12	Adequate Effluent treatment plant followed by suitable treatment to meet inlet norms of CETP, through technologies like Advance Oxidation Process (AOP) or Reverse Osmosis (RO) or Multi Effect Evaporator (MEE). In case, CETP is not available zero discharge conditions as prescribed by the concerned SPCB/PCC shall be met.
13	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.
14	Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process.

