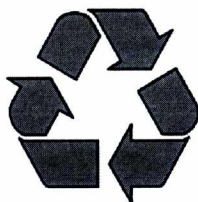


Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule 9 of the Hazardous and Other Wastes (Management and Transboundary movement) Rules, 2016

Utilization of Spent Acid Containing Molybdenum generated during manufacturing of filaments in bulb/lamp Industry



cpcb

March, 2017

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

Vineet

Procedure for grant of authorisation by SPCBs/PCCs for utilization of Hazardous Waste

- (i) While granting authorisation for utilization of hazardous wastes, SPCBs/PCCs shall ensure the following:
 - a. The waste (intended for utilization) belongs to similar source of generation as specified in Standard Operating Procedures (SoPs).
 - b. The utilization process is 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 be granted only after verification of utilization process and minimum requisite facilities as given in SoPs.
 - e. Issuance of passbooks (similar to the passbooks issued for recycling of used oil, waste oil, non-ferrous scrap, etc.) for maintaining records of receipt of hazardous wastes for utilization.
- (ii) After issuance of authorization, SPCB/PCC shall verify the utilization process, checklist and SOPs on quarterly basis for initial 2 years; followed by random checks in the subsequent period for at least once a year.
 In-case of lack of requisite infrastructures with the SPCB/PCC, they may engage 3rdparty institutions or laboratories having EPA/NABL/ISO17025 accreditation/recognition for monitoring and analysis of prescribed parameters in SoPs for verification purpose.
- (iii) SPCBs/PCCs shall provide half yearly updated list of units permitted under Rule 9 of HOWM Rule, 2016 to CPCB and also upload the same on SPCB website, periodically. Such updated list shall be sent to CPCB half yearly by July and January respectively.
- (iv) 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.
- (v) In case 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.
- (vi) The source and work zone standards suggested in the SoPs 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.

26.0 Utilization of Spent Sulphuric Acid:

Type of HW	Source of generation	Recovery/Product
Spent acid containing Molybdenum (Category: A67 of Class-A and Class C2 of schedule-II of HOWM Rules, 2016)	Bulb filament manufacturing industries	Ammonium Molybdate

26.1 Source of Waste

Spent acid containing Molybdenum is generated during manufacturing of filaments in bulb/lamp industry. In this process, the molybdenum wire (coiled with tungsten filament wire) is dissolved in a mixture of concentrated sulphuric acid and 68% nitric acid in a reactor. The resulting liquor containing 5 – 7 % molybdenum is generated as spent acid containing molybdenum. This waste is categorised as

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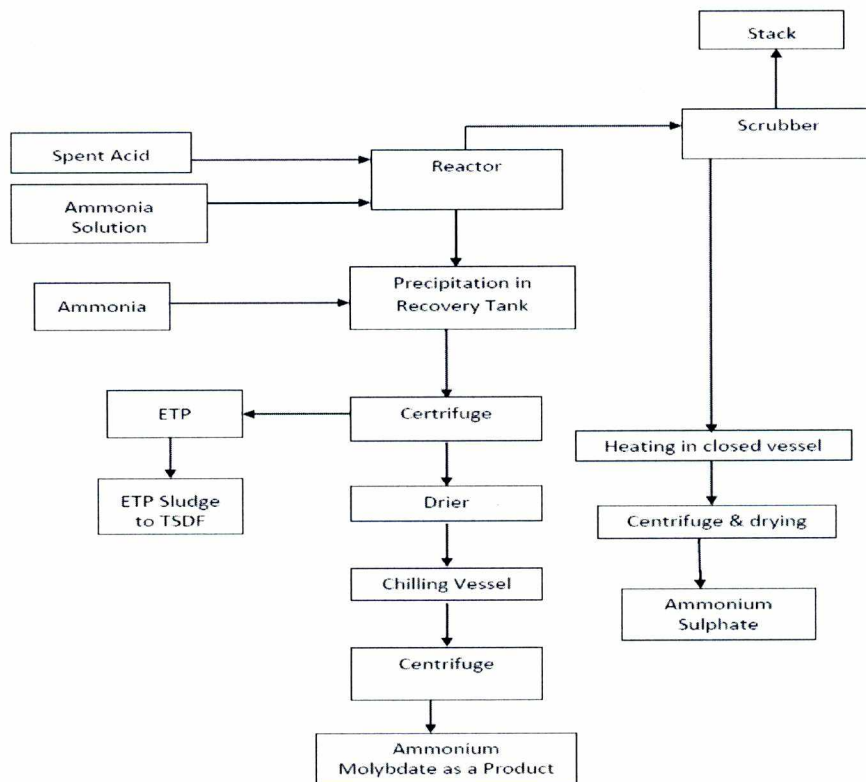
hazardous waste category # A67 of Class-A and Class C2 of schedule-II of HOWM Rules, 2016. This hazardous waste is required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

26.2 Process of utilization

In this utilization process, ammonia solution (25%) is added slowly to spent acid containing molybdenum (free from nitric acid) in a reactor with continuous stirring until desired pH is reached. The reaction is carried out for about 3-4 hours until precipitation takes place and then allowed for settling within reactor for about 8 hours. Ammonical fumes liberated during the process is scrubbed in scrubber using sulphuric acid as scrubbing medium. The supernatant liquor (Containing Ammonium Sulphate) is transferred to a storage tank while the slurry containing Molybdic acid along with residual mother liquor is taken for recovery.

The slurry is reacted with excess Ammonia in recovery tank to obtain Ammonium Molybdate. The slurry precipitate at this stage is centrifuged and washed with water and then transferred to electrically heated tray dryer (made of stainless steel or any equivalent suitable material) maintaining a temperature of about 70°C for about 2.5 hours followed by transferring to chilling vessel for cooling with the help of water circulation. The material is thereafter centrifuged to obtain Ammonium Molybdate as product.

The supernatant liquid from the reactor and bleed water from scrubber are subjected to heating in closed vessel followed by centrifuging and drying to obtain Ammonium Sulphate as by product. Whereas washed liquor from centrifuge, floor washings and incidental discharges are treated in an Effluent Treatment Plant (ETP).



26.3 Product Usage / Utilization

Ammonium Molybdate recovered from above process can be used as a catalyst in Pharmaceutical industry.

26.4 Standard Operating Procedure for utilization

This SOP is applicable only for utilization of Spent acid containing Molybdenum generated from bulb filament manufacturing industries to produce Ammonium Molybdate by adhering the following;

- (1) Spent acid containing Molybdenum shall be transported in SPCB/PCC authorised acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the same.
- (2) The receiver shall ensure that Spent acid containing Molybdenum shall be free from nitric acid. The traces of Nitric Acid present in Spent Acid, if any, should be removed by heating in a separate reactor, prior to utilization, for removal of nitric acid. A separate scrubber followed by stack shall be installed to treat NOx generated during heating process.
- (3) There should be a designated space for unloading of Spent acid containing Molybdenum into a rubber lined storage tank(s). The receiving storage tank shall be placed above the ground and contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, into collection pit. Alternatively, storage tanks for Spent Sulphuric acid may be 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.
- (4) The unit shall install the storage tank(s) under cool, dry, well-ventilated covered storage shed(s) within premises, as authorized by the concerned State Pollution Control Board/Pollution Control Committee under Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016 so as to eliminate rain water intrusion.
- (5) There shall be no manual handling of the hazardous wastes (Spent acid containing Molybdenum). Chemical process pump shall be used for transfer of Spent acid containing Molybdenum through pipelines to the reaction vessel.
- (6) The entire process area shall have leak-proof and acid proof floor tiles with adequate slope to collect spillages, if any, into a collection pit. The spillages from collection pit shall be transferred to ETP or reaction tanks, as the cases may be, through chemical process pump.
- (7) The vent of Spent Acid storage tanks shall be connected to scrubber.
- (8) The unit shall ensure basic safety equipment/Personal Protective Equipment during handling and transportation. Spills involving hazardous waste should first be contained to prevent spread of the material to other areas. This may involve the use of temporary diking, sand bags, dry sand, earth or proprietary booms / absorbent pads etc. as per the

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Emergency Response Plan (in accordance with "Guidelines on Implementing Liabilities for Environmental Damages due to Handling & Disposal of Hazardous Wastes and Penalty" published by CPCB)

- (9) Ammonia is expected to be liberated from the reactor. Thus, the said reactor shall be connected with fume suction hood over it to suck acid fume/vapour. The hood shall be maintained under suction followed by treatment in scrubber using sulphuric acid as scrubbing medium.
- (10) The treated acid fume/vapour shall comply with emission norms and shall be dispersed into atmosphere through stack of height as prescribed by the concerned SPCB/PCC.
- (11) 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) such as Chemical goggles, full-face shield, or a full-face respirator, Impervious gloves of chemically resistant material (rubber or neoprene), Body suits, aprons, and/or coveralls of chemical resistant material and impervious boots of chemically resistant material.

- (12) Sources of wastewater

The following are the sources of wastewater from utilization process;

- a) The supernatant liquor from reactor
- b) Bleed from scrubber
- c) Washed liquor from centrifuge
- d) Floor washing/reactor wash/incidental discharges, etc.

- (13) Treatment and disposal of wastewater:

The supernatant liquid from the reactor and bleed water from scrubber are subjected to heating in closed vessel followed by centrifuging and drying to obtain Ammonium Sulphate as by product. Whereas washed liquor from centrifuge, floor washings, incidental discharges, etc. are treated in an Effluent Treatment Plant (ETP).

The ETP consists of holding tank/pH adjustment tank and settling tank. Ammonia gas released during lime neutralization in pH adjustment tank shall be channelized to the aforesaid scrubber unit for recovery of Ammonia in the form of Ammonium Sulphate as by product.

The treated wastewater shall be discharged in accordance with the conditions 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 has been stipulated in the said Consent or non-availability of the Common Effluent Treatment Plant (CETP), zero discharge shall be met by evaporation (single or multi effect evaporator) of treated water.

- (14) It shall be ensured that Spent acid containing Molybdenum compound is procured from the industries who have valid authorization for the same from the concerned SPCB/PCC as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.

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- (15) The residue generated (viz. ETP sludge and residue from scrubber) 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 having proper ventilation.
- (16) Prior to utilization of spent sulphuric acid, the unit shall obtain authorization for generation, storage and utilisation of Spent sulphuric acid from the concerned State Pollution Control Board under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (17) 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.
- (18) 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.

26.5 Records/Return filing

- (1) The unit shall maintain a passbook issued by concerned SPCB/PCC wherein the following details of each procurement of Spent Acid containing Molybdenum 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 each type of the said hazardous wastes, quantity, date wise utilization of the same, quantity of Ammonium Molybdate 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, residues 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 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.

26.6 Standards

Waste Management Division, CPCB Delhi

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- (1) Emissions from stack connected to reaction tank and scrubber shall comply with following standards or as prescribed by SPCB/PCC, whichever is stringent.

SO ₂	:	50mg/Nm ³
Sulphuric Acid mist	:	50 mg/Nm ³
NO _x	:	50 mg/Nm ³
Ammonia	:	75 mg/Nm ³

Note: Other parameters as prescribed by SPCB/PCC, if any, shall be complied

- (2) Fugitive emissions in the work zone shall comply with following standards

Sulphuric acid	:	1 mg/m ³ TWA*, 3 mg/m ³ STEL*
Nitric acid	:	5 mg/m ³ TWA*
Ammonia	:	35 mg/m ³
NO ₂	:	9 mg/m ³ ceiling limit
SO ₂	:	13 mg/m ³ TWA*

* Time-weighted average (TWA), Short-term exposure limits (STEL).

The Permissible Exposure Limit is 8-hour TWA.

Reference: Occupational Safety and Health Standards 1910:1000);

A short-term exposure limit (STEL) is the acceptable average exposure over a short period of time, usually 15 minutes as long as the Time weighted average is not exceeded.

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 specified parameters for fugitive 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 by NABL accredited or ISO17025/EPA recognized laboratories and the results shall be submitted quarterly to the concerned SPCB/PCC.

26.7 Siting of Industry

Facilities for processing of Spent acid containing Molybdenum should preferably 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.

26.8 Size of Plant and Efficiency of utilisation

The plant with processing of about 1000 litres of spent acid containing about 5% molybdenum shall produce a minimum of 120 kg of Ammonium Molybdate. Therefore, requisite facilities of adequate size of storage tank and other plant and machineries as given in Para 26.10 below shall be installed accordingly.

26.9 On-line detectors / Alarms / Analysers

Online detectors/alarms/analysers shall be installed in case of continuous process operations for acid mist and ammonia emissions in the stack.

26.10 Checklist of Minimal Requisite Facilities

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S.No	Requisite Facilities
1.	Storage tank(s) of adequate capacity to store Spent acid containing Molybdenum of at least two weeks requirement. Such storage tank(s) shall be placed above the ground and contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, into collection pit. Alternatively, 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 acid containing Molybdenum storage tanks within premises.
3.	Earmarked unloading area (for transfer of Spent acid containing Molybdenum from tanker) contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, to collection pit.
4.	Acid proof pumps for transferring of Spent acid containing Molybdenum tanker to storage tank and reactor.
5.	Mechanical means for transferring of acids/liquid chemicals to the reaction vessels
6.	Acid-proof and leak-proof floor tiles in entire working area with adequate slope to collect spillages, if any.
7.	Collection pit for collection of spillages from aforesaid working area and unloading area.
8.	Reactor(s) of adequate size with mechanised stirrer. Reactor(s) shall have fume suction hood connected to scrubber. The hood shall be maintained under suction through ID fan.
9.	Scrubber (with sulphuric acid as scrubbing medium) with fume suction hood over reactor(s) connected to stack of height as of height as prescribed by the concerned SPCB/PCC.
10.	Stacks 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.
11.	Centrifuge
12.	Electrically heated dryer (made of stainless steel or any equivalent suitable material)
13.	Crystallizer with water circulating jacket.
14.	Closed vessel with electrically heating arrangement for heating of supernatant liquid from the reactor and bleed water from scrubber to obtain Ammonium Sulphate as by product.
15.	Effluent treatment plant of adequate capacity with provision of channelizing Ammonia gas (released during lime neutralization in pH adjustment tank) to the aforesaid scrubber unit
16.	Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process
