

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 from Dye & Dye Intermediates & Organic Chemical Industries) in manufacturing of Ferrous/Copper/Zinc Sulphate



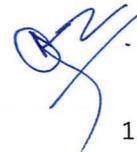
December, 2022

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

Utilization of Spent Sulphuric acid (generated from Dye & Dye Intermediates & Organic Chemical Industries) in manufacturing of Ferrous/Copper/Zinc Sulphate

Procedure for grant of authorization by State Pollution Control Boards (SPCBs)/Pollution Control Committee (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 utilisation have been circulated by Central Pollution Control Board (CPCB) ensuring the following:
 - a. The waste (intended for utilization) belongs to same source of generation as specified in SoP.
 - b. The utilization shall be same 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.
- 2) After issuance of authorization, SPCBs/PCCs shall verify the compliance of checklist and SoP on quarterly basis for initial 2 years; followed by random checks during subsequent period for atleast once a year. The compliance reports shall be submitted to CPCB by July every year.
- 3) In-case of lack of requisite infrastructures with the SPCBs/PCCs, they may engage 3rd party institutions or laboratories having EPA, 1986/NABL/ISO 17025 accreditation / recognition for monitoring and analysis of prescribed parameters in SoP 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 on half yearly basis i.e., by July and January respectively.
- 5) Authorization 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.
- 6) In case of the utilization proposal is not same 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 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.



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83.0 Utilization of Spent Sulphuric Acid:

Type of HW	Source of generation	Recovery/Product
Spent sulphuric acid (Category 26.3 of Schedule-I and B-15 & C2 of Schedule II of HOWM Rules, 2016)	Generated from: (i) Dye & Dye Intermediates (ii) Organic Chemical Industries	Ferrous/Copper/Zinc Sulphate

83.1 Source of Waste:

Spent sulphuric acid generated from dye & dye intermediates & organic chemical industries falls under Category 26.3 of Schedule-I and B-15 & C2 of Schedule II of HOWM Rules – 2016 respectively. It is essential that COD of spent sulphuric acid shall be less than 18,000 mg/l for the purpose of utilization as per this SoP.

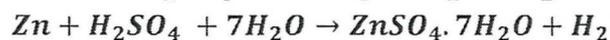
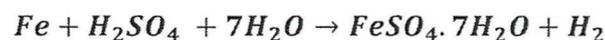
Table 1. Criteria Characteristics of spent sulphuric acid:

S. no.	Parameter	Unit	Range
1.	Strength	%	>50
2.	Insoluble Matter	mg/lit	<90
3.	TOC	mg/lit	<6700
4.	COD	mg/lit	<18000

83.2 Utilization Process

The utilization process involve addition of iron/copper/zinc scrap/powder to spent sulphuric acid of specific concentration in a reaction vessel. If required, fresh sulphuric acid may also be added, as per the requirement to maintain desired specific gravity. Total reaction time is approx. 6-7 hours. After completion of reaction, reaction mass is to be transferred to filter press and filtrate is collected and sent for self-crystallization. After crystallization, product crystals are separated from mother liquor and washed with water in centrifuge. The mother liquor and washing waste water are reused to next batch.

Chemical reaction inside reactor:



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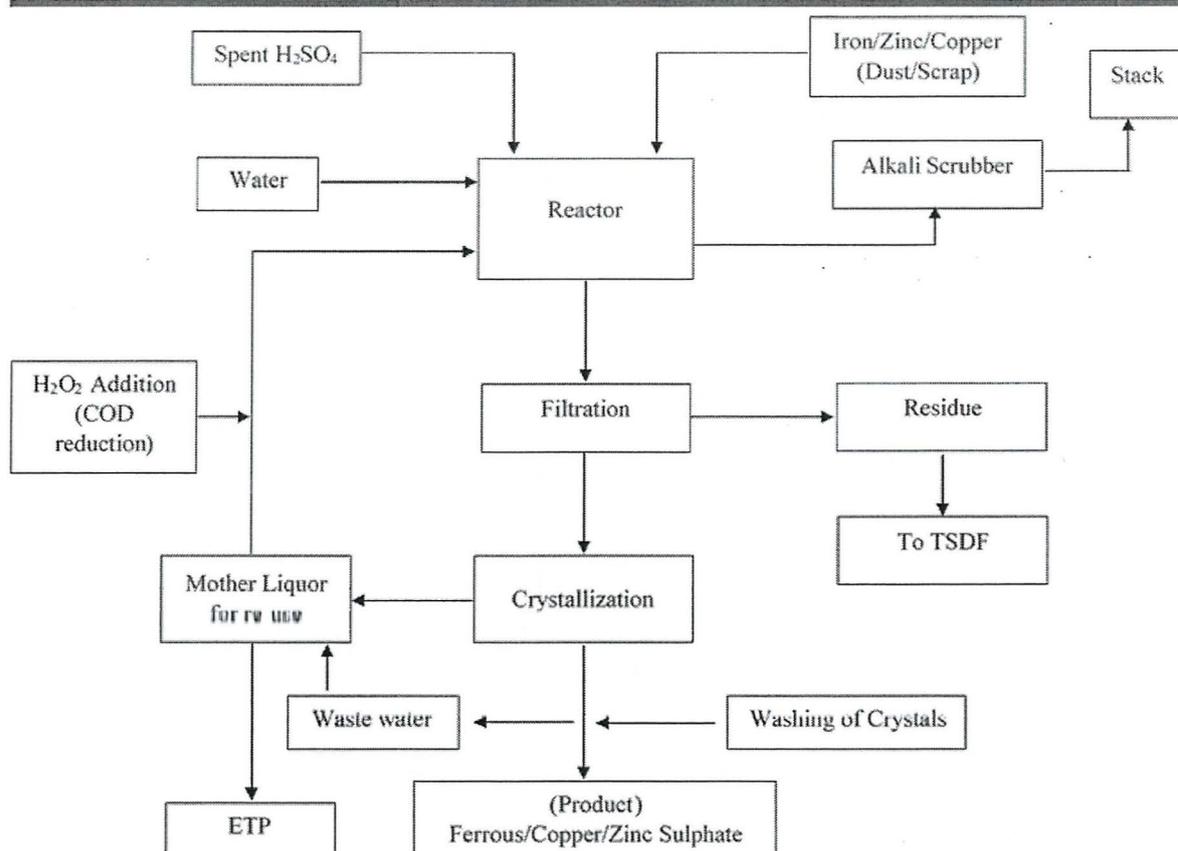


Figure: 1-Process flow diagram for utilization of spent sulphuric acid.

83.3 Product Usage / Utilization

1. Ferrous/Copper/Zinc Sulphate manufactured by utilizing spent sulphuric shall be utilized for industrial purposes. Recovered material shall not be permitted for use in drinking water treatment (as FeSO_4 -coagulant), fertilizer/agro-soil, food and pharma industries.
2. Recovered material shall meet quality criteria as specified in IS: 262 – 1982 for Ferrous Sulphate; IS: 261 – 1982 for Copper sulphate and IS: 8249 (1994) for Zinc sulphate.
3. Recovered products shall not be permitted for use as fertilizer or additive to agriculture soil.
4. The unit shall label tankers and bags carrying its products manufactured by utilizing spent sulphuric acid as *“This Ferrous/Copper/Zinc Sulphate has been manufactured by utilizing spent sulphuric acid (generated from Dye & Dye Intermediates/Organic chemical industries)”*.

83.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of spent sulphuric acid (generated from dye & dye intermediates & organic chemical industries) in manufacturing of Ferrous/Copper/Zinc Sulphate.

- 1) The spent sulphuric acid shall be procured only in closed tankers mounted over vehicles fitted with requisite safeguards ensuring no spillage of the acid. The vehicles should be registered with SPCBs/PCCs.

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- 2) Spent sulphuric acid shall be stored in designated HDPE/MS tanks and kept in acid proof brick lining floors with closed bund area by acid resistance brick wall.
Further, the storage area of spent sulphuric 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 Effluent Treatment Plant (ETP), as the cases may be, through chemical process pump.
- 3) There shall be no manual handling of the spent sulphuric acid at any stage of utilization process.
- 4) Spent sulphuric acid shall be unloaded from the closed tanker to the storage tank through pipelines using dedicated transfer pump.
- 5) Feeding of spent sulphuric acid from storage tanks to reaction vessel shall be done through closed loop pipelines using dedicated transfer pump.
- 6) The complete manufacturing process shall be a closed system, with alkali scrubbers connected to storage and reaction area. The iron/copper/zinc scrap/powder should be transferred in closed system like closed conveyor belts or screw conveyors.
- 7) The treated gases shall comply with emission norms prior to dispersion into atmosphere through stack. The stack height shall be a minimum of 30 m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 8) 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.
In case of zero discharge, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB/PCC.
- 9) Hydrogen Peroxide shall be added for treatment of Mother Liquor after every batch to reduce COD. Once COD stops decreasing or remains constant, mother liquor may be reused in the process. Excess Mother Liquor should be sent to ETP for neutralization.
- 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 (filter cake, ETP Sludge, 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.
- 12) The unit shall ensure that the spent sulphuric acid is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.

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- 13) Transportation of spent sulphuric 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.
- 14) Prior to utilization of spent sulphuric acid, the unit shall obtain authorization for storage, utilization and disposal of spent sulphuric acid from the concerned SPCB/PCC under HOWM Rules, 2016.
- 15) 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.
- 16) 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.
- 17) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 18) 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.

83.5 Record>Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of spent sulphuric 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 log book with information on source and date of procurement of spent sulphuric acid, 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 annual returns in Form 4 as per Rule 20 (1) and (2) of the HOWM Rules, 2016, to concerned SPCB/PCC.



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- 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.

83.6 Standards

- 1) Source emissions from the stack connected to process units (reaction vessel/scrubber) stack shall comply with the following Emission standards or as prescribed by the concerned SPCB/PCC, whichever is stringent:

Particulate Matter	150 mg/Nm ³
SO ₂	100 mg/Nm ³
NO _x	50 mg/Nm ³
H ₂ SO ₄ Acid Mist	50 mg/Nm ³

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

PM ₁₀	5 mg/m ³ TWA* (PEL)
SO ₂	13 mg/m ³ TWA* (PEL)
NO _x	9 mg/m ³ #
H ₂ SO ₄ Acid Mist	1 mg/Nm ³

**PEL - Permissible Exposure Limit; # - Ceiling 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.

83.7 Siting of Industry

Facilities for utilization of spent sulphuric 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.

83.8 Size of Plant and Efficiency of Utilisation

Utilization of 0.44 Kg of spent sulphuric acid may yield 1 Kg of Ferrous Sulphate. Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly. Records of specific utilization of spent sulphuric acid for production of copper and zinc sulphates should be maintained.

83.9 On-line Detectors / Alarms / Analyzers

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

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83.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1.	Spent H ₂ SO ₄ storage tank (s) with acid proof rubber lining having minimum storage capacity of at least two week's consumption.
2.	The storage tank shall be placed above the ground and contained with low raise bund wall & acid proof floor with slope to collect spillages into collection pit.
3.	Chemical process pump to transfer Spent H ₂ SO ₄ from tanker to storage tank and then to reaction tank
4.	The entire process area shall be made of leak-proof and acid proof floor tiles with adequate slope to collect spillages. into collection pit.
5.	Collection pit for collection of spillages from the working and unloading area.
6.	Adequate Storage facility for acids and Iron/Copper/Zinc scrap/powder.
7.	Reaction tank shall be connected with suction hood above the feeding point (of waste scrap/powder). The suction hood shall be connected with alkali scrubber and stack.
8.	Filter press
9.	Crystallizer unit (open tanks, jacketed crystallizers, crystallizers with evaporators, etc.)
10.	Centrifuge
11.	Drying unit (hot air dryer of adequate size attached with scrubber and stack)
12.	Effluent treatment plant comprising of neutralization, coagulation & sedimentation.
13.	ETP Sludge handling unit (Filter/Centrifuge/ Sludge drying bed etc.)
14.	Covered hazardous waste storage area to store filter cake, residue from scrubber and ETP sludge in HDPE bags/drums.
15.	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.

