

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 the manufacturing of Pesticides, Dyes and Dye intermediate, Fertilizer and Organic chemicals manufacturing industries) in production of Magnesium Sulphate



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**Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change,
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Utilization of Spent Sulphuric Acid generated during manufacturing of Pesticides, Dyes and Dye intermediate, Fertilizer and Organic chemicals manufacturing industries in production of Magnesium 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 utilization 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.
 - f. Monitor closely the quantity of hazardous waste being sent by generators and the quantity being utilized by authorized facilities.
- 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 utilization 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 utilization) or its complete utilization 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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86.0 Utilization of Spent Sulphuric Acid:

Type of HW	Source of generation	Product
Spent Sulphuric Acid [Category 26.3, 29.6 of Schedule I and B15 (Inorganic Acids) at Note 7 & C-2 (Corrosive) of Schedule II of HOWM Rules, 2016]	Generated from: i. Dye & Dyes intermediates, ii. Pharmaceutical, iii. Pesticide, iv. Inorganic chemical v. Synthetic organic chemical industry (aniline, toluene & chlorobenzene) and vi. Chlor alkali (purification of chlorine gas)	Magnesium Sulphate, for utilization in specific industrial use (mentioned at 86.3)

86.1 Source of Waste:

The Spent Sulphuric Acid generated from dye and dyes intermediate industry, pharmaceuticals industry, pesticide industry, inorganic chemical industry, Chlor alkali plants and synthetic organic chemical industry is categorized as hazardous waste at S. no. 26.3, 29.6 of Schedule-I, B-15 and C-2 of HOWM Rules-2016 which is required to be disposed in an authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

Table 1. Typical characteristics of Spent Sulphuric Acid are given below:

No.	Parameters	Unit	Value
1.	Appearance	--	Greyish - Light Blackish
2.	pH @ 25°C	--	Highly acidic
3.	Purity	%	>50
4.	TOC	mg/l	<6700
5.	COD	mg/l	<18,000
6.	Magnesium (Mg)	mg/l	<1
7.	Mercury (Hg)	mg/l	<0.005

86.2 Utilization Process

Magnesium Oxide (MgO), mother liquor (containing magnesium sulphate) / Fresh water (in the case of first batch) and Spent Sulphuric acid is charged into the reaction vessel. This being an exothermic reaction, produces gaseous fumes which are then passed through alkali scrubber and then the treated gas is released at stipulated standards through the stack.

A homogenous solution of Magnesium Sulphate is formed a desired specific gravity of the solution becomes neutral pH. The impurities present in Magnesium Sulphate solution is removed in Filter press and the wet filter cake generated in this process is then transferred to the hazardous waste storage facility.

After filtration, Magnesium Sulphate solution is then transferred to the Crystallizer and cooled for the crystallization process. The crystallizer stirs the solution continuously to decrease its temperature and also prevents the material to settle down in the crystallization tank.

The solution is now passed to the Centrifuge wherein, the liquid-solid separation is done. The liquid extracted from this process (i.e. mother liquor) is transferred into the mother liquor collection pit. The final product obtained is wet powder of Magnesium Sulphate.

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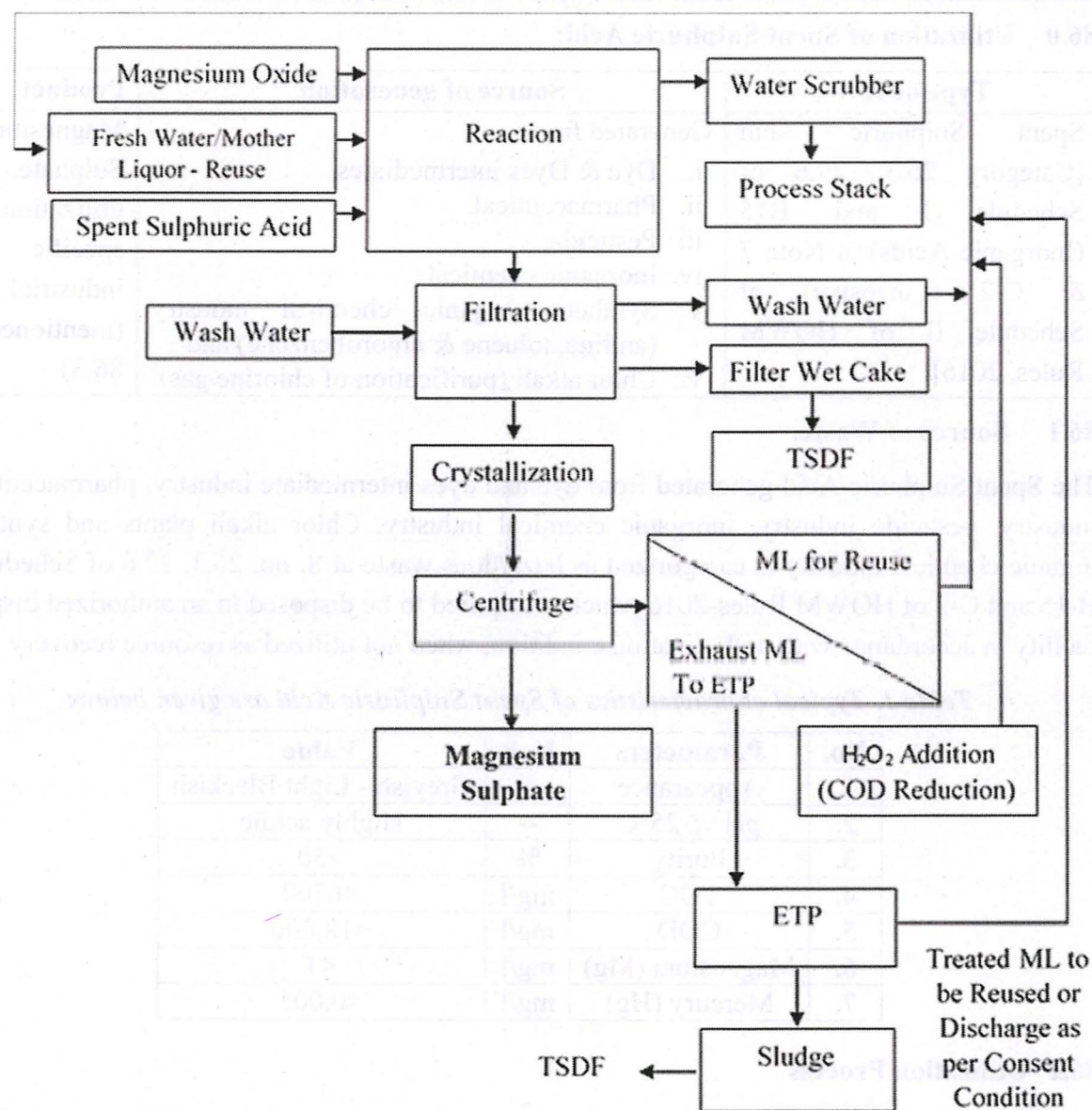


Figure: 1-Process flow diagram for utilization of spent H_2SO_4 in production of $MgSO_4$.

86.3 Product Usage / Utilization

- Magnesium Sulphate manufactured by utilizing the Spent Sulphuric Acid shall be utilized for industrial purpose only i.e. in Textile & leather industry, pulp and paper manufacturing, construction and building material and wastewater treatment.
- Magnesium Sulphate manufactured by utilizing the Spent Sulphuric Acid shall meet IS: 2730-1977.
- The end product (Magnesium Sulphate) thus produced, shall not be utilized for agriculture/soil applications, pharmaceutical/healthcare products or in food material.
- The unit shall label its product i.e. Magnesium Sulphate manufactured by utilizing Spent Sulphuric Acid as *"This Magnesium Sulphate has been manufactured by utilizing Spent Sulphuric Acid generated during manufacturing of Fertilizer / Pesticide / Dyes & Dyes intermediates / Organic Chemical products."*

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86.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of spent sulphuric acid generated during manufacturing of Dye and Dyes intermediates, Pesticide, Fertilizer and Organic Chemical industries in production of Magnesium Sulphate.

- 1) The spent sulphuric acid shall be procured only in SPCB/PCC authorized barrels/closed tanks mounted over vehicles fitted with requisite safeguards ensuring no spillage of the acid.
- 2) Spent sulphuric acid shall be stored in HDPE/MS or rubber lined steel tank and kept in acid proof brick lined dyke under shed. The unit shall provide slope and collection pit in storage area. 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 HOWM Rules, 2016, so as to eliminate rain water intrusion.

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 ETP, as the cases may be, through chemical process pump

- 3) There shall be a designated space for unloading of Spent Sulphuric Acid into 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 the collection pit.
- 4) There shall be no manual handling of the spent sulphuric acid. It shall be unloaded from the closed tanker to the storage tank through pipelines using dedicated transfer pump. The feeding of spent sulphuric acid shall be done through closed loop pipelines using dedicated transfer pump.
- 5) The complete manufacturing process shall be a closed system with alkali scrubbers connected to storage and reaction area.
- 6) The treated gases should comply with the emission standards and then only be released in the atmosphere through dedicated stacks. The height of the stack shall be a minimum of 30m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 7) Separate storage tanks to be provided for the storage of chemicals. These tanks should be at a designated place with proper cover and with acid brick lining floors.
- 8) Hydrogen Peroxide or any suitable treatment of Mother Liquor shall be given to reduce or oxidize organic matter (as per COD). Once COD stops decreasing or remains constant, Mother Liquor must be sent to ETP for further appropriate Physico-chemical treatment for reuse back in process or discharge as per the consent condition.
- 9) Treatment and disposal of wastewater:

Wastewater generated from floor-washings, spillages, reactor washing, 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.

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In case of zero discharge, 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 Filter cake, chemical 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 its 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 spent sulphuric acid is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 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.

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86.5 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.
- 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.

86.6 Standards

- 1) Source emission monitoring from the stack attached to the Reactor shall comply with the following emissions standards or as prescribed by the concerned SPCB/PCC, whichever is stringent:

Parameters	Standard
Particulate Matter	150 mg/Nm ³
SO ₂	100 mg/Nm ³
Acid mist (H ₂ SO ₄)	50 mg/Nm ³

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

Parameters	Standard
PM ₁₀	5 mg/m ³ , *TWA
SO ₂	13 mg/m ³ , *TWA
Acid mist (H ₂ SO ₄)	1 mg/m ³ , #C

**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) 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.

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86.7 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.

86.8 Size of Plant and Efficiency of Utilization

The yield of utilization (which is the ratio of the Product and hazardous waste utilized) to range between 0.1 - 0.25 i.e. for approximately 1MT spent sulphuric acid may generate 100– 250Kg of magnesium sulphate.

86.9 On-line Detectors / Alarms / Analyzers

In case of continuous process operations, online emission analyzers for PM and SO₂ shall be installed in the stack connected to reaction vessel and the online data be connected to the server of the concerned SPCB/PCC and CPCB.

86.10 Checklist of Minimal Requisite Facilities

S.no.	Particulars
1.	Spent H ₂ SO ₄ storage tank(s) with acid proof rubber lining having adequate storage capacity.
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.	Reaction vessel and vent of storage tanks of spent sulphuric acid shall be connected with alkali scrubber of adequate capacity and stack.
7.	Filter press
8.	Crystallizer unit (open tanks, jacketed crystallizers, crystallizers with evaporators, etc.)
9.	Centrifuge
10.	Effluent treatment plant comprising of physico- chemical unit operations and processes.
11.	ETP Sludge handling unit (Filter/Centrifuge/ Sludge drying bed etc.)
12.	Covered hazardous waste storage area to store filter cake, residue from scrubber and ETP sludge in HDPE bags/drums.
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.

