

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 Pharmaceutical sector and Chlor-Alkali Plant] in manufacturing of Precipitated Silica, Colloidal silica and Silica gel



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**Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change,
Government of India)
Parivesh Bhawan, East Arjun Nagar,
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Utilization of Spent Sulphuric Acid [generated from Pharmaceutical sector and Chlor-Alkali Plant] in manufacturing of Precipitated Silica, Colloidal silica and Silica gel

Procedure for grant of authorization by State Pollution Control Boards (SPCBs)/Pollution Control Committees (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 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. 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 report 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/ISO17025 accreditation/ recognition for monitoring and analysis of prescribed parameters in SoPs 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/Union Territory 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 utilization 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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84.0 Utilization of Spent Sulphuric Acid:

Type of HW	Source of generation	Recovery/Product
Spent Sulphuric Acid [B-15 (Inorganic acids) at Note 7 of Schedule-II of HOWM Rules – 2016]	Generated from: i. Pharmaceutical sector during production of 7-ADCA and Ethambutol Hydrochloride; and ii. Chlor-Alkali Plant while purification of Chlorine gas.	Precipitated Silica, Colloidal silica and Silica gel.

84.1 Source of Waste and Desired Quality:

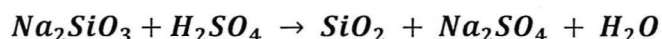
Spent Sulphuric Acid generated during manufacturing of Pharmaceutical sector (during production of 7-ADCA and Ethambutol Hydrochloride) and Chlor-Alkali Plant (while purification of Chlorine gas) falls under, Class B15 (Inorganic Acids) at Note 7 of Schedule II of HOWM Rules –2016. The said spent sulphuric acid is permitted for utilization as per these SoPs provided it meets the desired characteristics given in Table -1 below;

Table 1. Desired Characteristics of Spent Sulphuric Acid:

S. No.	Parameter	Unit	Pharmaceutical/ Chlor-Alkali Sector	S. No.	Parameter	Unit	Pharmaceutical/ Chlor-Alkali Sector
1.	Purity as H ₂ SO ₄	%	>70	11.	Nickel	ppm	<1.15
2.	COD	ppm	<358	12.	Cadmium	ppm	<0.074
3.	TSS	ppm	< 2	13.	Lead	ppm	3.26
4.	TOC	ppm	<150	14.	Iron	ppm	2.41
5.	Sulphide	ppm	< 0.1	15.	Manganese	ppm	0.651
6.	Sulphate	%	<79.3	16.	Total Chromium	ppm	0.117
7.	Phenolic Compound	ppm	< 0.1	17.	Hexavalent Chromium	ppm	< 0.01
8.	Phosphate	ppm	< 0.1	18.	Mercury	ppm	< 0.01
9.	Copper	ppm	<0.032	19.	Arsenic	ppm	< 0.01
10.	Zinc	ppm	<0.21	20.	Cyanide	ppm	< 0.01

84.2 Utilization Process

Diluted Spent Sulphuric Acid is added to Aqueous Solution of Sodium Silicate in the reactor to precipitate Silicon Dioxide at around 80°C temperature. The material formed during the reaction is filtered in filter press & cake is washed with water for reuse. The filter cake is transferred for drying and then pulverized to obtain finished product.



The precipitated silica is further processed to produce colloidal silica and silica-gel.

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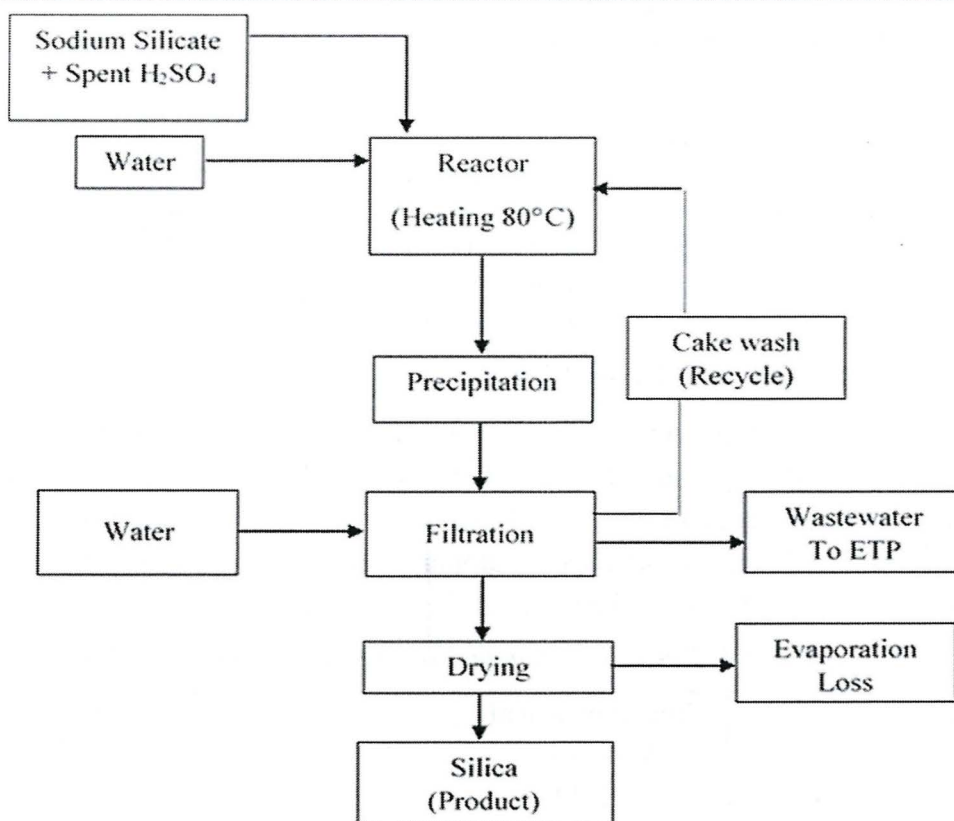


Figure: 1-Process flow diagram for utilization of spent sulphuric acid

84.3 Product Usage / Utilization

1. The products (precipitated Silica, colloidal silica and silica gel) shall meet quality specification of precipitated silica (IS.12076.1986), colloidal silica and silica gel (IS.3401.1992) shall comply Bureau of Indian Standards (BIS), for further respective utilization, if applicable.
2. The products (precipitated silica, colloidal silica and silica gel) can be utilized, provided it meets quality requirements; as filler in tyre industries, pesticides industries, rubber industry, paper industry, additive in paint & varnishes industries, shoe manufacturing, desiccant, etc.
3. The unit shall label its products i.e. Precipitated Silica, Colloidal silica and Silica gel manufactured by utilizing aforesaid spent sulphuric acid as *"This Precipitated Silica, Colloidal silica and Silica gel has been manufactured by utilizing Spent Sulphuric Acid generated from Pharmaceutical sector and Chlor-Alkali Plant"*.

84.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of Spent Sulphuric Acid generated during manufacturing of 7-ADCA and Ethambutol Hydrochloride (Pharmaceutical Sector) and purification of Chlorine gas (Chloro Alkali Plant) in manufacturing of Precipitated Silica, Colloidal silica and silica gel.

- 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.

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- 2) There shall be a designated space for unloading of spent sulphuric acid into the storage tank made of Stainless Steel/HDPE. 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.
- 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.

Further, the storage 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 reaction tanker or ETP, as the cases may be, through chemical process pump. Underground acid storage tanks should not be constructed.

- 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 reaction vessel.
- 5) The vent of spent sulphuric acid storage tanks shall be connected to scrubber for treatment using alkaline medium.
- 6) The unit shall provide suction vent to the reaction vessels and connect to a common or individual scrubbing system with proper venting & monitoring facility for the fumes generated.
- 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 brick lining floors.
- 8) Sulphuric acid mist 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 shall provide proper dust collection system/suction hoods connected to a common or individual APCD in spray dryer area and product packing section to avoid fugitive emission especially during transfer, packing and storing of precipitated silica (powder form).
- 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) 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.
- 12) 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,

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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.

- 13) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 14) 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.
- 15) 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.
- 16) The treated effluent 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.

84.5 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 logbook with information on source and date of procurement of Spent Sulphuric Acid, quantity, date wise utilization of same, hazardous waste generation and its disposal, etc. shall be maintained including analysis report of source & 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 return in Form-4 as per Rule 20(1) and (2) of 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/PCC.

84.6 Standards

- 1) Source emissions from the stack attached to reaction vessel and spray dryer shall comply with the following emission standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

Particulate Matter	150 mg/Nm ³
H ₂ SO ₄ (acid mist)	50 mg/Nm ³

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- 2) Work zone emissions in the work zone area shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

Total Dust	10 mg/m ³ TWA * (PEL)
SO ₂	13 mg/m ³ TWA (PEL)
H ₂ SO ₄	01 mg/m ³ TWA (PEL)

**PEL - Permissible Exposure Limit*

**time-weighted average (TWA)- measured over a period of 8 hours of operation of process.*

- 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. In case of zero discharge or no discharge condition stipulated in the consent or non-availability of the Common Effluent Treatment Plant (CETP), zero discharge shall be met.

84.7 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.

84.8 On-line Detectors / Alarms / Analyzers

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

84.9 Checklist of Minimal Requisite Facilities

S.No.	Particulars
1.	Adequate dust collection system/ suction hoods connected to a common or individual APCD in spray dryer area, product packing section, material transfer points (especially from filter press to dryer to crystallizers) to avoid fugitive emission especially during transfer, packing and storing of Precipitated Silica, Colloidal silica and silica gel.
2.	Suction vent to the reaction vessels connected to a common or individual scrubbing system with proper venting and stack height & monitoring facility.
3.	Material transfer / handling in entire utilization process shall be done in closed system. Covered conveying system for material transfers.
4.	The packing section of the product (in fine powder form) should be in closed room and the packing area should be provided with negative pressure.
5.	Storage tank(s) of adequate capacity to store spent sulfuric 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.

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6.	Cool, dry well-ventilated covered storage shed(s) for spent sulphuric acid storage tanks within premises.
7.	Mechanized system for transfer of Spent Sulphuric Acid from tankers to storage tanks to reactor vessels.
8.	Safety valve and vent to the hazardous waste (Spent sulphuric acid) storage tanks and connect the vents to a common or individual scrubbing system.
9.	Suction vent to the reaction vessels and connect to a common or individual scrubbing system with proper venting & monitoring facility for the fumes generated
10.	The process shall have proper ventilation (preferably with ventilation ducts above the process units).
11.	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.

