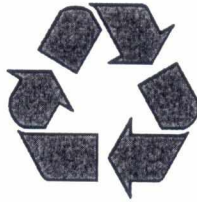


Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule 9 of the Hazardous and Other Wastes (Management and Transboundary movement) Rules, 2016

Utilization of Spent Sulphuric Acid (generated during manufacturing of 3, 5-Dichloro Nitro Benzene) and Spent Sodium Thiosulphate (generated during manufacturing of 3, 5-Dichloro Aniline and m-Chloro Aniline) for manufacturing of Nitrosyl Sulphuric Acid (NSA)



cpcb

October, 2017

Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change, Government of India)
Parivesh Bhawan, East Arjun Nagar,
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Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Spent Sulphuric Acid (generated during manufacturing of 3, 5-Dichloro Nitro Benzene) and Spent Sodium Thiosulphate (generated during manufacturing of 3, 5-Dichloro Aniline and m-Chloro Aniline) for manufacturing of Nitrosyl Sulphuric Acid (NSA)

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 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 minimum requisite facilities installed and after verification of utilization process as given in SoPs.
 - e. Issuance of passbooks (similar to the passbooks issued for recycling of use oils, waste oil, non-ferrous scraps, etc.) for maintaining records of receipt of hazardous wastes for utilization.
- (ii) After issuance of authorization, SPCB shall verify the utilization process, checklist and SOPs, quarterly during the initial 02 years of operation followed by random checks in subsequent year's atleast once in every year.

In-case of lack of requisite infrastructures with the SPCBs/PCCs, SPCBs/PCCs may engage 3rd party institutions and EPA/NABL/ISO17025 accredited laboratories for monitoring and analysis of prescribed parameters of the SoPs for verification purpose. Such labs shall have accreditation (EPA/NABL/ISO17025) for the parameters specified in SoP.
- (iii) SPCB shall provide half yearly up-dated list of units permitted for utilization of hazardous waste to CPCB and also periodically update the same on SPCB website Such updated list shall sent for January-June and July- December of every year and reach to CPCB by July and January respectively of every year.
- (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 or its complete utilisation or arrangement of sharing with any other authorised disposal facility.
- (v) In case of the utilization proposal is not similar with respect to source of generation, utilization process and end-use as outlined in this SoP, the same may be referred to CPCB for clarification / conducting trial utilization studies and developing SoPs.
- (vi) 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

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38.0 Utilization of Spent Sulphuric Acid:

Type of HW	Source of generation	Recovery/Product
Spent Sulphuric Acid Category: 26.3 of HOWM Rules, 2016	Spent acid generated during manufacturing of 3,5-Dichloro Aniline	For manufacturing of Nitrosyl Sulphuric Acid (NSA)

38.1 Source of Waste:

Spent Sulphuric Acid is generated during the reaction of 4-nitro, 2, 6-Dichloro Benzene Diazonium Sulphate with Formaldehyde and water during the production of 3, 5-Dichloro Nitro Benzene. The product, 3,5-Dichloro Benzene again reacts with sodium disulphide and 3-chloro Nitro Benzene with sodium hydrogen sulphide to produce 3,5-Dichloro Aniline and m-chloro aniline and generates waste, sodium thiosulphate. This Spent Sulphuric Acid is categorised as hazardous waste category 26.3 of Schedule-I 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.

Typical characteristic of spent acid and sodium thiosulphate generated are given below;

i. Spent Sulphuric Acid

S.No.	Parameters	Unit	Results
1.	pH	-	<2
2.	H ₂ SO ₄	%	39.8
3.	Sodium Thiosulphate	%	Not detected
4.	Water	%	56.9
5.	3, 5-Dichloro Aniline	mg/kg	Not detected
6.	Tetra Chloro Pthalic Anhydride	mg/kg	Not detected
7.	m-Chloro Aniline	mg/kg	Not detected
8.	TOC	mg/kg	17400

ii. Spent Sodium Thiosulphate

S.No.	Parameters	Unit	Results
1.	pH	-	7.33
2.	H ₂ SO ₄	%	Not detected
3.	Sodium Thiosulphate	%	36.4
4.	Water	%	58.2
5.	3, 5-Dichloro Aniline	mg/kg	Not detected
6.	Tetra Chloro Pthalic Anhydride	mg/kg	Not detected
7.	m-Chloro Aniline	mg/kg	Not detected
8.	TOC	mg/kg	16400

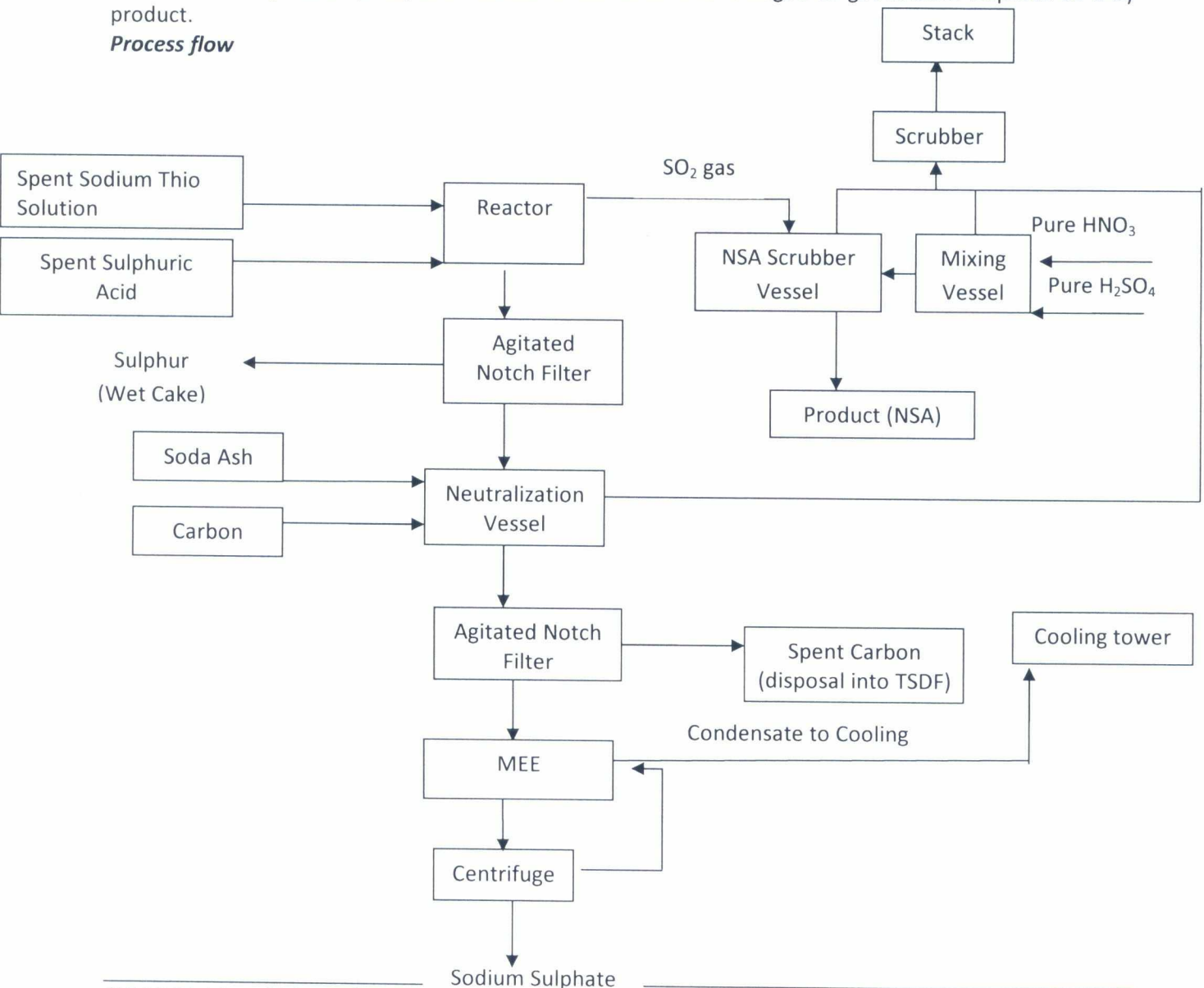
Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Spent Sulphuric Acid (generated during manufacturing of 3, 5-Dichloro Nitro Benzene) and Spent Sodium Thiosulphate (generated during manufacturing of 3, 5-Dichloro Aniline and m-Chloro Aniline) for manufacturing of Nitrosyl Sulphuric Acid (NSA)

38.2 Process of Utilization:

The utilization process involves reaction of waste sodium thiosulphate solution with Spent Sulphuric Acid solution (36%) in a reaction vessel. Firstly, the Thio Solution is taken into the reaction vessel and heated to attain the temperature around 60°C, then spent sulphuric acid is added slowly in the reaction vessel. It is an exothermic reaction and to maintain the temperature between 60-70°C, reaction vessel is packed with jacketed cooling system. Sulphur dioxide gas is liberated during the reaction which is scrubbed in NSA scrubber vessel using premixed acid to get Nitrosyl Sulphuric Acid (NSA) as a product. Premixed acid is the mixture of pure HNO₃ and H₂SO₄.

Solution from the reaction vessel is sent to agitated notch filter (ANF) to get sulphur cake. The filtrate from ANF is neutralized using soda ash in neutralization vessel where carbon is also added. After neutralization, the neutralized mass is filtered in ANF. The filtrate from the ANF is evaporated using multi effect evaporator (MEE) and residue of the MEE is centrifuged to get sodium sulphate as a by product.

Process flow



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38.3 Product Usage / Utilization

As a supplementary resource in the manufacturing of Nitrosyl Sulphuric Acid (NSA) for industrial use.

38.4 Standard Operating Procedure (SOP) for utilization

This SOP is applicable only for the utilization of Spent Sulphuric Acid and Spent Sodium Thiosulphate generated during manufacturing of 3,5-Dichloro Aniline/ m-Chloro Aniline by adhering to the following;

- (1) The Spent Sulphuric Acid should be transported in acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the liquid waste.
- (2) There should be a designated space for unloading of Spent Sulphuric Acid into a rubber lined storage tank. 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.
- (3) The unit shall install storage tank 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.
- (4) There shall be no manual handling of the Spent Sulphuric Acid and spent sodium thiosulphate. Acid proof pump shall be used for transfer of Spent Sulphuric Acid through pipelines to the reaction vessel.
- (5) Reaction vessels shall have jacketed cooling system with thermo pack and temperature indicator to maintain the initial temp of about 60°C in the reaction vessel by indirect heating (such as using oil) and then addition of spent sulphuric shall be started into reaction vessel.
- (6) NSA scrubber vessels and neutralization vessels used during the utilization process shall have jacketed cooling arrangement and attached with cooling tower to maintain the temperature during the exothermic reaction.
- (7) Mixing Vessel used for the mixing of the pure HNO_3 and H_2SO_4 shall be attached with chilling tower to maintain the temperature below 10°C.
- (8) 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 tank, as the cases may be, through acid proof pump.
- (9) The NSA scrubber vessels, neutralization vessels and acid mixing vessels shall be attached with ducting system attached with scrubber (premixed acid used as a scrubbing medium) and connected to a common stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.

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- (10) 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.
- (11) The process liquor from reaction tank shall be transferred to neutralization vessel and then to agitated notch filter through chemical process pump.
- (12) The unit shall label its product (i.e. NSA manufactured by utilizing aforesaid hazardous waste) as "This NSA as product has been manufactured by utilizing spent sulphuric acid and spent thio solution and therefore it may contain some organic constituents".
- (13) Treatment and disposal of wastewater:
The following are the sources of wastewater from utilization process;
 - a) MEE condensate
 - b) Floor washing/reactor wash/vehicle wash/spillages, etc.

The above wastewater may be utilized in cooling tower attached to mixing vessel. However, depending on consumption of waste water in cooling tower, the concerned SPCB/PCC may prescribe suitable Effluent Treatment to meet conditions as stipulated in the consent to operate.

- (14) It shall be ensured that Spent Sulphuric Acid 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.
- (15) Waste Sulphur cake generated from the utilization process shall be disposed in TSDF or be utilized as authorized by SPCB/PCC.
- (16) Sodium sulphate shall be used as filler/dilution in dyes manufacturing after obtaining authorization from concerned SPCB/PCC, without referring to CPCB. In case, such utilization is not possible, the same shall be disposed in authorized TSDF.
- (17) The hazardous waste (viz. Spent Carbon, ETP residue, if any, etc.) generated from utilization process shall be collected in HDPE bags and temporarily stored in a dedicated hazardous waste storage area sent to authorised TSDF within 90 days from generation of the waste.
- (18) Transportation of hazardous wastes such as Spent Sulphuric Acid, Spent Carbon, etc. shall be carried out by the sender or receiver (utilizer/TSDF operator) as per the authorization issued by concerned SPCB/PCC under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (19) Prior to utilization of spent sulphuric acid and spent thiosulphate, the unit shall obtain authorization for 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.

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- (20) 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.
- (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.

38.5 Records/Return Filing:

- (1) The unit shall maintain a passbook issued by concerned SPCB/PCC wherein the following details of each procurement of Spent Sulphuric Acid and spent sodium thiosulphate waste 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 NSA manufactured, hazardous waste generation and its disposal etc. shall be maintained including analysis report of fugitive and emission monitoring, as applicable.
- (3) 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
- (4) 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.

38.6 Standards

- (1) Source emissions in common stack connected to acid mixing vessel, NSA scrubber vessel and neutralization vessel shall comply with following standards:
- PM-50mg/Nm³
 - SO_x-80 mg/Nm³
 - Sulphuric Acid Mist-50 mg/Nm³
 - TOC-20mg/Nm³

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

PM₁₀-5 mg/m³TWA

Sulphuric acid – 1.0 mg/m³ TWA*, 3 mg/m³ STEL*

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

The Permissible Exposure Limit is 8-hour TWA.

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.

38.7 Siting of Industry

Facilities for processing of Spent Sulphuric Acid should preferably be located in a notified industrial area or industrial park/estate/cluster.

38.8 Efficiency of utilisation

To produce 1 ton on Nitrosyl Sulphuric Acid (NSA) about 1.07 tons of Thiosolution and about 0.6 tons of Spent Sulphuric Acid are required. Other raw material like pure sulphuric acid and nitric acid are also used. Hence, requisite facilities of adequate size shall be installed accordingly as mentioned under para 38.10 below.

38.9 On-line detectors / Alarms / Analysers

In case of continuous process operations, online analysers shall be installed for acid mist in the stack emission connected to common stack connected to acid mixing vessel, NSA scrubber vessel and neutralization vessel. The on-line data shall be connected to the concerned SPCB/PCC server.

38.10 Checklist of Minimal Requisite Facilities:

S.No.	Requisite Facilities
1.	Earmarked unloading area (for transfer of Spent Sulphuric acid from tanker) contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, to collection pit.
2.	Acid proof lined tanks for storage of Spent Sulphuric Acid, pure nitric and sulphuric acid

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3.	Separate storage tank for the storage of NSA and spent thiosolution.
4.	Storage tank (s) should be of such size/capacity that it can store at least two weeks requirement of the said hazardous waste to be used as raw material.
5.	Well-ventilated covered storage shed(s) within the premises for Spent Sulphuric Acid storage tanks
6.	Chemical process (acid proof) pumps for transfer of Spent Sulphuric acid from tanker to storage tank and transfer subsequently to process area.
7.	Mechanical means for transferring of acids/liquid chemicals to the reaction vessels
8.	Leak-proof and acid proof floor tiles with adequate slope to collect spillages, if any, in the entire working area.
9.	Collection pit for collection of spillages from aforesaid working area and unloading area.
10.	Reaction vessels made of glass, with jacketed cooling arrangement with thermo pack and temperature display indicator facility, of adequate capacity
11.	NSA scrubber vessels and Neutralization vessels, SS made, shall have jacketed cooling arrangement attached to cooling tower along with hood for suction of acid fumes/ mist from the reaction tank and channelizing to scrubber attached with common stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
12.	Mixing vessel for the mixing of pure sulphuric and nitric acid attached with chilling plant to maintain the temperature below 10°C.
13.	Spare vessel to transfer the reaction mass, if any, in case of leakage or damage to the reaction vessels
14.	Separate pipelines for the transfer of spent sulphuric acid, spent thiosolution, pure nitric acid and sulphuric acid into reaction vessels
15.	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.
16.	Agitated Notch Filter
17.	Multi Effect Evaporator
18.	Temporary storage area under shed(s) for the storage of spent carbon.
19.	Fire fighting system
20.	Cooling tower
21.	Chilling plant
