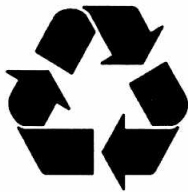


Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule 9 of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016

Utilization of Spent Sulphuric Acid generated during manufacturing of G-Salt, for production of R-Complex and Gamma-acid



June, 2018

Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change, Government of India)
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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 authorization is given only to those wastes for which SOPs on utilization have been circulated by CPCB ensuring the following:
 - a. The waste (intended for utilization) belongs to similar source of generation as specified in 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 shall verify the utilization process, checklist and SOPs on quarterly basis for initial 2 years; followed by random checks in the subsequent period for atleast once a year.
 In-case of lack of requisite infrastructures with the SPCB/PCC, they may engage 3rd party institutions or laboratories having EPA/NABL/ISO17025 accreditation/recognition for monitoring and analysis of prescribed parameters in SOPs for verification purpose.
- (iii) SPCBs 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 website, periodically. Such updated list shall be sent to CPCB on a half yearly basis i.e 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 standards respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions.

44.0 Utilization of Spent Sulphuric Acid generated during Vinyl Sulphone production

Type of HW	Source of generation	Recovery/Product
Spent Sulphuric Acid (Category No. 26.3 of schedule-I of HOWM Rules, 2016)	Generated during manufacturing of G-Salt (Dye & Dye Intermediate sector)	R-Complex and Gamma Acid

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44.1 Source of Waste

Spent Sulphuric Acid is generated during manufacturing of G-Salt (2-Naphthol 6,8, Disulphonic Acid) (dye & dye intermediate sector). Spent sulphuric acid is generated during isolation and filtration of the reacted mass after Sulphonation.

Spent Sulphuric Acid is categorized as hazardous waste at S.No. 26.3 of Schedule-I of the HOWM Rules, 2016, which are required to be disposed in accordance with authorization condition, when not utilized.

Following are the typical characteristics of the said hazardous waste generated during G-salt manufacturing:

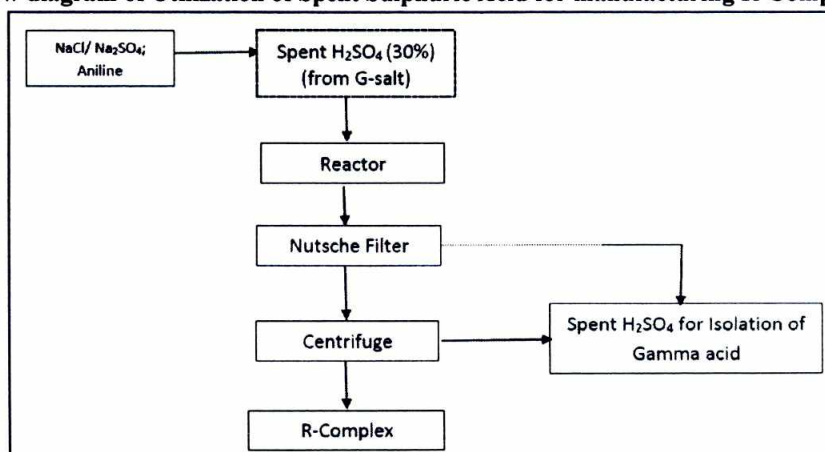
S.No	Parameters	Results (%)
1.	Physical Appearance	Light Yellow
2.	pH	2.0
2.	Specific Gravity	1.25
3.	Acidity	29-31 %
4.	G-Salt	2.0 %
5.	Trisulphonic Acid	1.0 %
6.	Potassium Sulphate	20-24 %
7.	Unreacted Beta Naphthol	0.0001 %

44.2 Utilisation Process

R-Complex:

Manufacturing process of R-Complex involves mixing of Spent Sulphuric Acid (generated from G-Salt process) with NaCl/Na₂SO₄ and Aniline in the reactor. The reacted mass is filtered through Nutsche filter followed by centrifuge. The final product R-Complex is collected and packed. The mother liquor generated during filtration and centrifuge is collected in a separate tank for isolation of gamma acid. The process flow diagram for utilization of spent sulphuric acid in manufacturing of R-Complex is given at Figure 1.

Fig 1. Flow diagram of Utilization of Spent Sulphuric Acid for manufacturing R-Complex



Gamma Acid:

Manufacturing process of Gamma acid involves amidation, concentration followed by fusion process. The reacted mass from the fusion process is mixed with Spent Sulphuric Acid (generated from R-complex process). The reacted mass is filtered

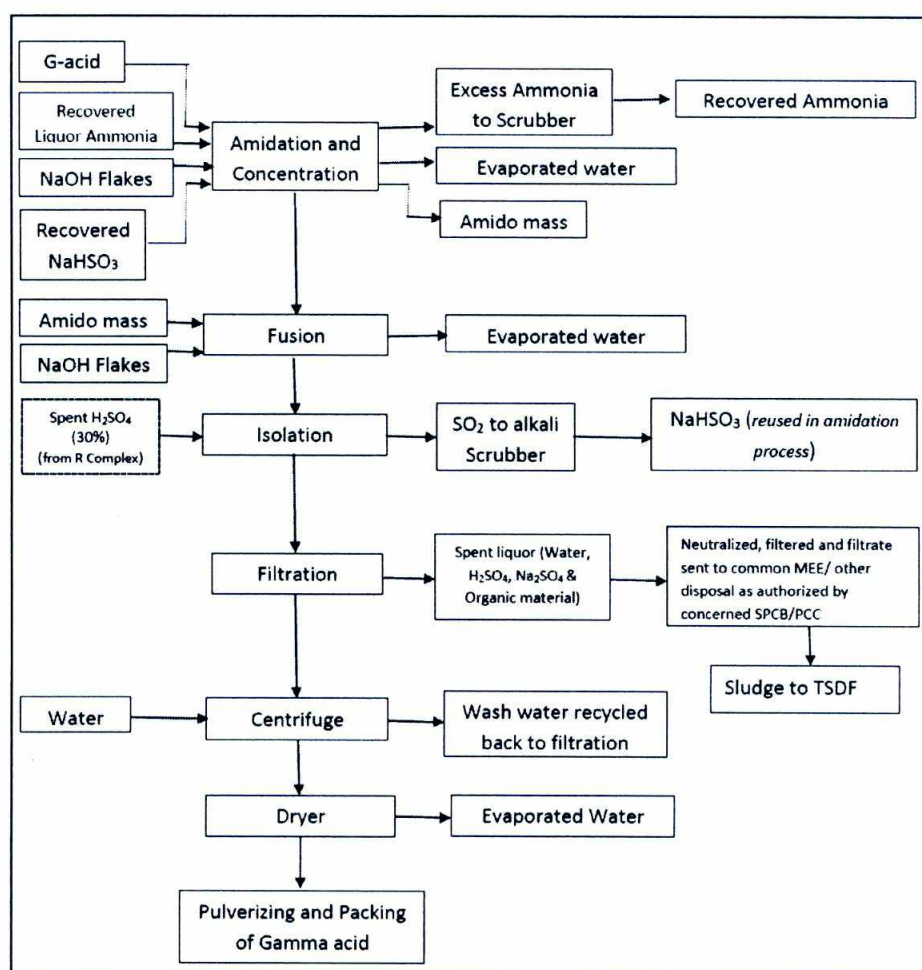
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through Nutsche filter followed by centrifuge to collect the final product Gamma acid. The process flow diagram for utilization of spent sulphuric acid in manufacturing of Gamma acid is given at Figure 2.

SO₂ gas liberated during isolation process is scrubbed using alkali scrubber, where Sodium bisulphite (48 %) is recovered and reused in the amidation process. The supernatant collected from the centrifuge is reused as washwater in the filtration stage. The wastewater generated from filtration (after isolation process) shall be treated Physico-Chemically in an ETP and may be sent to CETP for final disposal or treated further in a captive facility to comply with surface water discharge standards or treated by forced evaporators followed by Spray dryers to achieve zero discharge as may be stipulated by SPCBs.

The sludge generated in the neutralization tank of ETP be collected in HDPE bags for disposal at TSDF.

Fig 2. Flow diagram of Utilization of Spent Sulphuric Acid for manufacturing Gamma acid



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44.3 Product Usage / Utilization

The R-Complex and Gamma Acid (2-Amino-8-naphthol-6-sulfonic Acid) manufactured utilizing spent sulphuric acid (generated during manufacturing of G Salt), shall be utilized in Dye & dye intermediate industry.

The unit shall label its product (i.e. R Complex and Gamma acid) manufactured by utilizing aforesaid Hazardous waste as "This R-Complex and Gamma Acid has been manufactured by utilizing Spent Sulphuric Acid, generated from G-Salt (2-Naphthol 6,8, Disulphonic Acid) manufacturing process."

44.4 Standard Operating Procedure for utilization

This SOP is applicable only for the utilization of Spent Sulphuric Acid (30 %) generated during manufacturing of G Salt (Dye & Dye Intermediate sector), for manufacturing of R-Complex and Gamma acid (2-Amino-8-naphthol-6-sulfonic Acid).

- 1) Spent Sulphuric Acid shall be transported in SPCB/PCC authorized acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the same.
- 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 slop to collect spillages, if any, into collection pit.
Alternately, 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 and Transboundary Movement) Rules, 2016 so as to eliminate rain water intrusion.
- 4) There shall be no manual handling of the hazardous wastes (Spent Sulphuric Acid). Acid Proof pump shall be used for transfer of Spent Sulphuric Acid through pipelines to the reaction vessel.
- 5) The entire process area shall have leak-proof and acid proof 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.
- 6) The vent of Spent Sulphuric Acid storage tanks shall be connected to scrubber for treatment using alkaline medium.

- 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) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within the unit.
- 9) In R-Complex Plant, spent sulphuric acid (generated from G Salt process) shall be mixed with the reactants in closed vessel reactors. The reactor shall be kept under covered shed with proper ventilation in the process area.

The reacted mass is transferred to nutch filter for filtration and washing. The filtered material constitutes the product R Complex. The filtered cake collected is further centrifuged to recover the R Complex as product.

- 10) In Gamma acid plant, after fusion of the reaction mixture, spent sulphuric acid (generated from R Complex process) shall be mixed with reaction mixture in closed vessel reactors (isolation vessel). The reactor shall be kept under covered shed with proper ventilation in the process area.

After isolation vessel, the reacted mass is transferred to nutch filter for filtration and washing. The filtered material constitutes the product Gamma acid. The filtered cake collected is further centrifuged to recover the Gamma acid as product.

- 11) In R-Complex plant, the reactor and nutsche filters be a closed system and shall have vent ducts connected to common scrubbing system followed by dispersion through stack.

In Gamma acid plant, the reactors, nutsche filters and dryer be a closed system and shall have vent ducts connected to common scrubbing system followed by dispersion through stack.

- 12) The filtrate from nutsche filter of the gamma acid plant be collected in storage tank and transferred through process pumps for neutralization in effluent treatment plant.

- 13) The sodium bisulphite generated from scrubber attached to isolation reactor, may be reused in the Amidation stage of the manufacturing process. The excess/remaining sodium bisulphite may only be utilized in manufacturing of Bronners Acid & Amido G-Salt (Dye & Dye Intemediates) and in no case to be utilized in food industries/applications. Sodium bisulphite shall comply with the standards/specifications as given in Bureau of Indian Standards: IS 248:1987 for use as technical grade chemical.

- 14) 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 MSDS. The safety precautions of the worker shall be in accordance with the Factory Act, 1948, as amended from time to time.

- 15) Sulphuric Acid Mist and SO₂ are expected to be liberated from the said reactors (isolation vessel) of the Gamma acid plant, where the Spent Sulphuric Acid is added. Thus, the said reactors (isolation vessel) 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.

The treated gases shall comply with emission norms and prior to dispersion into atmosphere through stack. The height of stack shall be a minimum of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.

- 16) Treatment and disposal of wastewater:

Waste water generated from floor-washings, spillages, reactor washing, scrubber bleed including the wastewater from filtration (after isolation process) of the gamma acid plant shall be treated Physico-Chemically in an ETP and may be sent to CETP for final disposal or treated further in a captive facility to comply with waste water discharge standards.

In case of zero discharge condition by SPCB/PCC, the treated waste water from ETP may be evaporated in Forced Evaporators like MEE. The concentrated liquid from the evaporator shall be sent to spray dryer for conversion into dry powder which may be disposed as given in para 19 below.

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

- 18) SPCBs/PCCs shall ensure synchronization of generation and utilization of Spent acid and the same shall reflect in respective authorization specifying name and quantity.

- 19) The hazardous wastes generated (namely the filter residues, ETP sludge, scrubber residue, effluent powder generated from Spray Dryer/forced evaporator, product spillages, damaged filter liners, 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. Such storage area shall be covered with proper ventilation.

It shall be ensured that the highly soluble dry-powdered effluent from MEE-Spray Dryer should be stabilized or immobilized with suitable cementing material prior to secured landfilling in TSDF.

- 20) Transportation of Spent Sulphuric Acid and residues generated during utilization shall be carried out by the sender or receiver (utilize/TSDF operator) as per the authorization issued by concerned SPCB/PCC under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- 21) Prior to utilization of spent sulphuric acid, the unit shall obtain authorization for generation, storage and utilization of Spent sulphuric acid from the concerned State Pollution Control Board under the Hazardous and Other wastes (Management & Transboundary Movement) Rules, 2016.
- 22) 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.
- 23) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 24) 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.

44.5 Record/Return Filing

- (1) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of Spent Sulphuric Acid 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 the said hazardous waste, quantity, date wise utilization of the same, quantity of R Complex and Gamma acid 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 utilized, hazardous waste 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 concerned SPCB.
- (4) The unit 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.

44.6 Standards

- (i) Source Emissions from the stack connected to Reactors and Nutsche Filters of R Complex and Gamma acid plants respectively and dryer in Gamma acid plant, shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

PM	: 20 mg/Nm ³
Acid Mist/SO ₃	: 50 mg/ Nm ³
SO ₂	: 50 mg/ Nm ³
TOC	: 20 mg / Nm ³

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

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

PM ₁₀	: 5 mg/m ³ TWA* (PEL)
Sulphuric Acid mist	: 1 mg/m ³ TWA* (PEL) 3 mg/m ³ TWA* (STEL)

**PEL – Permissible Exposure Limit*

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

**short term exposure limit (STEL) – measured for 15 minutes duration of exposure*

- (iii) Monitoring of the above specified source emission parameter shall be carried out quarterly. The monitoring shall be carried out by NABL accredited or ISO17025 /EPA approved laboratories and the results shall be submitted to the concerned SPCB/PCC on a quarterly basis.
- (iv) Standards for wastewater discharge: The treated waste water 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 stipulated in the said Consent or non-availability of the Common Effluent Treatment (CETP), zero discharge shall be met.

44.7 Siting of Industry

Facilities for utilization of Spent Sulphuric Acid (during manufacturing of G Salt) shall be located in a notified industrial area or industrial park/estate/cluster and cited in accordance with Consent to Establish issued by the concerned SPCB/PCC.

44.8 Size of Plant & Efficiency of utilisation

1MT of Spent Sulphuric Acid yields 0.096 MT of R Complex and 0.110 MT Gamma acid. Hence, requisite facilities of adequate size shall be installed accordingly as mentioned under para 44.10 below.

44.9 On-line detectors / Alarms / Analysers

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

44.10 Checklist of Minimal Requisite Facilities:

S.No	Requisite Facilities
1.	<p>Storage tank(s) of adequate capacity to store Spent Sulphuric Acid of at least two weeks requirement.</p> <p>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. Alternately, 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.</p>
2.	Cool, dry, well-ventilated covered storage shed(s) for Spent Sulphuric Acid storage tanks with in premises.
3.	Mechanized system for transfer of Spent Sulphuric Acid from tankers to storage tanks to reactor vessels.
4.	The process shall have proper ventilation (preferably with ventilation ducts above the process units).
5.	Reactors with suction hood connected via duct to scrubber and stack of adequate height as prescribed by concerned SPCB/PCC.
6.	Nutch Filters/Filter Press
7.	Centrifuges
8.	Dryer (Tray drier / Fluidised bed drier)
9.	<p>Adequate Effluent treatment plant so as to comply with standards/conditions prescribed by the concerned SPCB/PCC.</p> <p>Forced Evaporator followed by Spray dryer (in case of zero discharge condition by SPCB/PCC)</p>
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/20/2013-14.
11.	Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process.

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