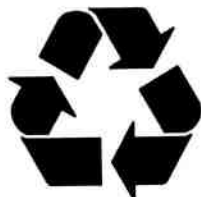


**Standard Operating Procedure and Checklist of Minimal  
Requisite Facilities for utilization of hazardous waste  
under Rule 9 of the Hazardous and Other Wastes  
(Management and Transboundary Movement) Rules, 2016**

**Utilization of Spent Sulphuric Acid generated during  
manufacturing of Vinyl Sulphone, for production of H-acid**



October, 2017

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

*P. U. R.*

**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 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 3<sup>rd</sup> 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.

**40.0 Utilization of Spent Sulphuric Acid generated during Vinyl Sulphone production**

| <b>Type of HW</b>                                                          | <b>Source of generation</b>                                                                                             | <b>Recovery/Product</b>                                               |
|----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| Spent Sulphuric Acid (Category No. 26.3 of schedule-I of HOWM Rules, 2016) | Generated during manufacturing of Vinyl Sulphone (intermediates, used as raw material in Dye & Dye Intermediate sector) | H-Acid (Hyaluronic acid / 1-amino-8-naphthalene-3,6-disulphonic acid) |

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#### 40.1 Source of Waste

Spent Sulphuric Acid is generated during manufacturing of Vinyl Sulphone (an intermediate used as a raw material in dye & dye intermediate sector). Spent sulphuric acid is generated during Chlorosulphonation of acetanilide to produce an intermediate i.e Acetyl Sulphonyl chloride (ASC) and sulphanilic acid.

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:

| S.No | Parameters                     | Results (%) |
|------|--------------------------------|-------------|
| 1.   | Total Acidity                  | 32.2        |
| 2.   | Sulphate                       | 24.4        |
| 3.   | Chlorides                      | 4.1         |
| 4.   | Acetanilide                    | 0.07        |
| 5.   | Acetanilide Sulphonyl Chloride | 0.12        |
| 6.   | Vinyl Sulphone                 | 0.02        |
| 7.   | COD                            | 7626 mg/l   |

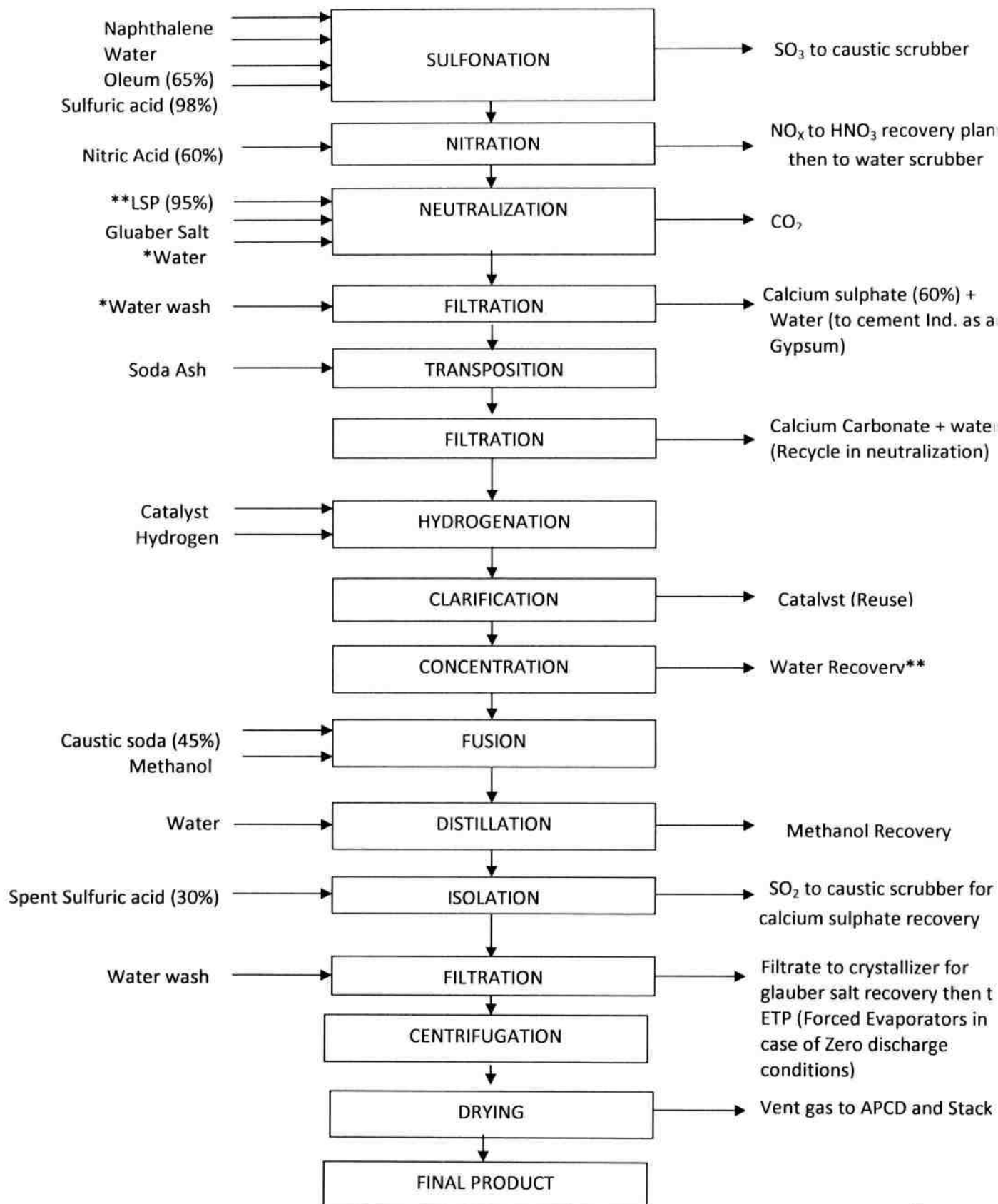
#### 40.2 Utilisation Process

Manufacturing process of H-Acid (1-amino-8-naphthalene-3,6-disulphonic acid) involves production of crude H-Acid in first stage by reacting Naphthalene with Oleum, water and sulphuric acid (98 %) in a reactor. The crude mass is filtered and again reacted with Nitric acid. The nitrated product is neutralized with lime and sodium sulphate (Glauber salt). Then the reacted mass is filtered & washed with water followed by soda ash transposition and Hydrogenation. The reaction mixture thus produced undergoes clarification, concentration and further fused with caustic soda and methanol to produce crude H-Acid. Methanol is recovered through distillation unit.

The crude H-Acid obtained from above process is mixed with spent sulphuric acid (by replacing the use of fresh Sulphuric acid) with constant stirring for 4-5 hours at ambient temperature to precipitate H-Acid. The reaction mixture is filtered using Nutsche filter. Then the reacted mass is centrifuged and dried to get H-Acid as product. The filtrate (Mother liquor) generated during filtration of H-acid is crystallised and filtered to recover Glauber salt which is re-used in manufacturing of the aforesaid crude H-acid.

SO<sub>2</sub> gas liberated during mixing of Spent Sulphuric Acid with H-acid is scrubbed using alkali scrubber, where calcium sulphate (Gypsum) is produced as by-product. The wastewater generated from crystallizer (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 is collected in HDPE bags for disposal.

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



\* Water recovery from concentration and recovered and reused at Neutralization/Filtration stage as indicated.

\*\*Recovery from filtration and reused at Neutralization stage.

WM-II Division, CPCB, Delhi

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### **40.3 Product Usage / Utilization**

The H-Acid (8-amino-1-naphthol-3,6-disulphonic acid) manufactured utilizing spent sulphuric acid (generated during manufacturing Vinyl Sulphone), is a product and shall be utilized as an intermediate in the dye and dye intermediate industry.

### **40.4 Standard Operating Procedure for utilization**

This SOP is applicable only for the utilization of Spent Sulphuric Acid (30 – 35 %) generated during manufacturing of Vinyl Sulphone (intermediates, used as raw material in Dye & Dye Intermediate sector), for manufacturing of H-acid (Hyaluronic Acid / 1-amino-8-naphthalene-3,6-disulphonic 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) with in 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.

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- 9) Spent Sulphuric Acid shall be mixed with crude H-Acid in alkali medium, in closed vessel reactors (isolation vessel) having mechanized stirring system. The reactor shall be kept under covered shed with proper ventilation in the process area.
- 10) After isolation vessel, the reacted mass is transferred to nutch filter for filtration and washing. The filtered material constitutes the product H-Acid. The H-Acid collected is further centrifuged and dried to recover the H-Acid as product.  
The unit may install spin flash dryer or any similar equipment for drying the product. The dryer unit shall have vent ducts connected to air pollution control devices such as bag dust collectors (for product recovery) followed by dispersion through stack.
- 11) The filtrate from nutsche is collected in storage tank and transferred through process pumps to crystallizer unit where the temperature of solution is reduced to facilitate crystallization. The crystallized Glauber salt is separated in a belt filter and may be reused in the neutralization stage of crude H-acid manufacturing process.
- 12) 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.
- 13) Sulphuric Acid Mist and SO<sub>2</sub> are expected to be liberated from the said reactors (isolation vessel) 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.  
The off gases from spray dryer shall be attached to cyclone followed by scrubber or suitable air pollution control devices and dispersed through stack into the atmosphere.
- 14) Treatment and disposal of wastewater:  
Waste water generated from floor-washings, spillages, reactor washing, scrubber bleed including the wastewater from crystallizer (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.  
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 17 below.

15) 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.

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

17) The hazardous wastes generated (namely the filter press, ETP sludge, scrubber, bag filter, 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.

18) 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.

19) 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.

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) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.

22) 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.

70.8

#### 40.5 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 H-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.

#### 40.6 Standards

- (i) Source Emissions from the stack connected to Isolation Vessel and H-Acid product dryer stack shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

|                           |                           |
|---------------------------|---------------------------|
| Acid Mist/SO <sub>3</sub> | : 50 mg/ Nm <sup>3</sup>  |
| SO <sub>2</sub>           | : 50 mg/ Nm <sup>3</sup>  |
| TOC                       | : 20 mg / Nm <sup>3</sup> |

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

- (ii) Source Emissions from the stack connected to H-Acid product dryer stack, Spray dryer and Boiler shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

|    |                         |
|----|-------------------------|
| PM | : 50 mg/Nm <sup>3</sup> |
|----|-------------------------|

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

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

|                     |                                  |
|---------------------|----------------------------------|
| PM <sub>10</sub>    | : 5 mg/m <sup>3</sup> TWA* (PEL) |
| Sulphuric Acid mist | : 1 mg/m <sup>3</sup> TWA* (PEL) |
|                     | 3 mg/m <sup>3</sup> 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



- (iv) 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.
- (v) 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.

**40.7 Siting of Industry**

Facilities for utilization of Spent Sulphuric Acid (during manufacturing of Vinyl Sulphone) 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.

**40.8 Size of Plant & Efficiency of utilisation**

100 Kg of Spent Sulphuric Acid yields 10.16 Kg of H-Acid. Hence, requisite facilities of adequate size shall be installed accordingly as mentioned under para 42.10 below.

**40.9 On-line detectors / Alarms / Analysers**

In case of continuous process operations, online emission analysers for PM & SO<sub>2</sub> in the stack shall be installed and the online data be connected to the server of the concerned SPCB/PCC.

**40.10 Checklist of Minimal Requisite Facilities:**

| S.No | Requisite Facilities                                                                                                                                                                                                                                                                                                                                                                                                                                              |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1.   | Storage tank(s) of adequate capacity to store Spent Sulphuric Acid of at least two weeks requirement.<br><br>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. |
| 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.                                                                                                                                                                                                                                                                                                                                                          |

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**Standard Operating Procedure and Checklist of Minimal Requisite Facilities for Utilization of Spent Sulphuric Acid generated during manufacturing of Vinyl Sulphone, for production of H-acid**

|     |                                                                                                                                                                                                                                                                                                                       |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 4.  | The process shall have proper ventilation (preferably with ventilation ducts above the process units).                                                                                                                                                                                                                |
| 5.  | Reactors (isolation vessel) with suction hood connected via duct to scrubber and stack of adequate height as prescribed by concerned SPCB/PCC.                                                                                                                                                                        |
| 6.  | Nutch/Belt filter/Filter Press                                                                                                                                                                                                                                                                                        |
| 7.  | Centrifuge                                                                                                                                                                                                                                                                                                            |
| 8.  | Dryer (operated by fuel or gas or as permitted by the concerned SPCB/PCC) for product drying<br><br>The vent from the product dryer should be connected to bag filter house or scrubber followed by stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher |
| 9.  | Crystallizer unit (for Glauber Salt recovery from filtrate after Isolation process)                                                                                                                                                                                                                                   |
| 10. | Adequate Effluent treatment plant so as to comply with standards/conditions prescribed by the concerned SPCB/PCC.<br><br>Forced Evaporator followed by Spray dryer (in case of zero discharge condition by SPCB/PCC)                                                                                                  |
| 11. | 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.                                                                                                     |
| 12. | Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process.                                                                                                                                                                                                 |

*P.K.S*