

**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 Sodium Hydrosulphide (generated during caustic scrubbing of H<sub>2</sub>S gas in pesticide, inorganic chemical, and dyes and dyes intermediate industries) as reducing agent in production of dye and dyes intermediates**



**August, 2023**

**Central Pollution Control Board  
(Ministry of Environment, Forest & Climate Change,  
Government of India)  
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**Utilization of Spent Sodium Hydrosulphide (generated during caustic scrubbing of H<sub>2</sub>S gas in pesticide, inorganic chemical, and dyes and dyes intermediate industries) as reducing agent in production of dye and dyes intermediates**

**Procedure for grant of authorization by State Pollution Control Board (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 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 Spent Sodium hydrosulphide 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 two 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 3<sup>rd</sup> 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) [HOWM] Rules, 2016 to CPCB and 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/Union Territory 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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**92.0 Utilization of Spent Sodium Hydro Sulphide:**

| Type of HW  | Source of generation  | Recovery/ Product   |
|---|---|---|
| Spent Sodium Hydro Sulphide (NaHS), Category 35.1 of Schedule I of HOWM Rules, 2016 | Generated during scrubbing of H <sub>2</sub> S gas in caustic solution from inorganic chemical industries, pesticide industries and dyes and dyes intermediate industries | As reducing agent in production of dye and dye intermediates. |

**92.1 Source of Hazardous Waste:**

Spent Sodium Hydro Sulphide generated from scrubbing of H<sub>2</sub>S falls under category, 35.1 of Schedule I of HOWM Rules, 2016. Characteristics of spent NaHS solution from 3 different sources, as observed during trial studies is given in Table 1 below.

*Table 1. Characteristics of Spent Sodium Hydro Sulphide*

| Sr. No. | Test parameters  | Unit | Spent NaHS from Inorganic sector | Spent NaHS from Dye and Dyes Intermediate sector | Spent NaHS from Pesticide sector |
|---------|------------------|------|----------------------------------|--|----------------------------------|
| 1       | Appearance       | --   | Light Yellowish Liquid           | Light Yellowish Liquid                           | Dark Yellowish Liquid            |
| 2       | pH               | --   | 12.30 (at 25.2 °C)               | 12.61 (at 25.2 °C)                               | 11.48 (at 25.2 °C)               |
| 3       | purity           | %    | 29.5                             | 28.2   | 28.9                             |
| 4       | TOC              | mg/L | 8460                             | 7773   | 13050                            |
| 5       | COD              | mg/L | 402384                           | 701184   | 940224                           |
| 6       | Iron (as Fe)     | mg/L | 0.35                             | 2.8  | 2.0                              |
| 7       | Chloride         | mg/L | 377.1                            | 295.6  | 344                              |
| 8       | Sulphate         | mg/L | 227                              | 133  | 1190                             |
| 9       | Barium           | mg/L | 0.037                            | -  | -                                |
| 10      | Insoluble matter | %    | 0.12                             | -  | 0.19                             |
| 11      | Moisture content | %    | 70.5                             | 71.8   | 71.1                             |
| 12      | Specific gravity | -    | 1.19                             | 1.24   | 1.19                             |
| 13      | Cadmium          | mg/L | 0.50                             | 0.53   | 0.53                             |
| 14      | Lead             | mg/L | 0.72                             | 1.53   | 8.48                             |
| 15      | Nickel           | mg/L | 0.38                             | 3.34   | 1.86                             |
| 16      | Manganese        | mg/L | 0.21                             | -  | 0.22                             |
| 17      | Chromium         | mg/L | 0.41                             | -  | 0.52                             |
| 18      | Copper           | mg/L | 0.23                             | -  | -                                |

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**92.2 Utilization Process of Hazardous Waste:**

Environmental aspects of utilising spent NaHS generated from inorganic chemicals, pesticide and dye and dye intermediates industries, as a reducing agent in dye and dye intermediates industry were assessed during trial studies. The production of dye and dyes intermediates involves process operations like sulphonation, drowning, reduction, isolation, filtration, purification, neutralization, centrifugation, pulverising, drying etc. Spent NaHS is proposed to be utilized as reducing agent. The following is one of the utilization process for use of spent NaHS as reducing agent in manufacturing of 4-NAPSA dye:

The utilization process involves addition of spent Sodium hydrosulphide along with other raw materials (caustic lye, 4-NAPSA Nitro and water) where a reduction process takes place. In the reduction reaction, the nitro compound gets converted to amino compound. Hydrogen sulphide is liberated during the process, which is scrubbed in alkali scrubber. The exhausted scrubbing media is reused back in process. After reduction process, sodium bi-sulphite (SBS) is added in reaction vessel to destruct/ remove the excess NaHS. Once excess NaHS is removed, HCl is added for pH balance.

After reduction process, mother liquor is passed through clarifier/filter press, where process sludge is removed from mother liquor. Process sludge should be stored in dedicated sludge storage area for ultimately disposed in TSDF.

Filtrate from clarifier/filter-press is transferred to isolation where HCl is added to adjust pH. After pH adjustment, mother liquor is transferred to Nutch filter, where excess water removed and 4-NAPSA in slurry form recovered. Moisture from 4-NAPSA is further removed through centrifuge and heating process. The final product shall be packed in moisture proof bags.



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**92.3 Spent NaHS and derived products Usage/ Utilization**

- i. Spent NaHS shall be used as reducing agent in manufacturing of dye and dye intermediate products only.
- ii. The dye and dye intermediate products produced utilizing spent NaHS shall comply with the Bureau of Indian Standards (BIS), for further respective utilization.
- iii. The end use of products "dye and dye intermediates" derived by utilizing spent NaHS shall be restricted for use in the food, pharma, cosmetic & fertilizer sector in any form.
- iv. The unit shall label the products manufactured by utilizing Spent NaHS as *"This product has been manufactured by utilizing Spent Sodium Hydro Sulphide generated during manufacturing of inorganic chemical industry, pesticide industry and dyes and dyes intermediate industry."*

**92.4 Methodology for finalization of quality of spent NaHS for utilization in production of dyes and dye intermediates**

1. The implementation of this SOP shall be done through State Level committee constituted for the implementation of HOWM Rules, 2016, or any such dedicated team identified for scrutiny and assessment with the following responsibilities for reviewing the application;
  - a. The committee or the concerned team shall recommend the quantity and TOC limit of Spent NaHS for utilization in production of Dyes and Dye intermediates products based on characteristics of spent NaHS, material balance and mass balance and quality requirements of the end usage of manufactured dye and dye intermediates.
  - b. The source emission from the stack connected to reactors/ process stacks, fugitive emissions in process/ storage area and effluent discharge shall comply with the standards prescribed in the section 92.7 (i) and 92.7 (ii) of this SOP respectively. Standards prescribed in the aforesaid section is not exhaustive, these may vary depending upon characteristics of spent NaHS based on sector specific source of generation and utilization process; however, committee may take final decision and impose stringent standards accordingly.
  - c. Hazardous waste generated during utilization of spent NaHS in production of various dyes and dye intermediates products shall be listed in the authorization issued by the SPCBs along with its disposal mechanism.
  - d. In addition to the minimal requisite facilities stipulated in this SOP at Section 92.11, the Committee or the concerned team may recommend additional facilities depending on the characteristics of Spent NaHS, unit operations/processes involved in utilization as reducing agent.
  - e. The general conditions shall be complied as mentioned in the SOP.
  - f. SPCB may grant authorization to actual users under Rule-9 for permission to utilize spent NaHS as reducing agent for production of dyes and dye intermediates.



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- g. While seeking authorization, the utilization facility shall submit feasibility report by giving observations on quantity of NaHS to be permitted for utilization, available utilization potential in the State vis-à-vis the generation, characteristics of waste proposed to be procured, clarification regarding sector of product from waste is proposed to be procured which is to be utilised in line with the SOP.

**92.5 Standard Operating Procedure for utilization of Spent Sodium Hydro Sulphide.**

This SOP is applicable only for utilization of spent sodium hydro sulphide (generated during caustic scrubbing of H<sub>2</sub>S gas in pesticide, inorganic chemical, dyes and dye intermediates industries) to be used as reducing agent in dyes and dyes intermediates.

- 1) The spent sodium hydro sulphide shall be procured only in SPCB/PCC authorized closed tankers mounted over vehicles fitted with requisite safeguards ensuring that there is no spillage.
- 2) There shall be a designated space for unloading of spent sodium hydro sulphide into 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 collection pit.
- 3) The vent of storage tanks shall be connected with adequate alkali scrubbing system as APCD followed by stack of adequate height.
- 4) The unit shall provide cool, well ventilated and designated storage space for the hazardous waste i.e., spent sodium hydro sulphide with caution sign. Storage, handling and management of sodium hydro sulphide shall be carried out with utmost care and under technical supervision.
- 5) The entire utilisation process shall have leak-proof and impervious flooring with adequate slope to collect spillages, if any, into a collection pit.
- 6) The spillages from the collection pit shall be transferred to ETP through chemical process pump.
- 7) Unit shall provide H<sub>2</sub>S gas detector(s) near storage and handling area.
- 8) There shall be no manual handling of the spent sodium hydro sulphide at any stage of the utilization process. Chemical process pump shall be used for transferring of spent sodium hydro sulphide through pipelines to the reaction vessel.
- 9) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within premises.
- 10) The reaction vessels shall be connected with adequate alkali scrubbing system as APCD followed by stack of adequate height as prescribed by concerned SPCB/PCC
- 11) The treated gases shall comply with the emission standards and then only be released in the atmosphere through dedicated stacks. The stack height shall be a minimum of 30m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 12) H<sub>2</sub>S liberated during utilization process (if any), may be re-used back in the process after scrubbing.



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- 13) Treatment and disposal of wastewater: Wastewater generated from the process, excess mother liquor, floor washing, spillage, reactor washing, scrubber bleed, etc. shall be treated physio chemically in an ETP to comply with wastewater discharge standards and may be sent to CETP for final disposal as prescribed by SPCB/PCC. Concentrated stream of wastewater (spent mother liquor) shall be disposed by means of forced evaporation i.e. either through MEE, spray dryer, etc.
- 14) 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.
- 15) The hazardous wastes (namely filter residue, ETP sludge, scrubber residue, MEE salt, etc.) generated shall be collected and temporarily stored in non-reactive drums/ bags category-wise under a dedicated hazardous waste storage area having proper caution sign and be sent to authorized common TSDF or other authorized facility within 90 days from the generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC. Such storage area shall be covered with proper ventilation.
- 16) The unit shall ensure that the spent sodium hydro sulphide is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 17) Transportation of Spent sodium hydro sulphide 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 documentation shall be followed as laid down under the said Rules.
- 18) Prior to the utilization of Spent sodium hydro sulphide, the unit shall obtain authorization for storage, utilization and disposal of Spent sodium hydro sulphide from the concerned SPCB/PCC under HOWM Rules, 2016.
- 19) 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.
- 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 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.
- 21) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.

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- 22) 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.

#### **92.6 Record>Returns Filing**

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of spent NaHS 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 Sodium Hydro Sulphide, 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 an annual return in Form-4 as per Rule 20 (1) and (2) of HOWM Rules, 2016 respectively, 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.
- 5) The unit shall use national hazardous waste tracking system (NHWTS) to manage the manifest, enter daily records of quantity generated, disposed, etc. once the portal is operational.

#### **92.7 Standards**

- 1) Source emissions from the stack connected to reactors/process unit shall comply with the following emission standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

|                            |                        |
|----------------------------|------------------------|
| SO <sub>2</sub>            | 200 mg/Nm <sup>3</sup> |
| HCl (Acid mist)            | 35 mg/Nm <sup>3</sup>  |
| Ammonia (NH <sub>3</sub> ) | 30 mg/Nm <sup>3</sup>  |
| Cl <sub>2</sub>            | 15 mg/Nm <sup>3</sup>  |
| H <sub>2</sub> S           | 5 mg/Nm <sup>3</sup>   |

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

|                  |                           |
|------------------|---------------------------|
| PM <sub>10</sub> | 5 mg/m <sup>3</sup> , TWA |
| SO <sub>2</sub>  | 13mg/m <sup>3</sup> , TWA |
| H <sub>2</sub> S | 50 ppm                    |

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



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- 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 (i) zero discharge as per consent or (ii) non-availability of the Common Effluent Treatment Plant (CETP), the unit shall achieve zero discharge by setting up adequate captive treatment facility.

### **92.8 Siting of Industry**

Facilities for utilization of Spent Sodium Hydro Sulphide 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.

### **92.9 Size of Plant and Efficiency of Utilization**

SPCB/PCC may evaluate the feasibility and efficiency about quantity of hazardous waste utilization as this being generic SOP.

### **92.10 Online detectors/ Alarms/ Analyzers**

In case of continuous process operations, online emission analyzers for SO<sub>2</sub>, NO<sub>x</sub> and H<sub>2</sub>S in the stack shall be installed and the online data be connected to the server of the concerned SPCB/PCC.

### **92.11 Checklist of Minimal Requisite Facilities:**

| Sl. No | Particulars   |
|--------|---|
| 1.     | Storage tank for Spent Sodium Hydro Sulphide with caution signs, proper covers, acid-proof lined floors, and spillage collection system. Tanks must connect to an adequate alkali scrubbing system (APCD) followed by stack of sufficient height. |
| 2.     | Cool, dry, well ventilated covered sheds for Spent Sodium Hydro Sulphide, product storage, and process activities. Dedicated hazardous storage area for temporary storage of waste during utilization.  |
| 3.     | Mechanized system for transfer of Spent Sodium Hydro Sulphide from storage tanks to Reaction Vessels.   |
| 4.     | Reaction vessels shall be connected with adequate alkali scrubbing system as APCD followed by stack of adequate height as prescribed by concerned SPCB/PCC.   |
| 5.     | 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.                                  |
| 6.     | ETP for treatment of wastewater generated from the process, etc.<br>In case of no access to CETP, install MEE, spray dryer etc. for concentrated stream of wastewater as means of forced evaporation.   |

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