

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 Sulphide and Spent Sodium bi Sulphide (generated during scrubbing of H₂S gases with caustic soda solution in the production of Carbon Di-Sulphide) for production of Sodium Sulphide and Sodium Bi Sulphide



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**Central Pollution Control Board
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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 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.
 - f) Monitor closely the quantity of hazardous waste (Spent Sodium Sulphide and Spent Sodium bi Sulphide) being sent by Carbon Disulphide plants (Generators) and the quantity being utilized by authorized facilities in production of recovered Sodium Sulphide and Spent Sodium bi Sulphide.
- 2) After issuance of authorization, SPCBs/PCCs shall verify the compliance of checklist and SOP on quarterly basis for initial 1 year; followed by random checks during subsequent period for at least once a year. The compliance reports may be submitted to CPCB.
- 3) In-case of lack of requisite infrastructures with the SPCBs/PCCs, they may engage 3rd party institutions or laboratories having EPA, 1986/NABUIS017025 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.
- 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 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.
- 7) The source and work zone standards suggested in the SOP are based on EPA notified and OSHA standard respectively, however, SPCBs/PCCs may impose more stringent standards based on the location or process specific conditions.
- 8) SPCBs/PCCs shall ensure that the utilizer of Spent Sodium Sulphide and Spent Sodium bi Sulphide shall maintain daily records in National Hazardous Waste Tracking System (NHWTS).

113.0 Utilization of hazardous waste (H.W.):

Type of HW	Source of generation	Recovery/ Product
Spent Sodium Sulphide and Spent Sodium bi Sulphide mixture (Category: 35.1 of Schedule I of HOWM Rules, 2016)	Generated from caustic scrubbing of H ₂ S gas liberated during production of Carbon di Sulphide	Sodium Sulphide and Sodium bi Sulphide for industrial end usages only.

113.1 Source of Waste:

H₂S gas is liberated during Carbon di Sulphide production process. The liberated gas is then scrubbed with Caustic solution thus generates Spent Sodium Sulphide (Na₂S) or Spent Sodium Bi Sulphide mixture (NaHS, also called Sodium hydrosulphide) with different proportions depending on the strength of caustic used in the scrubber. This is categorized as Hazardous Waste under Category: 35.1 of Schedule I of HOWM Rules, 2016, which is required to be disposed in an authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

Table 1. Typical Characteristics of Spent Sodium Sulphide and Sodium bi Sulphide mixture

S. No.	Parameters	Results	Unit
1	pH	12.20	-
2	Water Content	87	%
3	COD	272000	mg/l
4	TOC	< 10.00	mg/l
5	Cyanide Content	<1.0	mg/l
6	Pentasulfide as P	4.65	mg/l
7	H ₂ S	12.64	%
8	Purity		
	Sodium sulphide (Na ₂ S)	19.68	%
	Sodium Bisulphide (NaHS)	13.40	%
9	Lead as Pb	< 0.05	mg/l
10	Zinc as Zn	3.10	mg/l
11	Tin as Sn	< 0.05	mg/l
12	Cadmium as Cd	< 0.05	mg/l
13	Arsenic as As	< 0.05	mg/l
14	Mercury as Hg	0.0071	mg/l
15	Chromium as Cr	0.02	mg/l
16	Cobalt as Co	< 0.05	mg/l
17	Nickel as Ni	0.35	mg/l
18	Copper as Cu	< 0.05	mg/l
19	Vanadium as V	< 0.05	mg/l
20	Antimony as Sb	< 0.05	mg/l
21	Manganese as Mn	1.15	mg/l

Note: SPCBs/PCCs to check the characteristics of spent Na₂S/NaHS prior to issuance of authorization, any significant deviation with respect to typical values mentioned in the table above may be examined with respect to the source or may be referred to CPCB.

113.2 Utilization Process of Spent Sodium Sulphide and Spent Sodium bi Sulphide mixture):

Spent Sodium sulphide and spent sodium bi sulphide (generated from caustic scrubbing of H₂S gas emitted during production of Carbon Di-Sulphide), based on analysis and concentrations of Spent Sulphide solutions are mixed to prepare a homogenous solution. As per requirement the fresh NaOH is mixed with the Spent Sulphide solutions in a reactor to convert NaHS to Na₂S accordingly to obtain the required concentrations.

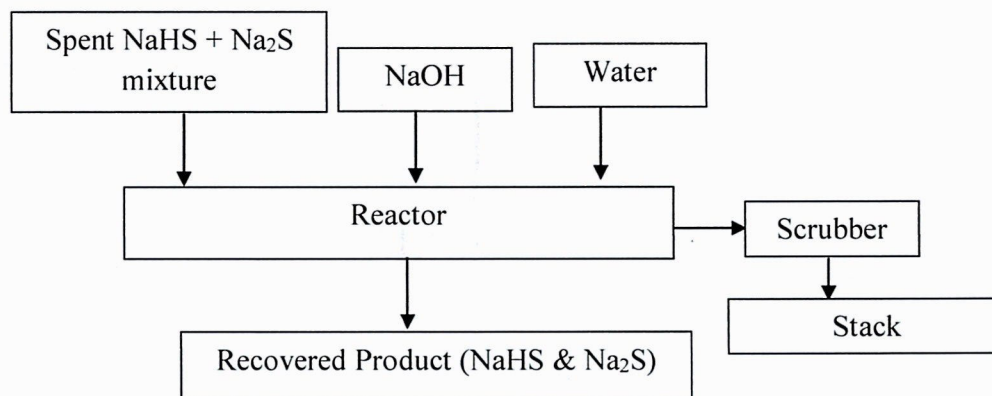


Figure: 1-Process flow diagram for utilization of Spent Sodium Sulphide and Spent Sodium Bi Sulphide.

113.3 Standard Operating Procedure for utilization of Spent Sodium Sulphide and Spent Sodium Bi Sulphide:

This SoP is applicable only for the utilization of Spent Sodium Sulphide and Spent Sodium Bi Sulphide mixture (generated from caustic scrubbing of H₂S gas emitted during production of Carbon Di-Sulphide) in production of Sodium Sulphide and Sodium Bi Sulphide.

- 1) The Spent Sodium Sulphide and Spent Sodium Bi Sulphide shall be procured only in SPCB/PCC authorized barrels/closed tanks mounted over vehicles fitted with-requisite safe guards ensuring no spillage of the HW.
- 2) There shall be a designated space for unloading of Spent Sodium Sulphide and Spent Sodium Bi 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 Spent Sodium Sulphide and Spent Sodium Bi Sulphide shall be stored in dedicated storage tanks with corrosive resistant material. The tanks should be placed under shed over an impervious flooring area with acid proof tiles/bricks with caution sign. Further, storage sheds/ area shall have proper slope and seepage collection pit to collect seepage / floor washing. The collected seepage / floor washing shall be channelized to Effluent Treatment Plant for further treatment.
- 4) The entire process shall have leak-proof and acid proof bricks/tiles with adequate slope to collect spillages, if any, into a collection pit. The spillages from the collection pit

shall be transferred to ETP or reaction tanks, as the case may be, through chemical process pump.

- 5) The unloading, storage, transfer and other handling of Spent Sodium sulphide and sodium bi sulphide from entire utilization process shall be carried out through dedicated mechanical transfer pump with fixed pipeline in closed system. Manual handling shall be strictly prevented.
- 6) The unit shall adopt adequate treatment method (such as Activated Carbon filtration, Hydrogen Peroxide treatment, etc.) to reduce the TOC content, heavy metals and other trace compounds in the Spent Na₂S/ NaHS for making it suitable for downstream utilization.
- 7) The unit shall provide fume extraction system in the process area.
- 8) The unit shall provide the fume extraction system followed by alkali scrubber for the storage and reaction tanks.
- 9) The treated gases shall comply with emission norms prior to dispersion into atmosphere through stack. The stack height shall be minimum of 30m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 10) Treatment and disposal of wastewater:
Wastewater generated from floor-washings, spillages, equipment washing, scrubber bleed shall be reused in the process or treated Physico- Chemically in an ETP or may be sent to CETP for final disposal or be treated further in a captive facility to comply with surface water discharge standards.

In case of zero discharge, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB / PCC. Otherwise, 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.
- 11) The hazardous wastes (namely storage tank or reaction tank residue, ETP sludge, etc.) generated shall be collected and temporarily stored in nonreactive drums/ bags under a dedicated hazardous waste storage area and be sent to authorized common TSDF or other authorized facility within 90 days or within period 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.
- 12) The unit shall ensure that the Spent Sodium Sulphide and Spent Sodium Bi Sulphide is procured only from authorized industries (involved in production of Carbon Di-sulphide) by the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 13) The unit shall ensure that the recovered Sodium Sulphide and Sodium Bi Sulphide is sold to authorized industries by the concerned SPCB/PCC as required under HOWM Rules, 2016. The unit shall sell the Na₂S/ NaHS derived utilizing Spent Na₂S/ NaHS, only to authorized actual end users and no sales to be allowed to traders.

- 14) Submission of details of end users to whom the Na₂S/ NaHS (derived from Spent Na₂S/ NaHS) is to be supplied and verification by the SPCB of the requirement of such end users, especially their capacity to use the Na₂S/ NaHS. The authorization of end users to be updated by concerned SPCBs specifying the quantity to be utilized.
- 15) Transportation of Spent Sodium Sulphide and Spent Sodium Bi 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 document shall be followed as laid down under the said Rules.
- 16) Prior to utilization of Spent Sodium Sulphide and Spent Sodium Bi Sulphide, the unit shall obtain authorization for handling, storage, utilization and disposal from the concerned SPCB/PCC under HOWM Rules, 2016.
- 17) 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.
- 18) 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.
- 19) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 20) 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.

113.4 Product Usage / Utilization

- 1) The recovered Sodium Sulphide and Sodium Bi Sulphide (manufactured by utilizing Spent Sodium Sulphide and Spent Sodium Bi Sulphide) shall comply with the Bureau of Indian Standards (BIS) IS 297 (2001), for further industrial utilization (wherever applicable).
- 2) The products shall comply with the Bureau of Indian Standards (BIS) & other regulatory standards, for further respective utilization (wherever applicable).
- 3) The unit shall label its products manufactured by utilizing Spent Sodium Sulphide and Spent Sodium Bi Sulphide as "This Sodium Sulphide and Sodium Bi Sulphide has been manufactured by utilizing Spent Sodium Sulphide and Spent Sodium Bi Sulphide."



113.5 Record/Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of Spent Sodium Sulphide and Spent Sodium Bi Sulphide 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 Sulphide and Spent Sodium Bi Sulphide, date wise treatment & 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, 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) Each procurement, production and transportation details (alongwith quantity of hazardous waste generated, utilized & disposed) shall be maintained on the National Hazardous Waste Tracking System/ Vehicle Location Tracking System (VLTS).

113.6 Standards

- 1) Source emissions from the stack connected to stack of APCD provided at source of emission such as reactor 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 S	5 mg/Nm ³

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

PM ₁₀	5 mg/m ³ TWA* (PEL)
H ₂ S	10 ppm
Sodium Hydroxide	2 mg/m ³ TWA* (PEL)

*PEL - Permissible Exposure Limit.

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

- 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 the above specified parameters for Source emissions and Work zone emission shall be carried out quarterly for first year followed by at least annually in the subsequent year of utilization. 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.

113.7 Siting of Industry

Facilities for utilization of Spent Sodium Sulphide and Spent Sodium bi Sulphide 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.

113.8 Size of Plant and Efficiency of Utilisation

Utilization process involves treatment of Spent Sodium Sulphide and Spent Sodium bi Sulphide, to achieve the desired purity and concentration of the product in terms of Na₂S & NaHS. Therefore, requisite facilities of adequate size such as storage shed and other plant & machineries shall be installed

113.9 Online detectors/ Alarms/ Analysers

In case of continuous process operations, online emission Analysers for PM & H₂S, in the stack shall be installed and the online data be connected to the server of the concerned SPCB/ PCC.

113.10 Checklist of Minimal Requisite Facilities:

Sl. No	Particulars
1.	Corrosion resistant storage tank of adequate capacity to store Spent Sodium Sulphide and Spent Sodium Bi Sulphide..
2.	The unit shall provide designated storage space for the hazardous waste with caution sign. The tank shall be placed under shed over impervious floor with acid proof tiles/bricks. Such storage tank(s) 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.	Cool, dry, well ventilated covered storage shed(s) for hazardous waste storage tanks within the premises
4.	Mechanized systems for handling & transfer of Spent Sodium Sulphide and Spent Sodium Bi Sulphide.
5.	The process shall have proper ventilation preferably with ventilation ducts above process units
6.	Fume extraction system for HW storage tanks and reactors connected to APCD comprising of alkali scrubber.
7.	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.
8.	Online analysers for PM & H ₂ S in the stack in case of continuous process operations.

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