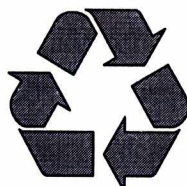


**Standard Operating Procedure and Checklist of Minimal Requisite Facilities
for utilization of hazardous waste under Rule 9 of the Hazardous and Other
Wastes (Management and Transboundary movement) Rules, 2016**

**Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-
Diaminobenzenesulfanilide (DABSA) in manufacturing of Para Amino
Benzene Sulphonic Acid (PABSA)**



November, 2018

Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change, Government of India)
Parivesh Bhawan, East Arjun Nagar,
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Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Di amino benzene sulfanilide in manufacturing of Para Amino Benzene Sulphonic Acid

Procedure for grant of authorisation by SPCBs/PCCs for utilization of Hazardous Waste

- 1) 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 used oils, waste oil, non-ferrous scraps, etc.) for maintaining records of receipt of hazardous wastes for utilization.
- 2) After issuance of authorization, SPCB shall verify the utilization process, checklist and SOPs on quarterly basis for during the initial 02 years; followed by random checks in subsequent period for at least once in every year.

In-case of lack of requisite infrastructures with the SPCBs/PCCs, 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.
- 3) SPCB/PCCs shall provide half yearly updated list of units permitted under Rule 9 of HOWM Rule, 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.
- 4) 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.
- 5) 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.
- 6) 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

47.0 Utilization of Spent Sulphuric Acid:

| Type of HW | Source of generation | Recovery/Product |
|---|--|---|
| Spent Sulphuric Acid (Category no.26.3 of Schedule I of HOWM Rules, 2016) | During production of 4, 4-Diaminobenzene sulfanilide (DABSA) | As a supplementary resource to manufacture of Para Amino Benzene Sulphonic Acid (PABSA) |

Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Di amino benzene sulfanilide in manufacturing of Para Amino Benzene Sulphonic Acid

47.1 Source of Waste

The Spent Sulphuric Acid is generated during manufacturing process of DABSA (4, 4-Diamino Benzene Sulphanilide). The chlorosulfonation of acetanilide using Chloro sulphonic acid produces spent acid containing sulphuric acid, hydrochloric acid and other organic impurities. A typical characteristic of the waste is given below:

| Parameters | Results |
|--------------------------------------|-----------|
| Acetanilide Sulphonyl Chloride (ASC) | < 5mg/kg |
| Acetanilide Flakes | < 5 mg/kg |
| Sulphanilic Acid | < 5 mg/kg |
| TOC | 8160 ppm |
| % of H ₂ SO ₄ | 19.36 % |

The aforesaid Spent Sulphuric Acid is categorised as Hazardous waste at S. No. 26.3 of Schedule I of HOWM Rules, 2016 which are required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

47.2 Utilization Process

In the utilization process, sodium salt of Sulphanilic Acid is allowed to react with Spent Sulphuric Acid in a reactor with constant stirring for 2-3 hours at room temperature. The reaction mass is filtered to obtain pure Sulphanilic Acid. The Sulphanilic Acid is further diazotized and allowed to react with Anilino methane sulfonic Acid. After 10-12 hours, reaction mass is filtered to get intermediate compound of PABSA. This intermediate compound is further hydrolyzed using Spent Sulphuric Acid. The hydrolyzed mass is filtered and dried followed by centrifuge to get final product i.e. PABSA. Sulphur Dioxide liberated during the addition of spent Sulphuric Acid (at both the stages i.e. during purification of Sulphanilic Acid and hydrolysis) is scrubbed using alkali scrubber. The waste water generated during the whole process (i.e. filtration, drying and washing etc.) is sent to Effluent Treatment Plant (ETP). Further, solid generated as hazardous waste, if any, during filtration from Nutch filter, is sent to the TSDF for final disposal. The process flow diagram of above utilization process is given in Fig. 1.

Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Di amino benzene sulfanilide in manufacturing of Para Amino Benzene Sulphonic Acid

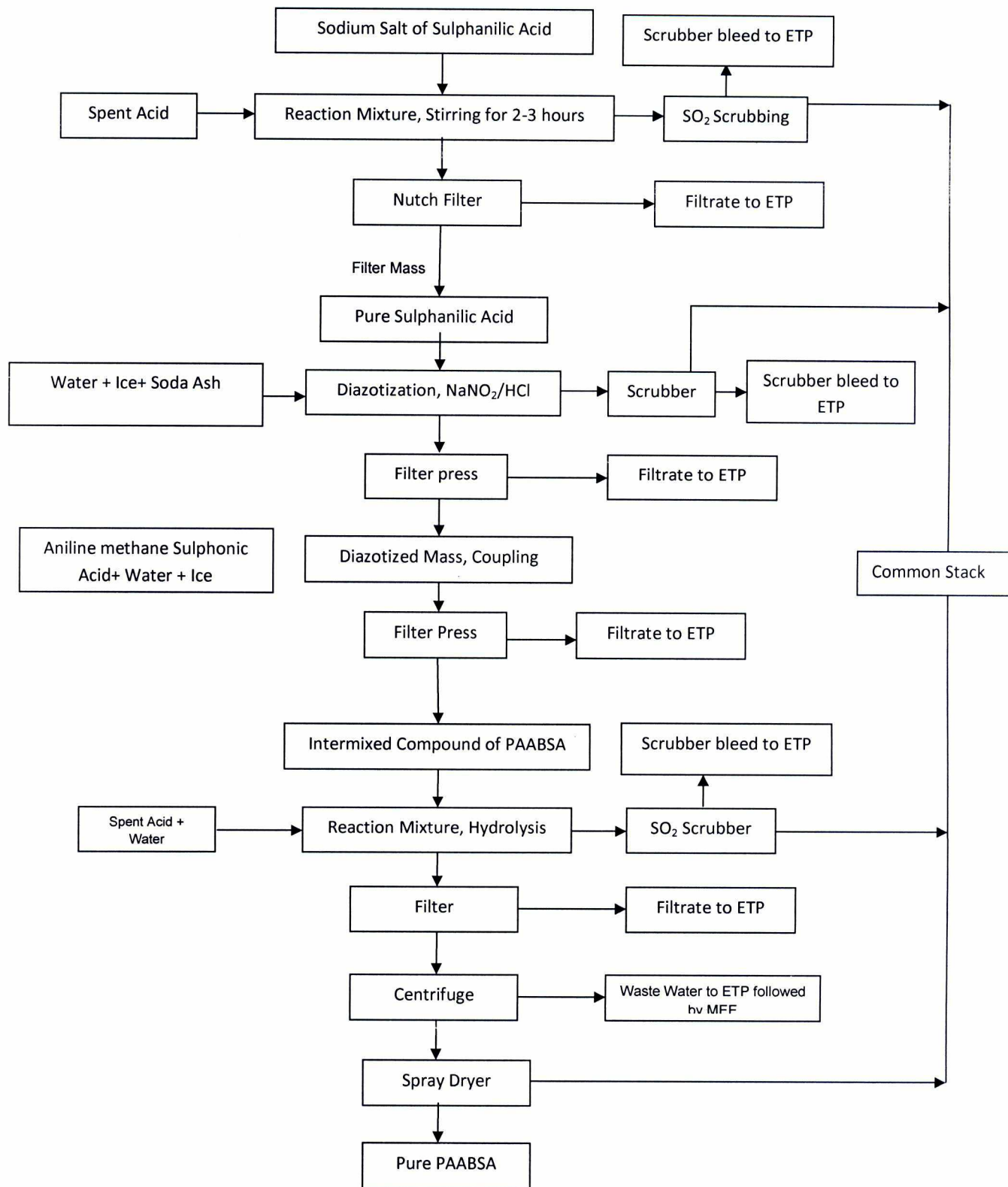


Fig. 1. Process flow diagram for production of PABSA

Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Di amino benzene sulfanilide in manufacturing of Para Amino Benzene Sulphonic Acid

47.3 Product Usage / Utilization

PABSA is used to manufacture Direct Red 81 Dyes which is used for paper industries and Orange 39 Dyes which is used for Paper and Wood Industries.

The unit shall label its product (i.e. PABSA) manufactured by utilizing aforesaid Hazardous waste as "This PABSA has been manufactured by utilizing Spent Sulphuric Acid, generated from 4, 4-Diaminobezenesulfanilide(DABSA) manufacturing process."

47.4 Standard Operating Procedure for utilization

This SoP is applicable only for the utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Diamino Benzene Sulphanilide (DABSA).

- (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 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 hazardous wastes (Spent Sulphuric Acid). Chemical process 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 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 tanks, as the cases may be, through chemical process pump.
- (6) The unit shall provide separate storage tanks for the storage of chemicals and the storage tanks should be at designated place with proper cover and with acid brick lining floors.
- (7) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within the unit.
- (8) Spent Sulphuric Acid shall be mixed with salt of sulphanilic acid in closed vessel reactors (isolation vessel) having mechanised stirring system with retention time of 2-3 hours, after constant stirring, Sulphanilic acid is reacted with aniline methane sulphonic acid in diazotization reactor with retention time of 10-12 hours respectively. These reactors (isolation vessel and diazotization reactor) should be connected to Scrubber. The mixer shall be kept under covered shed with adequate safety gadgets provided to workers, as well as ensuring proper ventilation in the process area.

Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Di amino benzene sulfanilide in manufacturing of Para Amino Benzene Sulphonic Acid

- (9) Sulphuric Acid Mist, HCl Vapour and SO₂ are expected to be liberated from the said reactors (hydrolysis reactor) where the Spent Sulphuric Acid is added. Thus, the hydrolysis reactor 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.
- (10) The spray dryer should be attached with Common Stack. The boiler attached with the spray dryer shall be operated electrically or by fuel permitted by the concerned SPCB/PCC. Depending upon type of fuel, suitable air pollution control device(s) shall be installed with the boiler followed by stack of height as prescribed by the concerned SPCB/PCC.
- (11) 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.
- (12) The treated acid fume/vapour shall comply with emission norms and shall be dispersed into atmosphere through stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
- (13) Treatment and disposal of wastewater:

Following are the sources of wastewater from utilization process;

- a) Waste water (generated from Nutch filter, Filter press, centrifuge (after hydrolysis process) and Floor washing/reactor wash/vehicle wash/spillages, etc.)
- b) scrubber bleeds

Waste water generated shall be treated Physico-Chemically in an ETP so as to comply with the prescribed inlet standards in case of CETP or be treated in captive ETP having adequate treatment facilities to comply with surface water discharge standards as stipulated in the Consent issued by the SPCBs/PCCs.

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. The condensate from MEE may be recycled in the utilization process.

- (14) 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.
- (15) 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.
- (16) The residue generated (from filter press, ETP sludge, scrubber, Spray Dryer/forced evaporator, product spillages, 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.

Utilization of Spent Sulphuric Acid generated during manufacturing of 4, 4-Di amino benzene sulfanilide in manufacturing of Para Amino Benzene Sulphonic Acid

- (17) Transportation of Spent Sulphuric Acid and residues generated during utilisation 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.
- (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 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.
- (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 the requirements in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable

47.5 Record>Returns Filing

- 1) The unit shall maintain a passbook issued by concern 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 Spent Sulphuric Acid, quantity, date wise utilisation of the same, quantity of PABSA 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 utilised, 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/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.

47.6 Standards

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

| | |
|---------------------------------------|-------------------------------------|
| H ₂ SO ₄ Vapour | 1.0 mg/m ³ Ceiling limit |
| HCL Mist | 7.0 mg/m ³ Ceiling limit |
| PM ₁₀ | 5.0 mg/m ³ TWA* |

Reference: Occupational Safety and Health Standard 1910:1000

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TWA: time-weighted average
The permissible Exposure Limit is 8-hours TWA*

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.

- 2) Source emission monitoring from the stack attached to the Common Stack attached to purifying reactor and hydrolyzing reactor etc. shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent;

| | |
|--|-------------------------|
| H ₂ SO ₄ vapour & Mist | 50.0 mg/Nm ³ |
| HCl Vapour & mist | 35.0 mg/Nm ³ |
| TOC | 20.0 mg/Nm ³ |

- 3) Monitoring of the specified parameters for source 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 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.

47.7 Siting of Industry

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

47.8 Size of Plant & Efficiency of utilisation

Maximum 3.8 MT of Spent Sulphuric Acid would be required to produce 1 MT of PABSA. Therefore, requisite facilities of adequate size of storage shed and other plants & machineries as given in para 47.10 below shall be installed accordingly.

47.9 On-line detectors / Alarms / Analysers

Online emission monitoring systems shall be installed with data transmission to CPCB and SPCBs server in case of continuous process operations for H₂SO₄ vapour and mist and HCl mist.

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. Such storage tank(s) 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, 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 |

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| | |
|-----|--|
| | tanks within premises. |
| 3. | Mechanized system for transfer of Spent Sulphuric Acid from tankers to storage tanks and storage tanks to reactor vessels |
| 4. | The process units shall have proper ventilation (preferably with ventilation ducts above the process units connected to ID fan with exhaust above roof level). |
| 5. | Covered hazardous waste storage space to store hazardous generated during utilization process |
| 6. | Isolation Vessels |
| 7. | Diazotization Reactor |
| 8. | Hydrolysis reactor |
| 9. | Nutch filter |
| 10. | Filter Press |
| 11. | Centrifuge for recovery and washing of product |
| 12. | Spray Dryer (dryer of adequate size operated electrically or by fuel as permitted by the concerned SPCB/PCC. |
| 13. | Suction arrangement to channelize emissions from reaction vessel, diazotization reactor and hydrolysis reactor to the APCD and finally to the common stack of height as prescribed by the SPCBs/PCCs. Scrubber shall be install all these units. |
| 14. | Adequate Effluent treatment plant so as to comply with standards/conditions prescribed by the concerned SPCB/PCC. or Forced Evaporator followed by Spray dryer (in case of zero discharge condition by SPCB/PCC) |
| 15. | Common 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. |
| 16. | Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process |

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