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 from Chlor-alkali plants) in the manufacturing of Aluminium Sulphate



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Central Pollution Control Board (Ministry of Environment, Forest & Climate Change, Government of India) Parivesh Bhawan, East Arjun Nagar, Shahdara, Delhi – 110032 <u>Procedure for grant of authorization by State Pollution Control Boards (SPCBs)/ Pollution</u> <u>Control Committees (PCCs) for utilization of Hazardous waste</u>

- 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 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 H₂SO₄) being sent by chlor-alkali plants and the quantity being utilized by authorized facilities intends to utilize the same.
- 2) After issuance of authorization, SPCBs/PCCs shall verify the compliance of checklist and SoP on quarterly basis for initial 1 years; 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/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) Rules, 2016 (HOWM Rules, 2016) to CPCB and also upload the same on SPCB/PCC website, periodically. Such updated list shall be sent to CPCB.
- 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 authorized captive disposal of the hazardous waste (if any generated during utilization) or its complete utilization or arrangement for transfer to authorized 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 E(P)A 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 H₂SO₄ shall maintain daily records in National Hazardous Waste Tracking System (NHWTS).

1 Page

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98.0 Utilization of Spent Sulphuric Acid:

Type of HW			Source of generation			Recovery/Product	
Spent	Sulphuric	Acid	Generated	from	Chlor-	Aluminum	Sulphate
(Category: B-15 of Schedule		Alkali plants [in drying the		(Non-Ferric Alum).			
ll of HOWM Rules, 2016)		chlorine gas]					

98.1 Source of Waste:

Spent sulphuric acid (purity around >80%) generated from the Chlor-alkali plants is categorized as hazardous waste listed at Category: B-15 of Schedule II of HOWM Rules-2016, which is required to be disposed in an authorized disposal facility in accordance with condition, when not utilized as resource recovery.

Parameters	Unit	Results *
pН		< 2
Acidity as H ₂ SO ₄	%	82.25
Lead	ppm	< 0.05
Iron	ppm	23.12
COD	ppm	85,9
TOC	ppm	< 150
Total Chromium	ppm	0.074
Mercury	ppm	< 0.01
Arsenic	ppm	< 0.01
Cyanide	ppm	< 0.01

Table 1. Criteria characteristics of Spent Sulphuric Acid

*The concentration of spent acid proposed for utilization may vary +/- 10% of the values mentioned in the table

98.2 Utilization Process at Production Stage:

Spent sulphuric acid is charged in to the reactor along with fresh aluminium hydrate and water. After completion of the reaction, the slurry is collected through bottom valve of the reactor and transferred to the crystallizer tray for the natural cooling and formation of alum lumps/ cubes (Aluminium Sulphate).

The lumps/ cubes are then passed through crusher for crushing, as per the requirement and final product (Aluminium Sulphate) recovered is packed in HDPE bags.

Page 27 Page



Utilization of Spent Sulphuric Acid (generated from Chlor-alkali plants) in the manufacturing of Aluminium Sulphate

Figure 1: Process Flow Diagram utilization of spent sulphuric acid in manufacturing of Aluminium Sulphate

Sulphate

98.3 **Product Usage / Utilization:**

- 1) The end product i.e. Aluminum Sulphate manufactured by utilizing Spent Sulphuric acid shall be used for industrial purposes only.
- 2) The product (i.e. Aluminum Sulphate) thus produced, shall not be utilized/ permitted for drinking water purification, agriculture/ soil applications, pharmaceutical/ healthcare products or in food material manufacturing or processing.
- 3) Aluminum Sulphate manufactured by utilizing the Spent Sulphuric Acid shall meet BIS specification for its intended use i.e. IS 260:2001.
- 4) The unit shall label its product i.e. Aluminum Sulphate manufactured by utilizing hazardous waste as "This Aluminum Sulphate has been manufactured by utilizing Spent Sulphuric Acid generated from Chlor-alkali plants and not fit for use in drinking water purification, agriculture/ soil applications, pharmaceutical/ healthcare products or in food".

98.4 Standard Operating Procedures (SoP) for utilization:

This SoP is applicable only for utilization of spent sulphuric acid (generated from Chlor-alkali plants in manufacturing of Aluminum Sulphate.

1) The spent sulphuric acid shall be procured/ transported in SPCB/PCC authorized tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage.

3 Page

Utilization of Spent Sulphuric Acid (generated from Chlor-alkali plants) in the manufacturing of Aluminium Sulphate

- 2) There shall be a designated space for unloading of spent sulphuric acid into the storage tank made of stainless steel/ HDPE. 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 the collection pit.
- 3) The unit shall install storage tank under cool, dry, well ventilated covered storage shed(s) within the premises, as authorized by the concerned SPCB/ PCC under HOWM Rules, 2016, so as to eliminate rain water intrusion.

Further, the storage area shall have leak-proof floor tiles with adequate slope to collect spillage, if any, into a collection pit. The spillage from collection pit shall be transferred to the reaction tanker through chemical process pump.

- 4) There shall be no manual handling of the hazardous wastes (spent sulphuric acid). Acid proof pump shall be used for the transfer of spent sulphuric acid through fixed pipelines to the reaction vessel.
- 5) The unit should provide acid proof glass window for monitoring the progress of reaction in vessel.
- 6) The complete manufacturing process shall be a closed system with water and/or alkali scrubbers connected to the common vent of spent acid storage tank and reaction vessel.
- 7) The crystallization trays shall be covered under shed and the tray area should be ventilated through separate air venting system.
- 8) The pulverizer shall be connected with an enclosed bag filters, ID fan and stack.
- 9) The treated gases/fumes from the stack attached to reaction vessel and pulverizer 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) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within the unit. The crystallization and final product storage area should be maintained with proper housekeeping. There shall be no spillages of product during material handling with minimum manual intervention.
- 11) It shall be ensured that the aforesaid hazardous waste is procured from the industries which have valid authorization for the same from the concerned SPCB as required under HOWM Rule, 2016.
- 12) Treatment and disposal of wastewater:

There shall be no wastewater generation from the process.

The unit shall maintain zero liquid discharge. Any spillages, scrubber bleed or wash water generated within the premises may be managed as per conditions stipulated in the Consent granted by the SPCB/PCC.

4 Page

Utilization of Spent Sulphuric Acid (generated from Chlor-alkali plants) in the manufacturing of Aluminium Sulphate

- 13) The hazardous wastes generated during said utilization process (bag filter dust, process residue, floor sweepings, spilled material, etc.) 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 from generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC.
- 14) The sender of spent sulphuric acid shall have valid authorization from the concerned SPCB/ PCC under HOWM Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.
- 15) Prior to utilization of spent sulphuric acid, the unit shall obtain authorization for storage. utilization and disposal of spent sulphuric acid from the concerned SPCB/ PCC under HOWM Rules, 2016.
- 16) 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.
- 17) 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.
- 18) The unit shall provide suitable fire safety arrangements, flame proof electrical fittings and on site emergency plan approved by concerned agency.
- 19) 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.

98.5 Record / Returns Filing:

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of spent sulphuric acid 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 sulphuric acid. date wise utilization of the same, hazardous waste generation and its disposal, etc. shall be

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JO 5 Page

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 & file annual returns in Form 4 as per Rule 20 (1) and (2) of the 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) The unit shall use NHWTS to manage the manifest, enter daily records of quantity generated, disposed, etc.

98.6 Standards:

1) Source emission monitoring from the common stack attached to the vent of hazardous waste storage tank and reaction vessel shall comply with the following emissions standards or as prescribed by the concerned SPCB/PCC, whichever is stringent:

Particulate Matter	150 mg/Nm^3	
SO ₂	100 mg/Nm ³	
Acid mist (H ₂ SO ₄)	50 mg/Nm^3	

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

PM10	5 mg/m^3 , *TWA
SO ₂	13 mg/m ³ , TWA
Acid mist (H ₂ SO ₄)	$1 \text{ mg/m}^3, *C$

*TWA = Time Weighted Average for 8 hours,

*C = Ceiling limit: 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 fugitive 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 generated (if any) 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.
- 5) The unit shall label its product bags with a notice stating that "This Aluminum Sulphate is manufactured by utilizing *Spent Sulphuric Acid generated from Chlor-alkali plants* and not fit for use in drinking water purification, agriculture/ soil applications, pharmaceutical/healthcare products or in food.



98.7 Siting of Industry:

Facilities for utilization of spent sulphuric acid shall be preferably located in a notified industrial area or industrial park / estate / cluster and should be in accordance with Consent to Establish issued by the concerned SPCB/PCC.

98.8 On-line detectors / Alarms / Analysers:

In case of continuous process operations, online emission analyzers for PM and SO₂ in the stack shall be installed which should be connected to servers of SPCB/PCC and CPCB.

98.9 Size of Plant and Efficiency of Utilization

1.5 MT of aluminium sulphate is produced by utilizing 1 MT of spent sulphuric acid i.e. 85% yield of utilization along with other raw materials namely Aluminium hydrate & water. Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

Sl. No	Particulars				
\mathbf{l}_{x}	Spent H ₂ SO ₄ storage tank(s) with acid proof rubber lining having adequate storage				
	capacity.				
2.	The HW storage tank shall be placed above the ground and contained with low raise bund				
	wall & acid proof floor with slope to collect spillages into collection pit.				
3.	Chemical process pump to transfer spent H ₂ SO ₄ from tanker to storage tank and the				
	reaction tank.				
4.	The entire process area shall be made of leak-proof and acid proof floor tiles with				
	adequate slope to collect spillages, into collection pit.				
5.	Collection pit for collection of spillages from the working and unloading area.				
6,	Common vent for reaction vessel and storage tanks of spent acid be connected with water				
	and alkali scrubber of adequate capacity and stack.				
7,	Reaction vessel / crystallization unit shall have glass window.				
8,	Air venting / evacuation system connected to stack for tray crystallization area.				
9.	Crusher, Pulverizer connected with closed type bag filters.				
10.	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.				

98.10 Checklist of Minimal Requisite Facilities:
