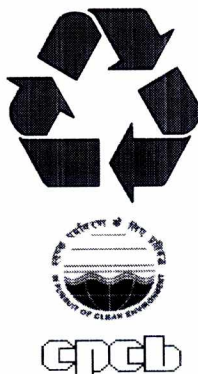


**Standard Operating Procedure and Checklist of Minimal Requisite Facilities
for utilization of hazardous waste under Rule 9 of the Hazardous and Other
Wastes (Management and Transboundary movement) Rules, 2016**

**Utilization of Spent Ammonium Carbonate (generated during
manufacturing of Copper Pthalocyanin blue (CPC Blue)) in
Manufacturing of Zinc Carbonate and Copper Carbonate**



February, 2019

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

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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 at least once a year.
 In-case of lack of requisite infrastructures with the SPCB/PCC, 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.
- (iii) SPCBs/PCCs shall provide half yearly updated list of units permitted under Rule 9 of Hazardous and Other Wastes (Management & Transboundary Movement) 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 standard respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions.

50.0 Utilization of Spent Ammonium carbonate:

Type of HW	Source of generation	Recovery/Product
Spent Ammonium carbonate - Category 26.1 of schedule-I of HOWM Rules, 2016	during manufacturing of copper Pthalocyanin blue (dye & dye-intermediate)	Metallic carbonates (i.e. zinc carbonate, copper carbonate)

50.1 Source of Waste

Spent Ammonium carbonate (hazardous waste) is generated during manufacturing of dye & dye-intermediate i.e. Copper Pthalocyanin blue (CPC Blue). During the production of CPC blue, ammonia gas liberated from the reaction vessel is passed through water scrubber, which generates Ammonium carbonate.

The aforesaid Spent Ammonium Carbonate is categorized as hazardous waste at S.No. 26.1 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.

A typical characteristic of the waste is given below:

Parameters	UNIT	Spent Ammonium carbonate (Hazardous Waste) used for production	
		Zinc Carbonate	Copper Carbonate
Moisture	%	55.02	55.68
pH		9.39	9.32
Thylo cyanine	mg/kg	<1.0	<1.0
Nitro benzene	mg/kg	8.2	9.1
Chloride as Cl	%	0.076	0.072
TOC	%	0.022	0.022
Copper	mg/kg	9.03	8.92
Zinc	mg/kg	371	269
Lead	mg/kg	13.88	15.17
Chromium	mg/kg	<0.05	<0.05
Nickel	mg/kg	0.81	0.96
Cadmium	mg/kg	1.43	1.09

50.2 Utilization Process

The production of metallic carbonates (i.e. zinc carbonate and copper carbonate) includes precipitation of ammonium carbonate with metallic sulphates to form metallic carbonate followed by filtration and drying.

The production of the metallic carbonate involves addition of spent ammonium carbonate to metallic sulphate (zinc/copper) solution in the reaction vessel and allowing to precipitate by maintaining pH 7 (by adding lime/H₂SO₄ respectively). After precipitation, metallic carbonate slurry is transferred through filter press to separate metallic carbonate and

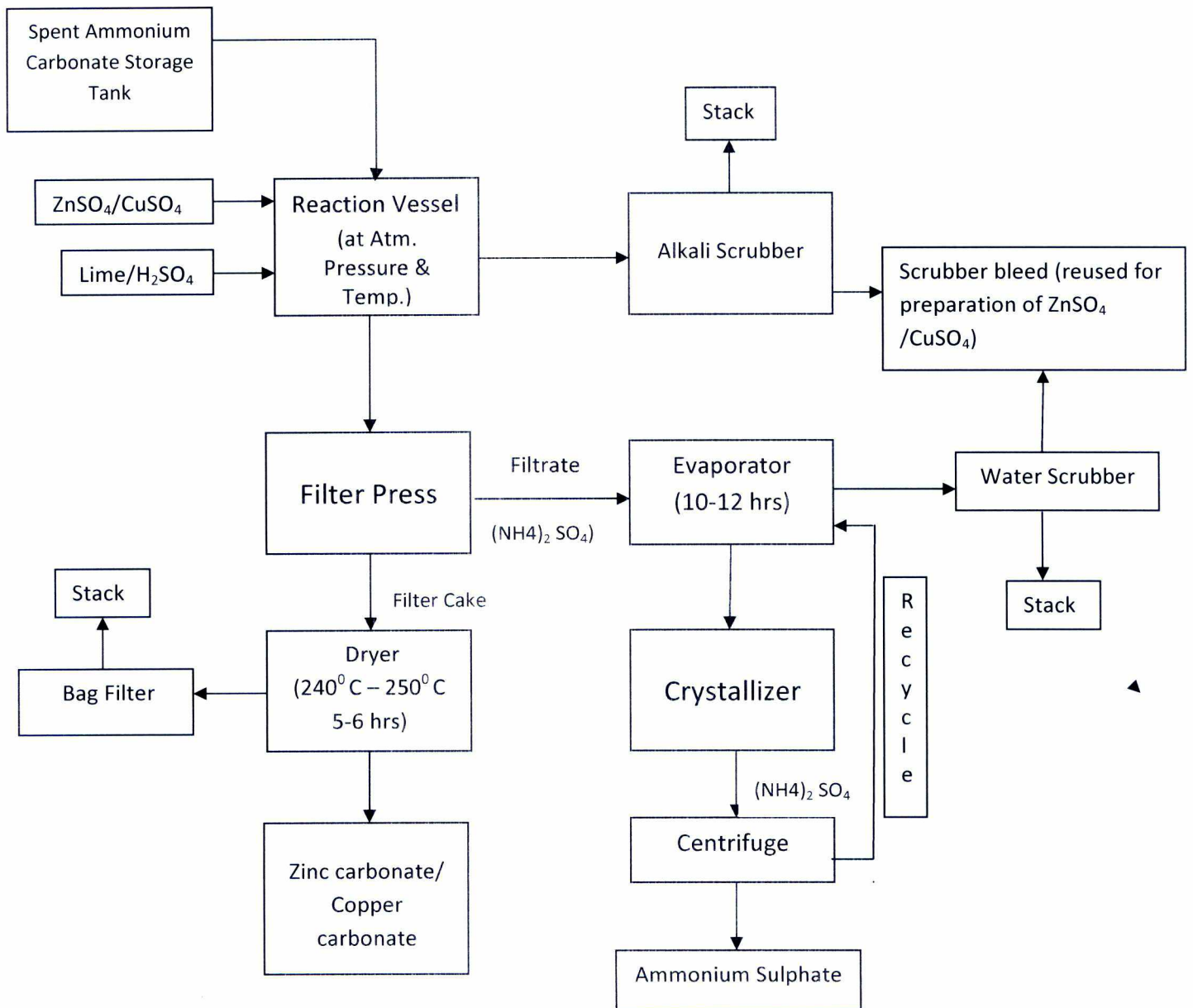
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ammonium sulphate. The filter cake containing metallic carbonate (zinc/ copper) is sent to drier and dried product is collected and packed.

The ammonium sulphate solution collected from the filter press is sent to evaporator followed by crystallizer and centrifuge. The ammonium sulphate crystal collected may be used for alum manufacturing. The mother liquor generated from centrifuge may be recycled in the evaporator. The reject or Waste water generated from the process is to be managed as per the conditions stipulated in the Consent to Operate granted by concerned SPCB/PCC. The flow diagram of the utilization process is provided as below;

Figure 1. Process Flow Diagram of manufacturing of Zinc Carbonate/ Copper Carbonate



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50.3 Product Usage / Utilization

Metallic Carbonates (Zinc carbonate / copper carbonate) will be utilized in industrial use i.e. textile, rubber industry.

The unit shall label its product (i.e. Zinc Carbonate / Copper Carbonate) manufactured by utilizing aforesaid Hazardous waste as “This zinc carbonate / copper carbonate has been manufactured by utilizing spent ammonium carbonate, generated from CPC Blue manufacturing process.”

The ammonium sulphate so produced during the said utilization process be used for manufacturing alum. The application of alum, shall only be allowed in Dye & Dye intermediate manufacturing, Leather tanning process or other industrial process application etc. and shall not be permitted for use in manufacture of fertilizer or in water treatment. In case, the said end use of ammonium sulphate is not possible, the same may be disposed in TSDF.

50.4 Standard Operating Procedure (SoP) for utilization

This SoP is applicable only for the utilization of Spent Ammonium carbonate generated from CPC Blue manufacturing process.

- (1) Spent Ammonium carbonate shall be transported in SPCB/PCC authorised dedicated 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 Ammonium carbonate into a rubber lined storage tank. The receiving storage tank shall be placed above the ground and contained with low raise parapet/bund wall & dedicated leak proof floor with slope to collect spillages, if any, into collection pit. Alternatively, storage tanks for spent ammonium carbonate 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.

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- (4) There shall be no manual handling of the hazardous wastes (Spent ammonium carbonate). Chemical process pump shall be used for transfer of Spent ammonium carbonate through pipelines to the reaction vessel.
- (5) The entire process area shall have dedicated leak-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 proof 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 ammonium carbonate shall be mixed with zinc sulphate/copper sulphate only in closed vessel reactors (isolation vessel) having mechanised stirring system for proper mixing and maintaining the pH up to 7. 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.
- (9) NH₃, heavy metals and TOC are expected to be liberated from the said reactors (isolation vessel) where the spent ammonium carbonate is added. Thus, the said reactors (isolation vessel) shall be connected with hood over it to suck acid fume/vapor. The hood shall be maintained under suction followed by treatment in scrubber using alkaline medium.
- (10) The dryer shall be attached with bag filter followed by Stack of height as prescribed by the concerned SPCB/PCC.
- (11) The evaporator shall be attached with scrubbing system to contain the fumes/vapors released from the evaporator followed by stack of height as prescribed by the concerned SPCB/PCC.
- (12) The evaporator followed by centrifuge and crystallizer 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 at the evaporator followed by stack of height as prescribed by the concerned SPCB/PCC.
- (13) 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,

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aprons, and/or coveralls of chemical resistant material and impervious boots of chemically resistant material.

- (14) 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.
- (15) Treatment and disposal of wastewater:

Following are the sources of wastewater from utilization process;

- a) Waste water (generated from Floor washing/reactor wash/vehicle wash/spillages, etc.)
- b) Scrubber bleed

Waste water and scrubber bleed may be reused in the said utilization process for the production of zinc sulphate/copper sulphate.

In case of Waste water generation, the same 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 managed as per conditions stipulated by the SPCBs/PCCs.

- (16) It shall be ensured that Spent ammonium carbonate 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.
- (17) SPCBs/PCCs shall ensure synchronization of generation and utilization of Spent ammonium carbonate and the same shall be reflected in respective authorization specifying name and quantity.
- (18) Prior to utilization of Spent ammonium carbonate, the unit shall obtain authorization for generation, storage, and utilization of spent ammonium carbonate solution from the concerned State Pollution Control Board under the Hazardous and Other Wastes (Management and Transboundary Movement) Rules 2016.
- (19) 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.
- (20) a) The residue generated (from bag filter attached to dryer, scrubber, product spillages, etc.) in case of copper carbonate production, shall be collected and temporarily stored in non reactive drums / bags under a dedicated hazardous waste

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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.

b) The residue generated (from bag filter attached to dryer, scrubber, product spillages, etc) in case of zinc carbonate production may be reused in the said utilization process. If the residue is not reused, the same 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.

- (21) Transportation of Spent Ammonium Carbonate 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.
- (22) 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.
- (23) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- (24) 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.

50.5 Records/return filing

- (1) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of Spent Ammonium Carbonate shall be entered:
 - Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of receipt in the premises

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- (2) A log book with information on source and date of procurement of each type of the said hazardous wastes, quantity, date wise utilization of the same, quantity of zinc carbonate and copper carbonate 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.
- (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.

50.6 Standards

- (1) Fugitive emissions in the work zone:

Ammonia	-	35.0 mg/m ³ TWA*
Zinc Oxides	-	5.0 mg/m ³ TWA*
Copper Fumes	-	0.1 mg/m ³ TWA*
Sulphur dioxide	-	13.0 mg/m ³ TWA*

(Reference: Occupational Safety and Health Standards 1910:1000)

TWA - Time-weighted average*

The Permissible Exposure Limit is 8-hour TWA.

- (2) Monitoring of specified parameters for fugitive 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 by NABL accredited or ISO17025/EPA recognized laboratories and the results shall be submitted quarterly to the concerned SPCB/PCC.

- (3) Stack Emissions:

- a) Stack attached to evaporator and reaction vessel

PM	-	50 mg/Nm ³
Ammonia	-	30 mg/Nm ³
Heavy Metals	-	0.5 mg/Nm ³
TOC	-	20 mg/Nm ³

- b) Stack attached to dryer

PM	-	50 mg/Nm ³
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5.	Covered hazardous waste storage space to store hazardous generated during utilization process
6.	Reactors (isolation vessel) with suction hood connected via duct to scrubber and stack
7.	Filter press
8.	Evaporator for filtrate (i.e. ammonium sulphate).
9.	Crystallizer with chilling unit (for ammonium sulphate)
10.	Centrifuge (for ammonium sulphate)
11.	Dryer (of adequate size operated electrically or by fuel as permitted by the concerned SPCB/PCC)
12.	Bag filter shall be installed in case of dryer followed by stack of height as prescribed by the concerned SPCB/PCC
13.	Suction arrangement to channelize emissions from reaction vessel, dryer and evaporator to the APCD. Appropriate Scrubber system shall be installed to reaction vessel and evaporator followed by stack of height as prescribed by the SPCBs/PCCs
14.	Adequate Effluent treatment plant so as to comply with standards/conditions prescribed by the concerned SPCB/PCC
15.	Forced Evaporator in case of zero discharge condition
16.	Boiler (attached with the dryer/forced evaporator) operated electrically or by fuel as 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
17.	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
18.	Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process

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