

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 Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride



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**Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change,
Government of India)
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Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

Procedure for grant of authorization by State Pollution Control Boards (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 same source of generation as specified in SoP.
 - b. The utilization shall be same 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 the quantity of spent Zinc Chloride ($ZnCl_2$) generation and demand for utilization of the same by industries involved in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride in the State.
- 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 authorised captive disposal of the hazardous waste (if any generated during utilization) or its complete utilization or arrangement for transfer to 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 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 $ZnCl_2$ shall maintain daily records in National Hazardous Waste Tracking System (NHWTS).



Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

96.0 Utilization of Spent Zinc Chloride solution:

Type of HW	Source of generation	Recovery/Product
Spent Zinc Chloride solution categorized as Class C-4 of Schedule-II of (HOWM Rules – 2016)	Dye & dye intermediate industry	Secondary production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

96.1 Source of Waste:

Spent Zinc Chloride Solution generated during production of Bi Chloro Methyl Biphenyl (BCMB) is considered as hazardous waste listed at C-4, Schedule-II of HOWM Rules –2016, which is required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized for energy or resource recovery.

Table 1. Typical characteristics of spent ZnCl₂ given below:

Sr.No.	Parameter	Unit	Value
1.	pH	--	<2.0
2.	Total Zinc as Zinc Chloride, % by Mass	%	19.8
3.	Total Organic Carbon	mg/l	<6700
4.	Chemical Oxygen Demand	mg/l	<18000
5.	Ammonia as NH ₄ Cl	%	<0.90
6.	Sulphate	mg/l	<900
7.	Chloride	mg/l	<37.5
8.	Mercury as Hg	ppb	<0.001
9.	Chromium as Cr	ppb	<3.0
10.	Barium as Br	%	<0.05

96.2 Utilization Process

1) Production of Zinc carbonate:

The basic raw material for this product are ZnCl₂ and Soda ash. Spent ZnCl₂ solution is transferred to a mixing vessel equipped with a stirrer. Condensate water recovered from the evaporator is pumped from the storage vessel in a mixing vessel. In a reaction vessel, soda ash (Na₂CO₃) powder is added by a bucket elevator to make soda ash solution. It is further mixed thoroughly and continuously to obtain a uniform solution. Soda Ash solution is added to the reaction vessel containing spent ZnCl₂. The free acid neutralization in ZnCl₂ is achieved by using Sodium Hydroxide (caustic) yielding the same NaCl and water. Free unreacted hydrochloric acid will react first as per the first equation.

Once the free acid is neutralized, addition of excess Soda Ash solution will result in the conversion of Zinc chloride to Zinc Carbonate. Since Zinc carbonate is insoluble in water the solution will yield precipitated zinc carbonate in form of a white slurry.



Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

Once the reaction is completed the solution is transferred to a continuous belt filter (pneumatic) which operates under vacuum and separates the solid zinc carbonate cake and the liquid brine solution. The separated solid zinc carbonate cake is transferred to the dryer hopper and the liquid brine solution is pumped to a storage vessel. The brine solution is tested for NaCl concentration. The dry powder is packaged into bags from a cyclone and bag filters. Vent from dryer is attached to a cyclone and bag filters (APCM) to arrest the fine dust particles of product which is then collected in bags.

2) Production of NaCl:

The liquid brine generated in the system is sent to an evaporator to obtain crystalline NaCl salt and the water vapour which is condensed to form condensate water (which is reused into the system for preparation of soda ash solution). Once the target concentration is achieved, Brine solution from evaporator is sent to filter press and dryer and crystalline salt is bagged and sold as industrial grade salt.

The brine solution may also be sent to end users to be used as industrial grade salt.

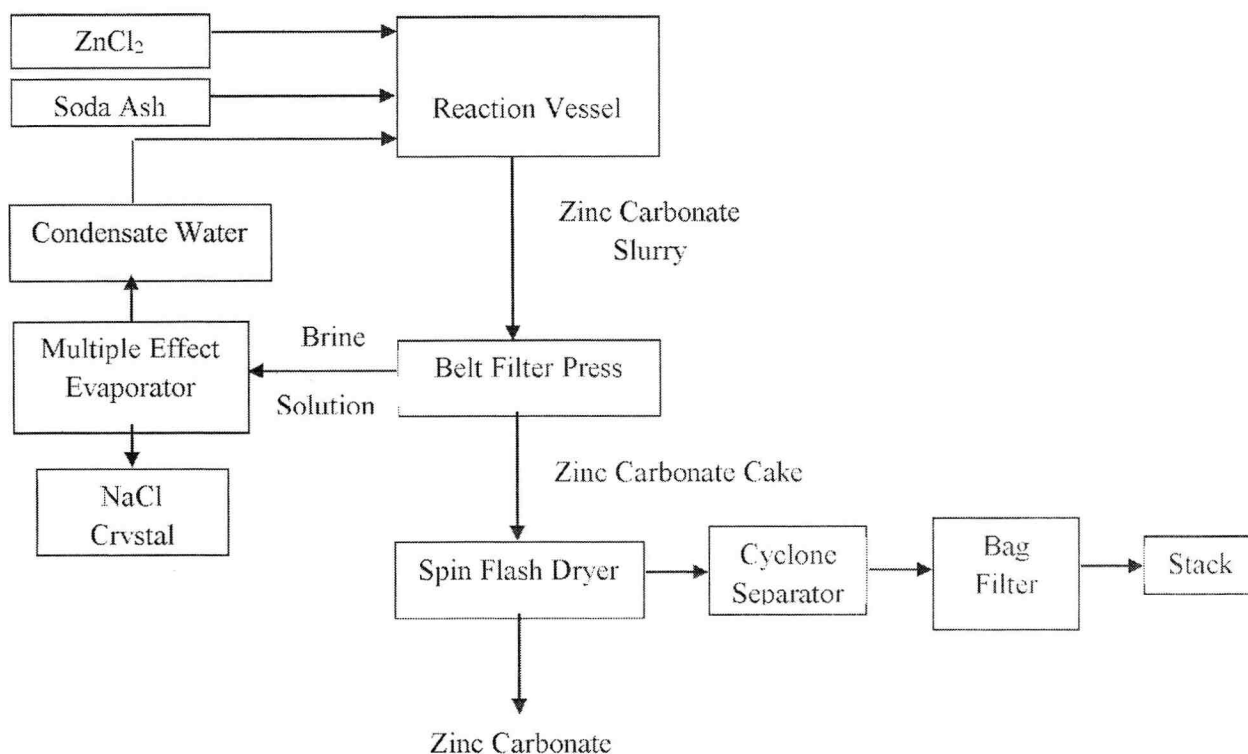


Figure: 1-Process flow diagram for utilization of spent zinc chloride in manufacturing of Zinc Carbonate and Sodium Chloride.

3) Production of Zinc Oxide from Zinc Carbonate

Zinc Carbonate produced by utilizing spent zinc carbonate solution gets converted to Zinc Oxide in Calcination process operating at temperature typically around 400 °C.

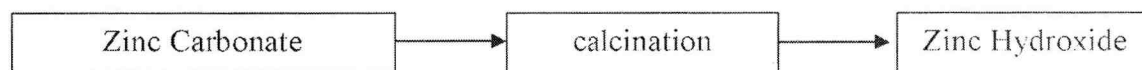


Figure: 2-Process flow diagram, conversion of zinc carbonate into Zinc Oxide.

Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

96.3 Product Usage / Utilization

1. The Product i.e. ZnCO_3 manufactured by utilizing spent ZnCl_2 (generated during manufacturing of BCMB) shall be utilized in Rubber, Ceramic and Paint industry only (as per industry requirement).
2. The Product i.e. ZnO shall comply Bureau of Indian Standards (BIS)-3399:2013, and shall be allowed for downstream utilization in Rubber, Ceramic and Paint industry only.
3. The Product i.e. NaCl shall comply Bureau of Indian Standards (BIS)-797:1982, for use in chemical industries and other industrial purposes excluding food, food processing, pharma and fertilizer industries.
4. The unit shall label its product i.e. ZnCO_3 , ZnO and NaCl manufactured by utilizing spent ZnCl_2 as "*This ZnCO_3 / ZnO / NaCl has been manufactured by utilizing spent ZnCl_2 generated from dye & dye intermediate industries*".

96.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of spent ZnCl_2 solution (generated from dye & dye intermediate industries) in production of ZnCO_3 , ZnO and NaCl only.

- 1) Spent ZnCl_2 solution shall be procured only in SPCB/PCC authorized barrels/closed tanks mounted over vehicles fitted with requisite safeguards.
- 2) Spent ZnCl_2 solution shall be stored in either HDPE or scrubber lined steel tank on acid proof brick lined area under covered storage shed within premises. Further, storage sheds shall have a 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.
- 3) Spent ZnCl_2 solution shall be unloaded from the closed tanker to the storage tank through pipelines using dedicated transfer pump.
- 4) Material transfer / handling in entire utilization process shall be done in closed system. Manual handling shall be strictly prohibited.
- 5) Vent from spray dryer shall be attached to cyclone separator and bag filters followed by stack of adequate height.
- 6) The treated gases shall comply with emission norms prior 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.
- 7) There shall be no generation of effluent from the process and unit shall strictly adhere to zero liquid discharge condition.
- 8) The hazardous wastes generated during utilization process 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. The hazardous waste storage area shall be covered with proper ventilation.

Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

- 9) Transportation of spent ZnCl_2 solution shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorization from the concerned SPCB under HOWM Rules, 2016. The requisite manifest document shall be followed as laid down under the said Rules.
- 10) Prior to the utilization of spent ZnCl_2 solution, the unit shall obtain authorization for generation, storage, and utilization of spent ZnCl_2 solution from the concerned State Pollution Control Board under HOWM Rules, 2016
- 11) Treatment and disposal of wastewater:
Wastewater generated from floor-washings, spillages, reactor washing, scrubber bleed including the wastewater from filtration shall be treated Physico-Chemically in an ETP.
In case of zero discharge, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB/PCC.
- 12) 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.
- 13) The unit shall ensure that the Spent ZnCl_2 solution is procured from the industries, which have valid authorization from concerned SPCB/PCC as required under HOWM Rules, 2016.
- 14) 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.
- 15) 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.
- 16) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 17) 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.

96.5 Record/Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of Spent ZnCl_2 solution as mentioned below:
 - Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of Receipt in the premises



Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

- 2) A log book with information on source and date of procurement of spent ZnCl_2 solution, 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 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.
- 5) The unit shall use NHWTS to manage the manifest, enter daily records of quantity generated, disposed, etc.

96.6 Standards

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

Particulate Matter	50 mg/Nm ³
Ammonia	30 mg/Nm ³

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

PM ₁₀	5 mg/m ³ TWA* (PEL)
Zinc Chloride fume	1 mg/m ³ TWA* (PEL)
Ammonia	35 mg/m ³ TWA* (PEL)
Toluene	200 mg/m ³ TWA* (PEL)
Hexane	1800 mg/m ³ TWA* (PEL)

*PEL - Permissible Exposure Limit, # - Ceiling Limit

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

- 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.

96.7 Siting of Industry

Facilities for utilization of spent ZnCl_2 solution 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.

Utilization of Spent Zinc Chloride Solution (generated from dye & dye intermediates industry) in production of Zinc Carbonate, Zinc Oxide and Sodium Chloride

96.8 Size of Plant and Efficiency of Utilisation

Utilization of 2.25 MT of spent $ZnCl_2$ solution along with 6 MT of raw material (soda ash) may yield 1 MT of $ZnCO_3$ & 0.5 MT of NaCl or respective products. Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

96.9 On-line Detectors / Alarms / Analyzers

In case of continuous process operations, online emission analyzers for PM and NH_3 in the stack shall be installed and the online data be connected to the server of the concerned SPCB/PCC and CPCB.

96.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1.	Dedicated storage tank for storage of spent Zinc Chloride solution with acid proof brick lining and proper slope & seepage collection pit.
2.	Mechanical transfer pumps with fixed pipeline for transportation and handling of spent $ZnCl_2$ solution.
3.	Vent from dryer shall be attached to cyclone and bag filter
4.	Multiple effect evaporator to treat the brine solution if the salt is required in powder form.
5.	Reactor, dryer, Pneumatic filter press
6.	Material transfer / handling in entire utilization process shall be done in closed system. Manual handling shall be strictly prevented.
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.	Adequate freeboard to be provided in the reactor to avoid overflow because of liberation of CO_2 from the process while manufacturing zinc carbonate.

