

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 Hydrochloric Acid (generated during manufacturing of Dyes and Dyes intermediates & synthetic organic chemical sector) for production of Calcium Chloride (CaCl_2)



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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**

**Utilization of Spent HCl (generated during manufacturing of dyes and dyes intermediates
& synthetic organic chemical sector) for production of Calcium Chloride**

Procedure for grant of authorization by State Pollution Control Boards (SPCBs)/Pollution Control Committees (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 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 HCl) being sent by generators and the quantity being utilized by authorized facilities
- 2) After issuance of authorization, SPCBs/PCCs shall verify the compliance of checklist and SoP on quarterly basis for initial 2 years; followed by random checks during subsequent period for atleast once a year.
- 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 on half yearly basis i.e., by July and January respectively.
- 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 (generated during utilization) or its complete utilization 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 E(P)A notified and OSHA standard respectively, however, SPCBs/PCCs may impose more stringent standards based on the location or process specific conditions.

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85.0 Utilization of Spent HCl:

Type of HW	Source of generation	Recovery/Product
Spent Hydrochloric Acid (HCl) 26.3 of Schedule-I and B15 (Inorganic Acids) at Note 7 of Schedule II, of HOWM Rules, 2016	During manufacturing of: i. Dyes & Dyes intermediates (Vinyl Sulphone) and ii. Synthetic organic chemical sector (Chorobenzene)	Calcium Chloride

85.1 Source of Waste:

Spent Hydrochloric Acid generated during manufacturing of dyes & dye intermediates and synthetic organic chemical sector is categorized as hazardous waste at Category 26.3 of Schedule-I respectively & B-15 (Inorganic Acids) at Note 7 of Schedule II of Schedule-II, HOWM Rules – 2016.

Table 1. Criteria Characteristics of Spent HCl are given below:

Sr. No.	Parameter	Unit	Value
1.	Purity of HCl	%	<30
2.	COD	mg/L	<9500
3.	TOC	mg/L	<2300
4.	Sodium	mg/L	<1500
5.	D.D.T	mg/L	<0.01

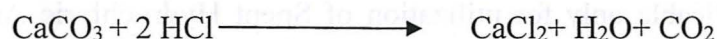
85.2 Utilization Process

The utilization process involves addition of calcium carbonate and spent hydrochloric acid in the reaction vessel, where calcium chloride is formed. The reaction tank is followed by alkali scrubber of adequate capacity. The reacted mass is neutralized by addition of lime in the neutralization tank.

From the neutralization tank the solution of calcium chloride is send through filter press for recovery of unreacted filter cake. The filter cake is bagged and stored in the hazardous waste storage area and disposed by co-processing in cement industry / disposal at TSDF site. The final product Calcium chloride solution is stored in tanks.

As per requirement the Calcium Chloride is crystallized from solution to powder form using evaporators and granulator. The evaporator is connected with wet scrubber (venturi scrubber) where CaCl_2 solution (brine) is used as scrubbing media, thereafter vent fumes are passed through cyclone and stack.

The chemical reaction involved in the utilization process is given below:



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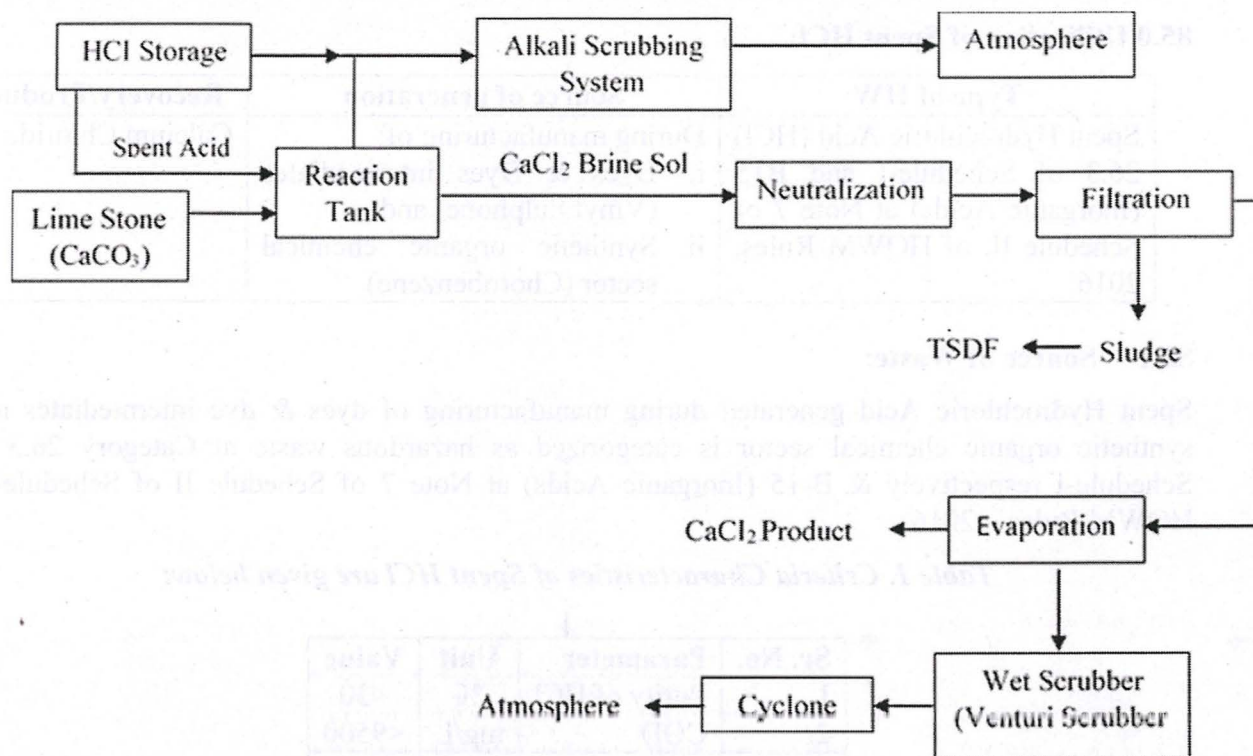


Figure: 1-Process flow diagram for utilization of spent HCl in production of CaCl_2 .

85.3 Product Usage / Utilization

1. Use of Spent Hydrochloric acid will replace fresh virgin Hydrochloric acid consumption there by decreases dependency of industrial unit on virgin hydrochloric acid.
2. The product Calcium Chloride (CaCl_2) manufactured by utilizing Spent Hydrochloric acid (HCl) shall be utilized for industrial purposes only such as during oil exploration activities, mud lubricant, de-icing and freezing point depression, road surfacing exempting food and pharma industries.
3. The Product i.e. Calcium Chloride (CaCl_2) shall comply Bureau of Indian Standards (BIS) – IS: 1314-1984, for further respective utilization.
4. The unit shall label its product i.e. Calcium Chloride (CaCl_2) manufactured by utilizing afore said Spent HCl as “*This Calcium Chloride (CaCl_2) has been manufactured by utilizing Spent HCl (generated from manufacturing of dyes and dye intermediates & synthetic organic chemical sector)*”.

85.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of Spent Hydrochloric Acid (generated during manufacturing of dyes and dyes intermediates & synthetic organic chemical sector for manufacturing of Calcium Chloride.

- 1) The Spent HCl shall be procured only in SPCB/PCC authorized barrels/closed tanks mounted over vehicles fitted with requisite safeguards ensuring no spillage of the acid.
- 2) Spent HCl shall be stored in HDPE/FRP or mild steel tank and kept in acid proof brick lined dyke under shed. The unit shall provide slope and collection pit in storage area. The unit shall install storage tanks under cool, dry, well ventilated covered storage shed(s) within premises, as authorized by the concerned SPCB/PCC under HOWM Rules, 2016.

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Further, the storage area of Spent HCl acid 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 ETP, as the cases may be, through chemical process pump.

- 3) The unit shall provide separate storage tanks/area at designated place with proper cover and acid brick lining floors for storage of Spent HCL, Calcium Chloride and Lime Stone.
- 4) There shall be no manual handling of the Spent Hydrochloric acid. The feeding of Spent HCl shall be done through closed loop pipelines using dedicated transfer pump.
- 5) Two stage alkali scrubbing system shall be provided to the reactor (where Spent HCl acid is utilized) to treat the emissions liberated from the reactor. Also, the vent of Spent Hydrochloric Acid storage tanks shall be connected to the alkali scrubber.
- 6) Dryer/ Granulator with adequate APCM shall be provided if the product is required to be converted in powder form.
- 7) Evaporator connected with wet scrubber (venturi scrubber) followed by cyclone where CaCl_2 solution (brine) to be used preferably as scrubbing media for the purpose of water conservation.
- 8) The treated gases/fumes 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.
- 9) Treatment and disposal of wastewater:

Wastewater generated from floor-washings, spillages, reactor washing, scrubber bleed shall be 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.
- 10) 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 generated (namely the Filter cake/ chemical sludge/ scrub liquor sludge, 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 its 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) It shall be ensured that the Spent Hydrochloric Acid is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 13) Transportation of Spent Hydrochloric Acid shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorization from the concerned SPCB/PCC under

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HOWM Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.

- 14) Prior to utilization of Spent Hydrochloric Acid, the unit shall obtain authorization for storage, utilization and disposal of Spent Hydrochloric Acid from the concerned SPCB/PCC under HOWM Rules, 2016.
- 15) 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.
- 16) 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.
- 17) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- 18) 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.

85.5 Record>Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of spent 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 logbook with information on source and date of procurement of Spent Hydrochloric acid, 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 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.

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85.6 Standards

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

Particulate Matter	50 mg/Nm ³
HCl Mist	20 ppm
Chlorine	15 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)
Cl ₂	3 mg/ m ³ TWA* (PEL)
HCl mist	7 mg/m ³ Ceiling Limit

**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 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 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.

85.7 Siting of Industry

Facilities for utilization of Spent Hydrochloric Acid 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.

85.8 Size of Plant and Efficiency of Utilization

1 MT of CaCl₂ brine solution (Purity around 45%) is produced by using 0.8 MT of spent Hydrochloric Acid (purity around 30%) generated during manufacturing of Vinyl Sulphone (Dyes and Dyes intermediate).

0.47 MT of CaCl₂ granules is produced by using 1 MT of spent hydrochloric acid generated during manufacturing of Chlorobenzene (synthetic organic chemical sector)

Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

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85.9 On-line Detectors / Alarms / Analyzers

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

85.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1.	Storage tanks of adequate capacity to store Spent Hydrochloric Acid. Such storage tanks shall be placed above the ground and contained with low rise parapet/bund wall and acid proof floor with slope to collect spillages, if any, in to collection pit.
2.	Cool, drywell-ventilated covered sheds for Spent Hydrochloric Acid storage tanks, product storage tanks and process activities within premises and dedicated hazardous storage area for temporary storage of hazardous waste generated during utilization process.
3.	Mechanized system for transfer of Spent Hydrochloric Acid from storage tanks to Lime Digester.
4.	Spare vessel to transfer there action mass, if any, in case of leakage or damage to their reaction vessel.
5.	Pumps, pipes, feeder sand equipment for mechanical handling of Spent Hydrochloric Acid.
6.	Reaction vessel, Brine Storage Vessel, Two stage alkali scrubbing system, Filter press
7.	pH sensor for scrubbing media with hooter
8.	Dryer/ Granulator with adequate APCM shall be provided, if the product is required to be converted in powder form in powder
9.	Evaporator connected with wet scrubber (venturi scrubber) followed by Cyclone.
10.	Adequate freeboard to be provided to avoid overflow because of liberation of CO ₂ from the process
11.	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.

