

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 acid containing HCl
(generated as waste pickling liquor from Steel Industries)
for Regeneration of HCl and production of Ferric Oxide**



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**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 acid containing HCl (generated as waste pickling liquor from Steel Industries) for Regeneration of HCl and production of Ferric Oxide

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, shall SPCBs/PCCs 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 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.
- 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/ISO 17025 accreditation / recognition for monitoring and analysis of prescribed parameters in SoP 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 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.
- 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.

71.0 Utilization of Spent Acid containing HCl:

Type of HW	Source of generation	Recovery/Product
Spent acid containing HCL (Waste Pickling Liquor- Category 13.1 of Schedule-I of HOWM Rules, 2016)	Pickling line of steel industries	Regeneration of HCl acid and production of Ferric Oxide

Utilization of Spent acid containing HCl (generated as waste pickling liquor from Steel Industries) for Regeneration of HCl and production of Ferric Oxide

71.1 Source of Waste:

Steel sheets are passed through Hydrochloric acid to remove surface impurities in pickling industries. The waste generated during this process is called spent acid or Waste Pickle Liquor (WPL) containing Ferrous Chloride. This spent acid containing HCL generated from Pickling line of steel industries falls under Category 13.1 of Schedule-I of HOWM Rules – 2016.

Table 1. Typical Characteristics of Spent acid are given below:

Sr. No.	Parameter	Unit	Range
1	Specific Gravity	-	1.10-1.25
2	HCl Acid content	%	2-10
3	Iron (Fe) content	g/L	60-130

71.2 Utilization Process

Hydrochloric acid regeneration is done by a chemical process (Pyrohydrolysis) for the recovery of bonded and un-bonded HCl from ferrous chloride solutions.

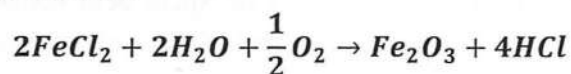
a. Venturi/Separator: HCl acid concentrator

Spent acid (WPL) is pumped from storage tanks to the Venturi. In Venturi direct mass and heat exchange with the roaster's exit hot gas takes place. The hydrogen chloride hot gas from roaster is cooled down from 400°C to 90°C-95°C approximately. Approximately 25-30% of water gets evaporated from the Spent acid and the concentration increases during the mixing of hot gas with liquid. The liquid/gas mixtures separate out in separator (part of venturi) leaves and goes to absorber.

b. Roaster: Spent Acid processing

Concentrated spent acid from the venturi is injected into the roaster at pressure more than 10 kg/cm² by means of spray booms with spraying nozzles. The roaster is fired by tangentially mounted burners that create a hot swirl. Temperatures inside the roaster vary between 550°C - 650°C (burner level) and 400°C (roaster gas exit duct). In the roaster the droplets of concentrated spent acid comes in contact with hot combustion product & reacts with oxygen, water to form Iron oxide powder and Hydrogen Chloride gas.

Chemical reaction inside roaster:



The Iron Oxide falls to the bottom of the roaster and hydrogen chloride fumes rises up and fed to Venturi (Gas temperature around 400°C). **Iron oxide powder** formed is removed from the roaster bottom & transported to bin for storage in leak-proof bags.

c. Absorber: Regeneration of HCl

The HCL containing gas from venturi separator is absorbed adiabatically in water in a packed column tower. The gas pass through the packed column from bottom to top and predetermined water quantity is sprayed from the top as an absorbing agent. Most of the HCl fumes is dissolved in water. The concentration of HCl (typical strength: 18% wt/wt) in regenerated acid (RA) is achieved by controlling the spray water flow rate to the absorber. The concentrated HCl is collected at bottom of the absorption column and pumped to the storage tank.

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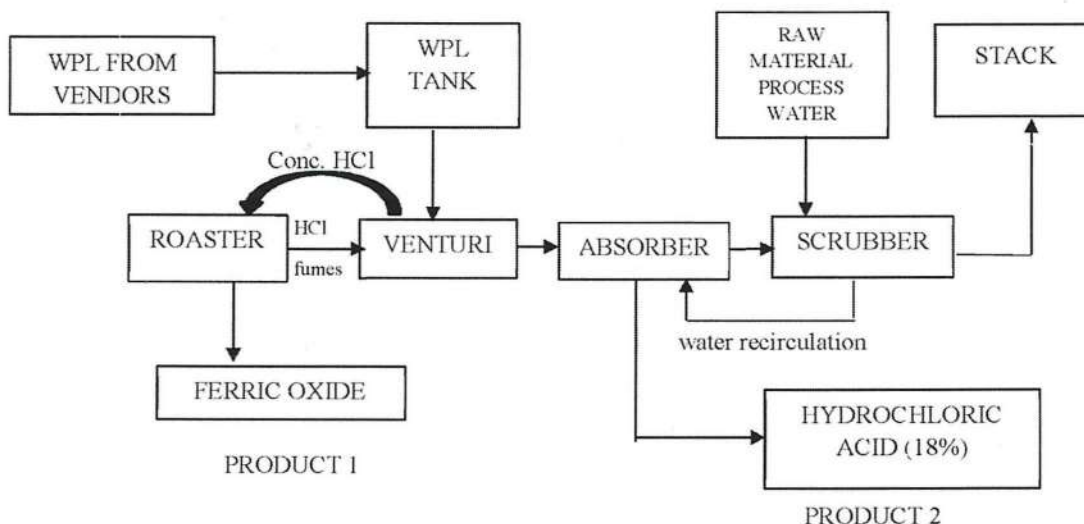


Figure: 1-Process flow diagram for utilization of spent acid containing HCl.

71.3 Product Usage / Utilization

1. Products manufactured by utilizing spent acid containing HCl shall be utilized for Industrial purposes only exempting food and pharma industries.
2. The regenerated acid (typical strength: 18%) is applicable for further re-use in Pickling Industries.
3. Ferric Oxide (Fe_2O_3) shall be used in Pigments making, Paint Industries, Tiles Industries, Cement Industries and making of soft ferrites for magnets, electronics etc.
4. The unit shall label tankers and bags carrying its products i.e. Regenerated Acid (HCl 18%) and Ferric Oxide manufactured by utilizing spent acid as "This Regenerated Acid (HCl 18%) Ferric Oxide has been manufactured by utilizing Spent acid containing HCl (generated during pickling in steel industries)".

71.4 Standard Operating Procedure for utilization

This SoP is applicable only for Utilization of Spent acid containing HCl (generated from pickling line of steel industries) as resource material for regeneration of HCl and production of Ferric Oxide.

- 1) The spent acid shall be procured only in SPCB/PCC authorized closed tankers mounted over vehicles fitted with requisite safeguards ensuring no spillage of the acid.
- 2) Spent acid and regenerated HCl shall be stored in designated tanks either Fiber Reinforced Plastic (FRP) / steel tank and kept in acid proof brick lining floors with closed bund area by acid resistance brick wall.
Further, the storage area of spent 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 Effluent Treatment Plant (ETP), as the cases may be, through chemical process pump.
- 3) There shall be no manual handling of the spent acid at any stage of utilization process.

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- 4) Spent acid shall be unloaded from the closed tanker to the storage tank through pipelines using dedicated transfer pump.
- 5) Feeding of spent acid from storage tanks to process units i.e. roaster, venturi and absorber shall be done through closed loop pipelines using dedicated transfer pump.
- 6) The unit shall provide wet scrubber for the scrubbing out dust & HCl fumes from the possible gaseous output at roaster, venturi, separator, absorber before dispersion through stack to atmosphere.
- 7) The treated gases shall comply with emission norms prior to dispersion into atmosphere through stack. The stack height shall be a minimum of 30 m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 8) 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 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.
- 9) 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.
- 10) The hazardous wastes generated (if any) 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.
- 11) The unit shall ensure that the spent acid is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 12) Transportation of spent acid shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorization from the concerned SPCB/PCC under HOWM Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.
- 13) Prior to utilization of spent acid, the unit shall obtain authorization for storage, utilization and disposal of spent acid from the concerned SPCB/PCC 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.

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- 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.

71.5 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 log book with information on source and date of procurement of spent 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 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.

71.6 Standards

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

Particulate Matter	150 mg/Nm ³
SO ₂	200 mg/Nm ³
HCl Mist	35 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 #
SO ₂	13 mg/m ³ TWA* (PEL)
NO _x	9 mg/m ³ #

*PEL - Permissible Exposure Limit; # - Ceiling 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.

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- 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 said consent or non-availability of the common Effluent Treatment Plant (CETP), zero discharge shall be met.

71.7 Siting of Industry

Facilities for utilization of Spent 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.

71.8 Size of Plant and Efficiency of Utilisation

Typical spent acid comprises of 22% FeCl₂, 3.5% HCl and 74.5% of H₂O. Utilization of 100 Kg of spent acid may yield to generate 15.17Kg Fe₂O₃ and 16.2 Kg HCl. As complete recovery of spent acid takes place in the process, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

71.9 On-line Detectors / Alarms / Analyzers

In case of continuous process operations, online emission analyzers for PM, SO₂, HCl mist in the stack shall be installed and the online data be connected to the server of the concerned SPCB/PCC and CPCB.

71.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1.	FRP/steel made Storage tanks of capacity relevant as per section 71.8 to store Spent acid as well Regenerated 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. Alternately, the storage tanks 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 sheds for product Ferric Oxide and dedicated storage area for temporary storage of wastes (if any) generated during utilization process.
3.	Mechanized system for transfer of Spent Acid from storage tanks to process vessels.
4.	Roaster, Scrubber and Absorber
5.	The process units shall be provided with appropriate suction connected with scrubber.
6.	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.
