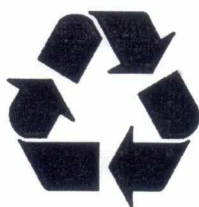


Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule 9 of the Hazardous and Other Wastes (Management and Transboundary movement) Rules, 2016

Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate



cpcb

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

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 that authorisation is given only to those wastes for which SoPs on utilisation have been circulated by CPCB ensuring the following:
- The waste (intended for utilization) should have similar source of generation as specified in SoPs.
 - The utilization process should be similar to the process of utilization described in SoPs.
 - End-use / product produced from the waste shall be same as specified in SoPs.
 - Authorisation shall be granted only after verification of minimum requisite facilities installed and after verification of utilization process as given in SoPs.
 - Issuance of passbooks (similar to the passbooks issued for recycling of use oils, waste oil, non-ferrous scraps, 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, quarterly during the initial 02 years of operation followed by random checks in subsequent year's atleast once in every year.
- In-case of lack of requisite infrastructures with the SPCBs/PCCs, SPCBs/PCCs may engage 3rd party institutions and EPA/NABL/ISO17025 accredited laboratories for monitoring and analysis of prescribed parameters of the SoPs for verification purpose. Such labs shall have accreditation (EPA/NABL/ISO17025) for the parameters specified in SoP.
- (iii) SPCB shall provide half yearly up-dated list of units permitted for utilization of hazardous waste to CPCB and also periodically update the same on SPCB website Such updated list shall sent for January-June and July- December of every year and reach to CPCB by July and January respectively of every year.
- (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 or its complete utilisation or arrangement of sharing with any other authorised disposal facility.
- (v) In case of the utilization proposal is not similar with respect to source of generation, utilization process and end-use as outlined in this SoP, the same may be referred to CPCB for clarification / conducting trial utilization studies and developing SoPs.
- (vi) The source and work zone standards suggested in the SoPs are based on the E(P)A notified and OSHA standards respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate

41.0 Utilization of Spent Sulphuric Acid containing Chromium:

Type of HW	Source of generation	Recovery/Product
Waste Dichromate Solution Category: A4 Schedule-II of HOWM Rules, 2016	Waste Dichromate solution (WDS) generated during manufacturing of Ibuprofen (Pharma Industry)	For production of Basic Chromium Sulphate

41.1 Source of Waste:

Waste Dichromate Solution (WDS) is generated during the oxidation of aldehyde group using sodium dichromate and concentrated sulphuric acid in the manufacturing of Ibuprofen. This WDS is categorised as hazardous waste category A4 of Schedule-II of HOWM Rules, 2016. This hazardous waste is required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

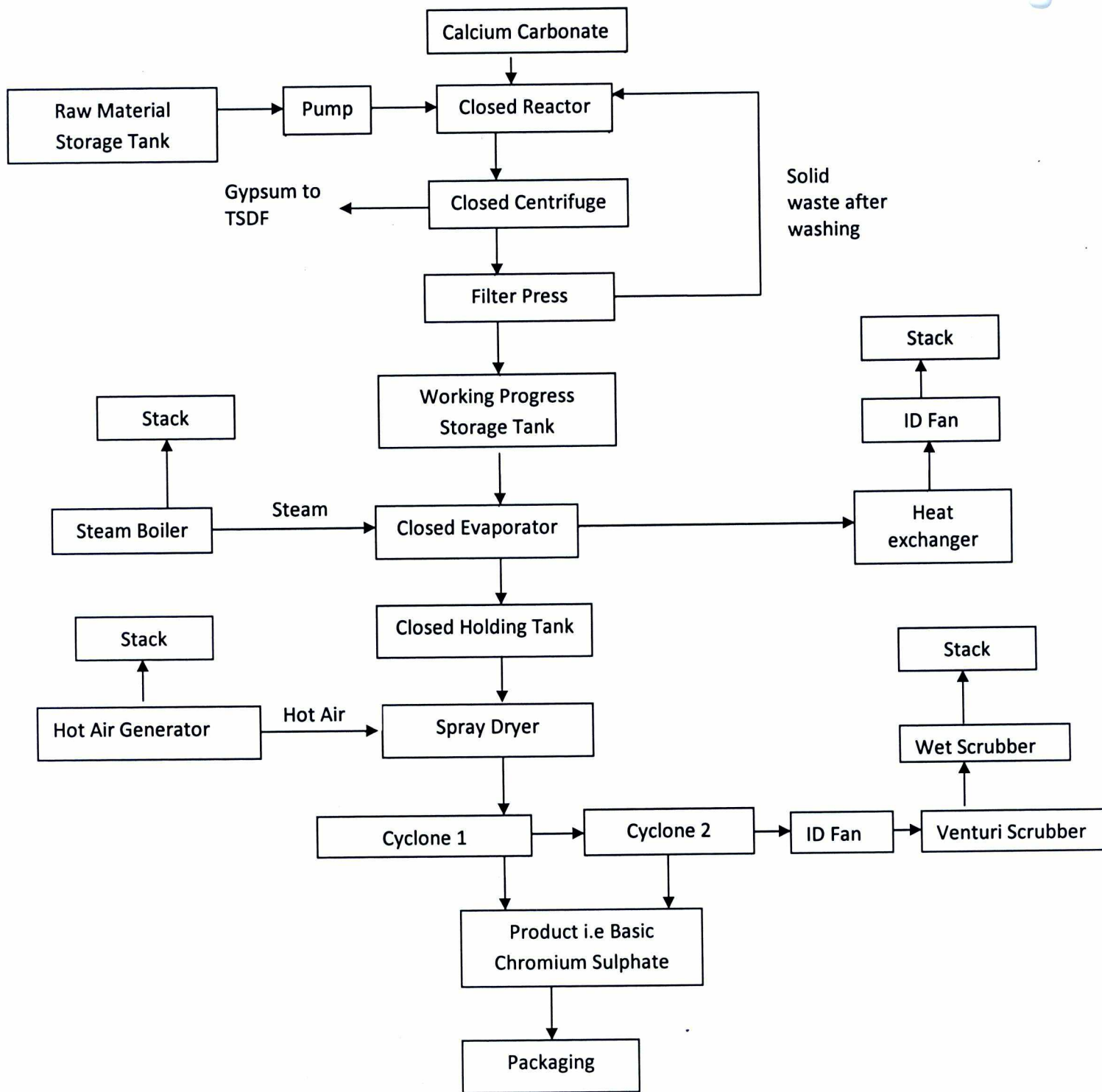
Typical characteristic of WDS generated is given below;

Parameters	Results
pH	0.5-1.0
Free H ₂ SO ₄	20-25 %
Chromic oxide	5.5-6.5 %
Free Sulphate	20-25 %

41.2 Process of Utilization:

The utilization process involves reaction of WDS with calcium carbonate to produce basic chromium sulphate. Firstly, waste dichromate solution is transferred to the reactor where calcium carbonate is added through closed conveyer system. The solution is kept in agitation to complete the reaction and prevent the settling of gypsum (calcium sulphate) in the reactor. Then the solution from the reactor is transferred to the centrifuge for filtration. The filtered precipitate i.e. calcium sulphate (Gypsum) is washed with hot water in the centrifuge and taken out. The filtrate solution from the centrifuge i.e. liquid basic chromium sulphate is further passes through the filter press for removal of solid particles, if any, and then kept in storage tank. Liquid basic chromium sulphate from storage tank is transferred to evaporator, where water is evaporated using steam, at temperature 120-130°C. During evaporation sodium sulphate and soda ash is added into evaporator to adjust the sulphate content and basicity of the basic chromium sulphate respectively, (if required). Concentrated basic chromium sulphate is sent to holding tank from where it is sent to spray dryer through chemical pump. In spray dryer concentrated basic chromium sulphate is sprayed where it gets contacted with hot air, at temperature of 150-160°C, and converted into basic chromium sulphate powder. Homogenized powdered basic chromium sulphate, as a product, is collected through cyclones and packed in HDPE bags.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate



Process Flow Diagram

41.3 Product Usage / Utilization

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate

Basic Chromium Sulphate is utilized in the leather industry for tanning purpose.

41.4 Standard Operating Procedure (SOP) for utilization

This SOP is applicable only for the utilization of Waste Dichromate Solution (WDS) generated during the oxidation of aldehyde group using sodium dichromate and concentrated sulphuric acid in the manufacturing of Ibuprofen for production of basic chromium sulphate by adhering to the following;

- (1) The WDS should be transported in acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the liquid waste.
- (2) There should be a designated space for unloading of WDS into acid proof storage tank. The receiving storage tank shall be placed above the ground and contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any into collection pit.
- (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.
- (4) There shall be no manual handling of WDS and basic chromium sulphate solution. Acid proof pump shall be used for transfer of WDS and basic chromium sulphate solution through pipelines.
- (5) WDS shall be transferred into closed reaction vessels where Calcium carbonate shall be added into the reactor through closed conveyer system. The reactor shall be of poly propelin FRP material or acid proof material.
- (6) The solution in the reactor shall be agitated with the help of mechanized agitator for 3-3.5 hours and then transferred to centrifuge through pump for filtration. The precipitated solid mass i.e. Calcium sulphate (gypsum) from the centrifuged is washed with hot water. The same shall be removed mechanically and packed and kept in storage area.
- (7) Filtrate i.e liquid basic chromium sulphate from the centrifuge shall be further filtered using filter press and sent to evaporator. Steam, generated from the boiler, shall be used in the Evaporator to maintain the temperature around 120-130°C. Evaporator shall be attached with heat exchanger and ID fan connected with stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
- (8) The concentrated liquid basic chromium sulphate shall be sent to spray dryer where hot air from hot air generator is used. In spray dryer liquid basic chromium sulphate is converted into powdered basic chromium sulphate and collected from cyclones as a product. Spray dryer shall be attached with cyclones for collection of product. Cyclones shall be attached with APCD (ID Fan, Venturi scrubber with ceramic rings for more efficiency, wet scrubber –water as a scrubbing media) connected with stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
- (9) The entire process area shall have leak-proof and acid proof floor tiles with adequate slope to collect spillages, if any, into a collection pit. The spillages from collection pit shall be transferred to reaction tank, as the cases may be, through acid proof pump.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate

- (10) 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, aprons, and/or coveralls of chemical resistant material and impervious boots of chemically resistant material.
- (11) The unit shall label its product (i.e. Basic Chromium Sulphate manufactured by utilizing aforesaid hazardous waste) as "This Basic Chromium Sulphate has been manufactured by utilizing Waste Dichromate Solution and therefore it may contain some organic constituents".
- (12) It shall be ensured that WDS is procured from the industries who have valid authorization for the same from the concerned SPCB/PCC as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
- (13) Calcium sulphate (gypsum) generated during the utilization process shall be sent to authorized TSDF for disposal or authorized Co-processor/utilize for utilisation/co-processing.
- (14) Transportation of hazardous wastes such as WDS 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.
- (15) Prior to utilization of WDS the unit shall obtain authorization for storage and utilisation of spent sulphuric acid from the concerned State Pollution Control Board under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (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 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.
- (17) 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.

41.5 Records/Return Filing:

- (1) The unit shall maintain a passbook issued by concerned SPCB/PCC wherein the following details of each procurement of WDS shall be entered:
 - 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 the said hazardous wastes, quantity, date wise utilization of the same, quantity of basic chromium sulphate manufactured,

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate

details on chemical gypsum (w.r.t. quantity, end use/ disposal), hazardous waste generation and its disposal etc. shall be maintained including analysis report of fugitive and emission monitoring, as applicable.

- (3) 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
- (4) The unit shall maintain record of hazardous waste utilised, residues 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 SPCB/PCC.

41.6 Standards

- (1) Source emission in stack connected to hot air generator and steam generator shall comply with standards prescribed by the concerned SPCB/PCC.
- (2) Source emissions in stack connected to evaporator and spray dryer shall comply with following standards:
 - PM-50mg/Nm³
 - Sulphuric Acid Mist-50 mg/Nm³
 - TOC-20mg/Nm³
 - Heavy Metals (Sb+As+Pb+Co+Cr+Cu+Mn+Ni+V+their compounds)-0.5 mg/ Nm³
- (3) Fugitive emissions in the work zone shall comply with following standards
 - PM₁₀-5 mg/m³TWA
 - Sulphuric acid – 1.0 mg/m³ TWA*, 3 mg/m³ STEL*
 - Chromium (III)-0.5 mg/ m³TWA
 - Chromium (VI)-0.05 mg/ m³TWA

** Time-weighted average (TWA), Short-term exposure limits (STEL).*

The Permissible Exposure Limit is 8-hour TWA.

A short-term exposure limit (STEL) is the acceptable average exposure over a short period of time, usually 15 minutes as long as the Time weighted average is not exceeded.

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.

- (4) 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.

41.7 Siting of Industry

Facilities for processing of WDS should preferably be located in a notified industrial area or industrial park/estate/cluster.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate

41.8 Efficiency of utilisation

To produce 1 ton on Basic Chromium Sulphate about 3.81 tons of WDS is required. Other raw materials like calcium carbonate, soda ash, sodium sulphate are also used. Hence, requisite facilities of adequate size shall be installed accordingly as mentioned under para 41.10 below.

41.9 On-line detectors / Alarms / Analysers

In case of continuous process operations, online analysers shall be installed for Particulate Matter in the stack emission connected to stack evaporator and spray dryer. The on-line data shall be connected to the concerned SPCB/PCC server.

41.10 Checklist of Minimal Requisite Facilities:

S.No.	Requisite Facilities
1.	Earmarked unloading area (for transfer of WDS from tanker) contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, to collection pit.
2.	Acid proof lined tanks for storage of WDS
3.	Separate storage tank for the storage of liquid basic chromium sulphate
4.	Storage tank (s) should be of such size/capacity that it can store at least two weeks requirement of the said hazardous waste to be used as raw material.
5.	Collection pit for collection of spillages from storage area, working area and unloading area.
6.	Well-ventilated covered storage shed(s) within the premises for WDS and liquid basic chromium sulphate storage tanks
7.	Chemical process (acid proof) pumps for transfer of WDS and liquid basic chromium sulphate from tanker to storage tank and transfer subsequently to process area.
8.	Leak-proof and acid proof floor tiles with adequate slope to collect spillages, if any, in the entire working area.
9.	Closed reactor made of poly propelin FRP material or acid proof material
10.	Closed conveyer system for transfer of calcium carbonate
11.	Closed centrifuge with mechanical system for removal of calcium sulphate
12.	Evaporator attached with heat exchanger and ID fan connected with stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
13.	Steam generator for evaporator connected with stack of height as prescribed by the concerned SPCB/PCC

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Waste Dichromate Solution generated during manufacturing of Ibuprofen for production of Basic Chromium Sulphate

14.	Spray dryer with cyclone for collection of product. Cyclones of the spray dryer attached with APCD (ID Fan, Venturi scrubber with ceramic rings, wet scrubber) and connected with stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
15.	Hot air generator for spray dryer connected with stack of height as prescribed by the concerned SPCB/PCC
16.	Stacks 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.
17.	Spare vessel to transfer the reaction mass, if any, in case of leakage or damage to the reaction vessels
18.	Dedicated separate covered storage area for the storage of other raw material, product and waste gypsum i.e calcium carbonate under shed (s)
19.	Fire fighting system
20.	Online analysers shall be installed for Particulate Matter in the stack emission, in case of continuous process
