

**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 ETP Sludge (generated from pickling process/ wastewater treatment) for manufacturing of Red/Chromium/Nickel Oxide & Gypsum**  
(Revised)



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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 ETP Sludge generated from Pickling Process as Resource material for manufacturing of Red/Chromium/Nickel Oxide & Gypsum**

**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 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. The compliance reports shall be submitted to CPCB by July every year.
- 3) In-case of lack of requisite infrastructures with the SPCBs/PCCs, they may engage 3<sup>rd</sup> 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.
- 8) SPCBs/PCCs shall ensure that the utilisers of ETP Sludge shall maintain daily records ion National Hazardous Waste Tracking System (NHWTS) once operationalised by CPCB.





**Utilization of ETP Sludge generated from Pickling Process as Resource material for manufacturing of Red/Chromium/Nickel Oxide & Gypsum**

**62.0 Utilization of ETP Sludge:**

Type of HW	Source of generation	Recovery/Product
ETP Sludge (13.2 & 35.3 of Schedule-I of HOWM Rules – 2016)	Sludge generated from pickling operation & chemical sludge generated from wastewater treatment of iron & steel industry	i. Gypsum for manufacturing of paver blocks ii. Red Oxide, Nickel Oxide, Chromium Oxide for manufacturing of pigments

**62.1 Source of Waste:**

ETP Sludge generated from pickling operation & chemical sludge generated from wastewater treatment of iron & steel industry is categorized as hazardous waste listed at 13.2 & 35.3 of Schedule-I of HOWM Rules – 2016 respectively.

*Table 1. Typical Characteristics of ETP Sludge given below:*

Sl. No.	Parameter	Results	Unit
1.	pH	7.9	--
2.	Moisture	50	%
3.	Cr	1.76	%
4.	Fe	20.9	%
5.	Ni	0.67	%
6.	Mn	0.29	%
7.	F	56	mg/L

**62.2 Utilization Process**

First Stage: ETP Sludge is mixed with fresh water &  $H_2SO_4$  and stirred into liquefied solution. The liquefied solution is passed through hydraulic filter press, where the solid part is retained in form of filter cake & filtrate – 1 is collected in the collection tank and processed in second stage. The filter cake is wet  $CaSO_4$  (gypsum) and dried in muffle furnace to obtain dried  $CaSO_4$  (gypsum), which contains substantial quantity of fluoride content. Fluoride content in dried  $CaSO_4$  (gypsum) is minimized by using hot water washing method, in this method dried  $CaSO_4$  (gypsum) is washed by addition of hot water followed by stirring. Fluoride salt in  $CaSO_4$  reacts with hot water & form aqua hydro fluoride which is soluble in water. The liquefied solution is again passed through hydraulic filter press.  $CaSO_4$  trapped in filter press along with CaO as filter cake and water with HF easily passes away and collected as filtrate. The filter cake (washed Gypsum) is collected and again dried in muffle furnace & grinded in ball mill to obtain fine consistency and it is used in paver block manufacturing as a binding agent. The Filtrate-2 (gypsum wash water) is collected separately and processed in second stage along with filtrate-1.

Second Stage: Filtrate - 1 & 2 from first stage is oxidized by addition of  $NaNO_2$  and stirred in the agitated reaction vessel. Further, NaOH is added to increase the pH and stirred in the agitated reaction vessel. The liquefied solution is passed through hydraulic filter press where the solid part is retained in form of filter cake (Chromium & Iron) & filtrate-3 is collected in the collection tank and processed in third stage.

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Third Stage: NaOH is added to the filtrate-3 (Nickel Sulphate solution) of second stage to increase the pH and stirred in the agitated reaction vessel. The liquefied solution is passed through hydraulic filter press where the solid part is retained in form of filter cake  $[\text{Ni}(\text{OH})_2]$  & filtrate-4 ( $\text{Na}_2\text{S}_2\text{O}_4$  solution) is collected in the collection tank and reused as cooling water in captive hot rolling mills or recycled in the same process.

Filter cake with 25-30% moisture (Chromium & Iron) of second stage is further processed by addition of  $\text{Na}_2\text{CO}_3$  and stirred in the agitated reaction vessel. The liquefied solution ( $[\text{Fe}(\text{OH})_3]$  &  $\text{Na}_2\text{Cr}_2\text{O}_7$  mix solution) is further processed by addition of fresh water and stirred in the same agitated reaction vessel. The liquefied solution is passed through hydraulic filter press where solid part retained in form of filter cake  $[\text{Fe}(\text{OH})_3]$  & filtrate-5 ( $\text{Na}_2\text{Cr}_2\text{O}_7$  solution) is collected in the collection tank and processed in fourth stage. Filter cake  $[\text{Fe}(\text{OH})_3]$  is collected and dried in the muffle furnace to obtain red oxide powder (value added by-product). Similarly, filter cake  $[\text{Ni}(\text{OH})_2]$  of third stage is dried in the muffle furnace to obtain nickel oxide powder (value added by-product).

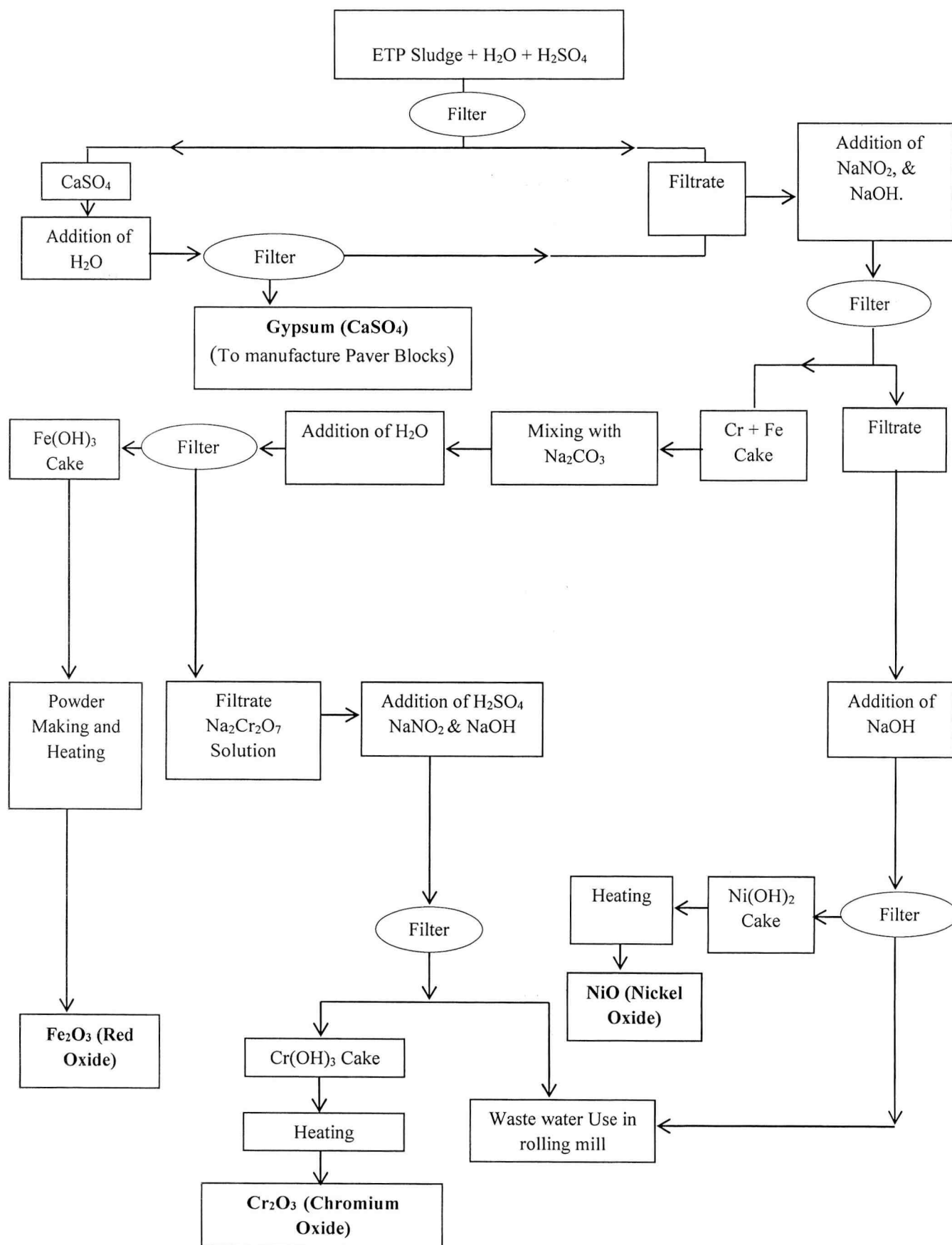
Fourth Stage:  $\text{H}_2\text{SO}_4$  is added to the filtrate-5 ( $\text{Na}_2\text{Cr}_2\text{O}_7$  solution) of third stage to decrease the pH and stirred, simultaneously  $\text{NaNO}_2$  is added and stirred; further NaOH is added to increase the pH and stirred in the agitated reaction vessel. The liquefied solution is passed through hydraulic filter press where solid part retained in form of filter cake  $[\text{Cr}(\text{OH})_3]$  & filtrate-6 ( $\text{Na}_2\text{S}_2\text{O}_4$  solution) is collected in the collection tank and reused as cooling water in captive hot rolling mills or recycled in the same process. Filter cake  $[\text{Cr}(\text{OH})_3]$  is collected and dried in the muffle furnace to obtain Chromium oxide powder (value added by-product).

**Paver block manufacturing:** Automatic or Manual Paver Manufacturing Machine is used to produce paver block from slag (from scrap steel refining), gypsum (recovered in above process), cement, grit and water. Composition of above ingredients may be based on strength required & application of manufactured paver blocks.

### 62.3 Product Usage / Utilization

- 1 Recovered Red/Nickel/Chromium Oxide to be used as pigment in industrial grade, and Gypsum will be utilized for manufacturing of Paver Blocks.
- 2 The Products shall comply as per Bureau of Indian Standards (BIS) of further respective utilization. However the products manufactured utilizing the hazardous waste shall not be used in food, food processing, pharma industries and production of fertilizers.
- 3 The unit shall label its product i.e. Recovered Red/Nickel/Chromium Oxide & Gypsum manufactured by utilizing afore said ETP sludge as *"This Recovered Red/Nickel/Chromium Oxide & Gypsum has been manufactured by utilizing ETP sludge (generated from Pickling Process) for manufacturing of paver blocks & Red/Nickel/Chromium Oxide respectively"*.

# Utilization of ETP Sludge generated from Pickling Process as Resource material for manufacturing of Red/Chromium/Nickel Oxide & Gypsum



**Figure: 1-Process flow diagram for utilization of ETP Sludge.**



**Utilization of ETP Sludge generated from Pickling Process as Resource material for manufacturing of Red/Chromium/Nickel Oxide & Gypsum**

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#### **62.4 Standard Operating Procedure for utilization**

This SoP is applicable only for utilization of ETP Sludge generated from Pickling Process as Resource material for manufacturing of Red/Chromium/Nickel Oxide & Gypsum.

- 1) ETP sludge shall be procured through vehicles fitted with requisite safeguards ensuring no leakage.
- 2) ETP sludge shall be stored in acid proof brick lined area under covered storage shed within premises so as to prevent rain water instruction. Further, storage sheds shall have 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) Transfer of ETP sludge from storage sheds shall be carried out through covered trolley or mechanical conveyor.
- 4) The unit shall provide separate storage tanks for storage of chemicals and the storage tanks should be at designated place with proper cover and with acid brick lining floors.
- 5) The treated gases shall comply with emission norms prior to dispersion into atmosphere through stack. The height of stack shall be a minimum of 30 m above the ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 6) 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 Factories Act, 1948, as amended from time to time.
- 7) 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 to comply with surface water discharge standards or may be sent to CETP for final disposal.

In case of zero discharge condition by SPCB/PCC, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB/PCC.

- 8) 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.
- 9) Dryer and ball mill shall be attached with a cyclone/ bag filter with a stack of adequate height or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 10) Unit shall ensure that recovered Gypsum which is to utilized in the manufacturing of Paver block shall meet the prescribed limits of Schedule-II of HOWM Rules, 2016.
- 11) The hazardous wastes generated (namely the Filter cake, other chemical 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 MEE or other



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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.

- 12) It shall be ensured that the ETP sludge is procured from the industries, which have valid authorization from the concerned State Pollution Control Board as required under HOWM Rules, 2016.
- 13) Transportation of ETP sludge shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorisation from the concerned SPCB under HOWM Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.
- 14) Prior to utilization of ETP sludge, the unit shall obtain authorisation for generation, storage and utilization of ETP sludge from the concerned State Pollution Control Board under HOWM Rules, 2016.
- 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. The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.

#### **62.5 Record/Returns Filing**

- 1) The unit shall maintain a passbook issued by concern SPCB wherein the following details of each procurement of ETP sludge 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 logbook with information on source and date of procurement of ETP sludge, 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.

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- 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.
- 5) The unit shall use NHWTS to manage the manifest, enter daily records of quantity generated, disposed, etc. once the portal is operational.

#### 62.6 Standards

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

PM	150 mg/Nm <sup>3</sup>
SO <sub>2</sub>	100 ppm
NO <sub>x</sub>	50 ppm
HCl	50 mg/Nm <sup>3</sup>
CO	100 mg/Nm <sup>3</sup>

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

PM <sub>10</sub>	5 mg/m <sup>3</sup>
Cl <sub>2</sub>	3 mg/ m <sup>3</sup>
HCl	7 mg/m <sup>3</sup>
Acid Mist (H <sub>2</sub> SO <sub>4</sub> )	1 mg/m <sup>3</sup>

- 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.

#### 62.7 Siting of Industry

Facilities for utilization of ETP sludge shall be located in a notified industrial area or industrial park / estate / cluster and in accordance with Consent to Establish issued by the concerned SPCB/PCC.



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**62.8 Size of Plant and Efficiency of Utilisation**

100 kg ETP sludge was used for manufacturing 40 kg gypsum ( $\text{CaSO}_4$ ) and 17 kg red oxide ( $\text{Fe}_2\text{O}_3$ ). Hence, yield was 0.4 for gypsum ( $\text{CaSO}_4$ ) & 0.17 Ferric oxide ( $\text{Fe}_2\text{O}_3$ ). 8 Kg Chromium oxide ( $\text{Cr}_2\text{O}_3$ ) & 5 Kg Nickel oxide ( $\text{NiO}$ ) were also obtained as value added byproducts. Therefore, requisite facilities of adequate size of storage shed and other plants and machineries as given in para 62.10 given below shall be installed accordingly.

**62.9 On-line Detectors / Alarms / Analyzers**

In case of continuous process operations, online emission analyzers for PM,  $\text{SO}_2$ ,  $\text{NO}_x$  in the stack shall be installed and the online data be connected to the server of the concerned SPCB/PCC.

**62.10 Checklist of Minimal Requisite Facilities**

S. No	Particulars
1.	Covered Hazardous Waste storage area for storage of ETP sludge with acid proof brick lining and proper slope & seepage collection pit.
2.	Agitated Stirred Reactor with Alkali Scrubber as APCD and stack of adequate height.
3.	Filter Press
4.	Storage vessel for storage of ML / Filtrate.
5.	Dryer and, ball Mill for size reduction of recovered material after drying.
6.	Dryer and ball mill shall be attached with a cyclone/ bag filter with a stack of adequate height.
7.	Paver block manufacturing machine (Automatic / Manual).
8.	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.

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