

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 Vanadium Sludge Generated From Alumina Refineries



cpcb

December, 2016

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

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

22.0 Utilization of Vanadium Sludge:

Type of HW	Source of generation	Recovery/Product
Vanadium Sludge- Category 11.7 of schedule-I of HOWM Rules, 2016	Alumina refineries	Vanadium metal

22.1 Source of Waste

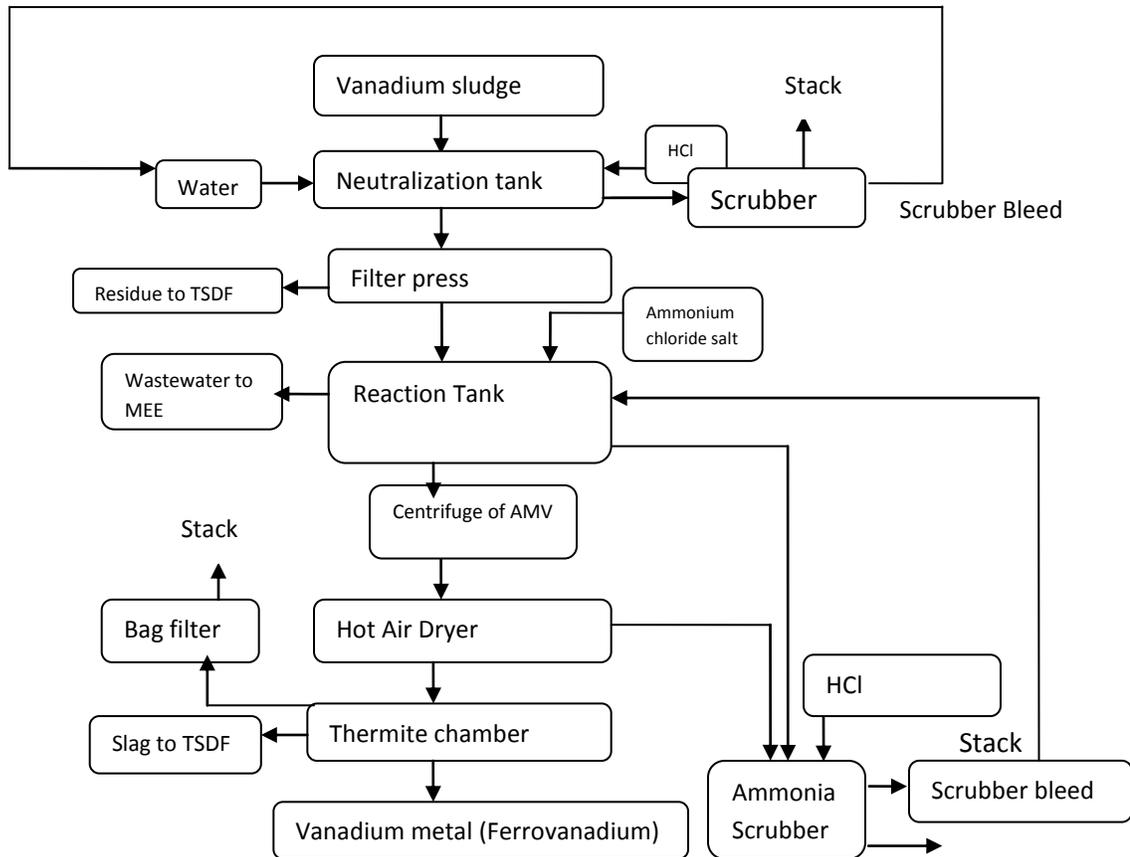
- i. Vanadium sludge is generated in Bayer's process in production of alumina from bauxite, which involves treating bauxite with alkali under high pressure forming Bayer's liquor that contains substantial amount of vanadium salts as impurities. Vanadium sludge gets precipitated, when vanadium containing bayer's liquor is cooled down or air is blown through. Vanadium sludge contains 10-20% vanadium as vanadium pentoxide.
- ii. Vanadium sludge contains about 38-45% moisture, 10-20% vanadium pentoxide, 8-15% sodium oxide and 2.5-3.0% alumina.

22.2 Proposed Process

The utilization process involves mixing of vanadium sludge with water followed by neutralization of solution with hydro chloric acid. Then solution is filtered through filter press and mother liquor containing dissolved V₂O₅ reacts with ammonium chloride powder resulting into precipitation of ammonium meta vanadate (AMV) in the solution, which is centrifuged and washed for recovery of vanadium pentoxide from mother liquor. The centrifuged precipitate is dried in hot air oven dryer and recovers the vanadium metal after thermite process.

Process Flow Diagram

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal



22.3 Product Usage / Utilization

The recovered vanadium metal is used in steel industry as additive. It is used for the production of rust resistant, spring and high speed tool steels. It is also added to steels to stabilise carbides.

22.4 Standard Operating Procedure (SoP) for utilization

This SoP is applicable only for the utilization of vanadium sludge generated from Alumina refineries industries during Bayer's process in production of alumina from bauxite to produce vanadium metal suitable for utilization in steel industry.

- (1) The vanadium sludge should be transported in HDPE/jambo bags mounted on vehicles fitted with requisite safeguards ensuring no spillage of waste.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

- (2) There should be a designated space for unloading of vanadium sludge jambo bags. The receiving storage area shall be placed above the ground and contained with low raise bund wall & acid-alkali proof floor with slope to collect spillages, if any, into collection pit.
- (3) The unit shall store hazardous waste as well as ammonium chloride salt under cool, dry and well-ventilated covered storage shed(s) within premises, as authorized by the concerned State Pollution Control Board/Pollution 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 vanadium sludge and ammonium chloride salt. Mechanical loading or bucket elevator shall be used for transfer of vanadium sludge and ammonium chloride salt to the reaction tank.
- (5) The entire process area shall have leak-proof and acid-alkali 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 chemical process pump.
- (6) Neutralization tank should be connected with scrubber followed by stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher. Stack shall have easy access to port hole for conducting stack emission monitoring. If water alone is used as scrubbing medium in the scrubber, the bleed water from scrubber shall be used as water for mixing vanadium sludge.
- (7) Transfer of hydrochloric acid shall be done only through separate chemical pipeline to reaction tanks.
- (8) There shall be separate storage area for HCl tank in HDPE tank or acid proof tank above the ground with low raise bund wall & acid/alkali proof floor with slope to collect spillages, if any, into collection pit.
- (9) The neutralized liquid from neutralization tank shall be filtered through filter press to remove particles from the liquid prior to transfer of the same to the reaction tank.
- (10) This mother liquor shall be transferred to reaction tank through mechanized/chemical process pump.
- (11) Transfer of ammonium chloride salt to reaction tank shall be carried out through bucket/mechanized system.
- (12) Precipitated ammonium meta vanadate shall be separated from mother liquor by gravity separation and the slurry transferred to centrifuge through slurry pump or any other mechanical process.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

- (13) The recovered ammonium meta vanadate (AMV) from centrifuge after washing can be transferred to dryer unit manually.
- (14) 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 such as Chemical goggles, 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.
- (15) Ammonia gas, release during oxidation of ammonium meta vanadate in hot air dryer at temperature of around 350°C to produce vanadium pentoxide, shall be channelized through duct to a scrubber (preferable with venturi scrubber) and released through stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher. HCl shall use as an absorbing media for recovery of ammonium chloride, shall be reused in the reaction tank, if possible.

The reaction tank should be covered with FRP (or any suitable acid/alkali proof) lid connected to the aforesaid common scrubber through a suction duct with isolation valve.

- (16) Vanadium pentoxide along with aluminium powder, iron chips and CaF_2 shall be charged in thermite furnace for exothermic reaction at temperature of about 1800°C-1900°C. Thermite furnace shall be connected with bag filters which shall be connected to stack of minimum 30 meters height above the ground.
- (17) The slag generated during thermite process shall be stored in designated area and shall be sent to TSDF for disposal.
- (18) Treatment and disposal of waste water:

The following are the sources of wastewater from utilization process;

- a) Spent mother liquor
- b) Scrubber bleed from Neutralization tank, if not used in utilization process
- c) Floor washing/reactor wash/vehicle wash/spillages, etc.

The Spent mother liquor, after reuse during the utilization process, shall be collected in separate tank for treatment with sodium hydroxide or calcium hydroxide followed by further treatment in Multiple Effect Evaporator (MEE). MEE salt should be sent to TSDF for encapsulation and secured land filling. Depending upon waste water quality generated from Floor washing/reactor wash/vehicle wash/spillages Scrubber bleeds and Scrubber bleed from Neutralization tank, if any, there may be requirement of effluent treatment plant if the same cannot be directly treated in MEE.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

The condensate of MEE and treated waste water shall be used for neutralization in its HW utilization process/floor washing/reactor wash/vehicle wash/spillages etc. and there shall not be any discharge of treated waste water.

- (19) It shall be ensured that vanadium sludge 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.
- (20) 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.
- (21) The residue generated from filter press, ETP sludge (if any), residue from scrubber and bag filter, MEE residue, product spillages etc. shall be collected and temporarily stored in HDPE drums / bags in a dedicated hazardous waste storage area and sent to TSDF within 90 days from generation of the waste. Such storage area shall be covered with proper ventilation.
- (22) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of vanadium sludge waste shall be entered:
 - Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of receipt in the premises
- (23) A log book with information on source and date of procurement of each type of the said hazardous wastes, quantity, date wise utilization of the same, quantity of vanadium metal manufactured, hazardous waste generation and its disposal, etc. shall be maintained including analysis report of emission monitoring & effluent discharged, as applicable.
- (24) Transportation of vanadium sludge and filter press & MEE residues generated during utilisation shall be carried out by the sender or receiver (utilizer/TSDF operator) as per the authorization issued by concerned SPCB under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (25) 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 concerned SPCB.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

- (26) 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.
- (27) 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.

22.5 Standards

- (1) Emissions from stack connected to neutralization tank followed by scrubber shall comply with the following:
- PM - 150mg/Nm³
 - HCl vapour & mist - 35mg/Nm³
- (2) Emission from stack attached to reaction vessel and thermite chamber reaction vessels shall comply with the following:
- PM - 150mg/Nm³
 - Ammonia - 5mg/Nm³.

(Ammonia standard has been arrived based on emission of ammonia measured during trial utilization study)

- (3) Emission from stack connected to Bag Filters shall comply with PM emission of 150mg/Nm³.
- (4) Stringent emission standards may be prescribed by the concerned SPCB/PCC. Other emission/discharge standard shall be as per norms prescribed by concerned SPCB/PCC.
- (5) Fugitive emissions in the work zone shall comply with following standards (Reference: OCCUPATIONAL SAFETY AND HEALTH STANDARDS 1910.1000):

Ammonia - 25 ppm (18 mg/m³) TWA*
Respirable dust (PM₁₀) - 5000 µg/m³ TWA

*TWA - Time-weighted average
The Permissible Exposure Limit is 8-hour TWA.*

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.

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

(6) Monitoring of the specified parameters for source emission and work zone shall be carried out by NABL/EPA/ISO 17025 accredited laboratories quarterly and the results shall be submitted quarterly to the concerned SPCB/PCC.

22.6 Siting of Industry

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

22.7 Size of Plant & Efficiency of utilisation

1000 kg of vanadium sludge may yield 175 kg of vanadium metal. Other raw materials required are 3000 litre water, 363 litre HCl, 240 kg ammonium chloride salt, 79 kg iron chips, 95 kg aluminium and 11 kg calcium fluoride. Requisite facilities of adequate size shall be installed accordingly.

22.8 On-line detectors / Alarms / Analysers

Online detectors/alarms/analysers are not recommended for batch type processing units. However, in case of continuous process operations, SPCB/PCC may recommend online stack monitoring for PM emission in stack attached to thermite process.

22.9 Checklist of Minimal Requisite Facilities

S. No.	Requisite Facilities
1.	Storage shed(s) for storage of vanadium sludge in jambo bags or bags suitable for alkaline salt only under cool, dry, well-ventilated covered storage shed(s) within premises.
2.	Covered hazardous waste storage area to store residues generated from ETP(if any), scrubber residues, MEE salt, slag, product spillages etc. in HDPE bags/drums.
3.	Acid-alkali proof flooring in process area including the areas of reception, storage and handling of vanadium sludge, ammonium chloride salt and HCl.
4.	Chemical pumps for transfer of acidic liquids and slurry pump (optional) for transfer of reaction mass from reaction vessel.
5.	Neutralization tank adequate size with suction hood connected to scrubber followed by stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
6.	Chemical pumps for transfer of mother liquor and leached liquid solution.
7.	Reaction vessels of adequate size covered with FRP (or any suitable acid-alkali proof)

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of Vanadium Sludge to produce Vanadium Metal

	lid with suction hood connected to scrubber followed by stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher
8.	Hot Air Dryer with fume / dust extraction system with suction ducts and may have common scrubber and stack of Reaction vessel or separate scrubber followed by stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
9.	Centrifuge for recovery and washing of ammonium meta vanadate precipitate.
10.	Filter press unit for removal of silica and other particles.
11.	Separate storage tank and pipeline for HCl.
12.	Multi effect evaporator (MEE) for treatment of neutralised mother liquor/floor washing/tank and vehicle washing so as to achieve zero liquid discharge.
13.	Thermite chamber with pollution control device equipped with bag filters attached to stack of 30 meters height above ground level.
14.	Buffer storage tank with adequate capacity to store minimum one week of spent mother liquor/floor washing/tank and vehicle washing generated so as to store the same in case of unforeseen circumstance/breakdown of MEE.
15.	First aid and appropriate fire fighting equipment.
