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 Hydro Fluoro Silicic Acid Generated From Single Super Phosphate Fertilizer Industries
(Revised)

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Central Pollution Control Board

(Ministry of Environment, Forest & Climate Change, Government of India)

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Procedure for grant of authorization by SPCBs/PCCs for utilization of Hazardous waste

1) 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:

   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. Authorisation 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 ETP Sludge for utilization.

2) After issuance of authorization, SPCB shall verify the compliance of checklist and SoP on quarterly basis for initial 2 years; followed by random checks in the subsequent period for atleast once a year.

   In-case of lack of requisite infrastructures with the SPCBs/PCCs, they may engage 3rd party institutions or laboratories having EPA/NABL/ISO17025 accreditation / recognition for monitoring and analysis of prescribed parameters in SoPs for verification purpose.

3) SPCBs 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 website, periodically. Such updated list shall be sent to CPCB on a half yearly basis i.e., by July and January respectively.

4) 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 (generated during utilisation) or its complete utilisation or arrangement of sharing with any other authorised disposal facility.

5) 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.

6) The source and work zone standards suggested in the SoP are based on the E(P)A notified and OSHA standard respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions.

20.0 Utilization of Hydro Fluoro-Silicic Acid:

Type of HW	Source of generation	Recovery/Product
Hydro fluoro silicic acid – Acidic scrubber solution. Category C2 of Schedule-II of HOWM Rules, 2016	Single Super Phosphate manufacturing industry	Sodium Silico Fluoride (Sodium fluorosilicate) Na_2SiF_6

20.1 Source of Waste

Hydro fluoro-silicic acid is generated during the manufacturing of single super phosphate. It is generated during scrubbing of HF, H_2SiF_6 vapours, SiF_4 and SiO_2 emanated during reaction of Phosphate rock with sulphuric acid in reaction den. The spent hydro fluoro-silicic acid is an acidic scrubber solution categorised as hazardous waste.

20.2 Utilization Process

The utilization process involves reaction of hydro fluoro-silicic acid with sodium chloride/sodium sulphate resulting into precipitation of the Sodium Silico Fluoride salt, which is centrifuged and washed for recovery of Sodium silico fluoride precipitate from mother liquor. In case of sodium chloride, the mother liquor (HCL) is neutralized with either Sodium hydroxide or calcium hydroxide. In case of sodium sulphate, the mother liquor (dilute H_2SO_4) shall be captively utilized in manufacturing of single super phosphate within the premises. The centrifuged precipitate is dried in hot air oven dryer.

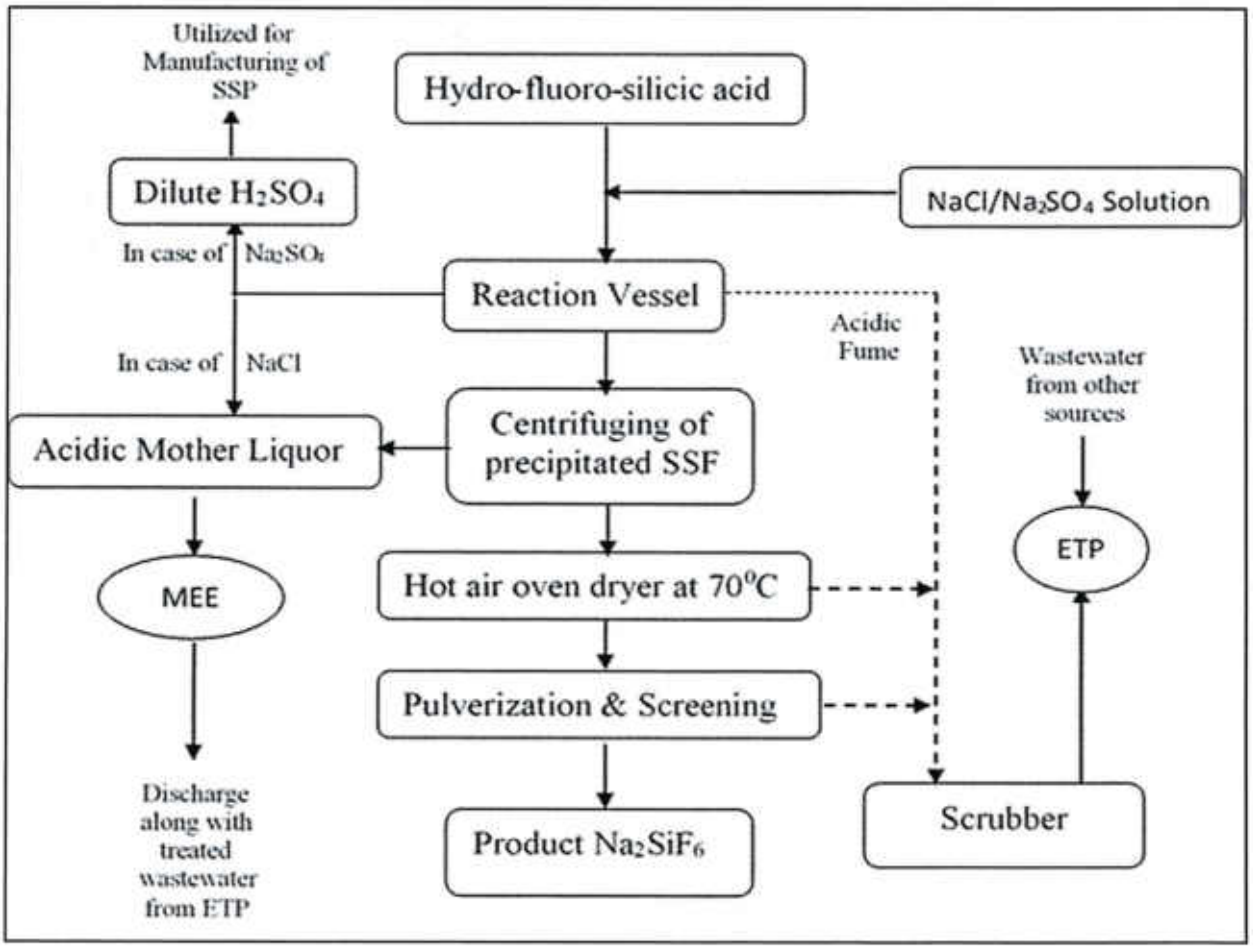

Figure: 1-*Process flow diagram for utilization of hydro fluoro silicic acid.*

20.3 Product Usage / Utilization

The recovered Sodium SilicoFluoride can be used in glass industry, ceramic industry and flux industry.

20.4 Standard Operating Procedure for utilization

This SoP is applicable only for the utilization of hydro fluoro silicic acid generated from Single Super Phosphate fertilizer industries during scrubbing of acid fumes to produce Sodium Silico Fluoride (Sodium fluorosilicate - Na_2SiF_6) suitable for utilization in glass industry, ceramic industry and flux industry.

1) The hydro fluoro silicic acid should be transported in acid-proof tankers or HDPE drums mounted on vehicles fitted with requisite safeguards ensuring no spillage of the liquid waste.
2) There should be a designated space for unloading of hydro fluoro silicic acid into a rubber lined storage tank. The receiving storage tank shall be placed above the ground and contained with low raise 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 HOWM Rules, 2016 so as to eliminate rain water intrusion.
4) There shall be no manual handling of hydro fluoro silicic acid. Chemical process pump shall be used for transfer of hydro fluoro silicic acid through pipelines to the reaction vessels.
5) 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 ETP or reaction tank, as the cases may be, through chemical process pump.
6) The reaction vessel should be covered with FRP (or any suitable acid proof) lid connected to a common suction duct with isolation valve leading to scrubber unit.
7) The material from storage tank may be filtered in a centrifuge to remove silica particles prior to transfer of the same to reaction tank (Optional operation).
8) There should be separate tank for preparation of $NaCl/Na_2SO_4$ solution. And this solution should be transferred to reaction tank though separate pipeline.
9) After completion of reaction between hydro fluoro silicic acid and $NaCl/Na_2SO_4$ solution, the supernatant containing hydrochloric acid shall be pumped out to ETP for treatment or the supernatant containing dilute sulphuric acid shall be pumped out to SSP manufacturing plant for utilization, while the remaining slurry / suspension (reaction mass) containing the precipitate of Sodium Silico Fluoride should be neutralised with caustic soda to reach neutral pH. The material is then transferred to centrifuge unit using a suitable slurry pump or other mechanical means with minimal manual intervention.
10) 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, 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) Drying of sodium silico fluoride shall be done in air over dryer connected to wet scrubber. It should be ensured that the temperature in the oven does not exceed 70°C there is a risk of conversion of the product into corrosive fumes of hydrogen fluoride and silicon tetra fluoride at temperatures beyond 105°C.

12) Screening of dried product should be done in mechanised sieves with dust enclosures.

13) All reaction tanks/vessels and dryer should be connected through common vent ducting system connected to wet scrubber (made of FRP material), connected to a stack of height 30 mtr above the ground level.

14) Sources of wastewater from utilization process

    a) In case of NaCl solution only, spent mother liquor containing HCl (high TDS effluent).

    b) Scrubber bleeds.

    c) Floor washing/reactor wash/vehicle wash/spillages, etc.

    d) In case of NaCl solution only, condensate from MEE.

15) Treatment and disposal of waste water

    - Discharge of high TDS effluent shall not be permitted. The Spent mother liquor containing HCl shall be collected in separate tank for treatment with sodium hydroxide or calcium hydroxide followed by further treatment in MEE.
    - The wastewater (excluding Spent mother liquor containing HCl) shall be treated Physico-Chemically by neutralization (calcium hydroxide or sodium hydroxide) followed by coagulation & sedimentation and shall be disposed as per the standards stipulated in Consent issued by SPCBs/PCCs.
    - The MEE salt should be sent to TSDF for encapsulation and secured landfilling.
    - In case the unit proposes to utilize supernatant containing HCl as a resource, the same shall be referred to CPCB for preparing SOPs for such utilization

16) It shall be ensured that hydro fluoro silicic acid is procured from the industries who have valid authorization for the same from the concerned SPCB as required under HOWM Rules, 2016.

17) The residue generated from centrifuge (used for pre-filtering of hydro fluoro silicic acid), ETP sludges, residue from scrubber, 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.

18) The residues generated from ETP, scrubber residues, MEE salt, waste silica, product spillages etc. shall be disposed as hazardous wastes through common TSDFs as per conditions stipulated under consent/authorization issued by concerned SPCB.

19) 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.

20) Transportation of hydro-fluoro-silicic acid and 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.The treated effluent shall be discharged in accordance with the conditions stipulated in the Consent to Operate issued by respective SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974.

21) 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.

22) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.

23) 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.

20.5 Record/Returns Filing

1) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of 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

2) A log book with information on source, quantity, date wise utilisation of hydro fluoro silicic acid and its generation and 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 utilised, hazardous waste 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/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.

20.6 Standards

1) Emissions from stack connected to scrubber and dryer units shall comply with PM, acid mist (HCl/H_2SO_4) and total fluoride emission of 150, 30/50 and 25 mg/Nm^3 respectively.

2) Fugitive emission in the storage area shall comply with the following standards:

   H_2SO_4 Vapour - 1 mg/m^3 Ceiling limit (in case using Na_2SO_4)

   Hydrogen choride- 7 mg/m^3 Ceiling limit (in case using NaCl)

   Respirable dust (PM_{10}) - 5000 µg/m3 TWA

   Fluoride in dust – 2.5 mg/m^3TWA

   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
   **PEL: Permissible Exposure Limit*
   **time-weighted average (TWA): measured over a period of 8 hours of operation of process.*

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 NABL or EPA approved laboratories and the results shall be submitted to the concerned SPCB/PCC on a quarterly basis.

4) Standards for discharge of wastewater (excluding Spent mother liquor containing HCl).

   pH – 5.5 – 9.0
   Fluoride – 2.0 mg/l
   COD – 250 mg/l
   O&G – 10 mg/l
   TSS – 100 mg/l
   Total residual chlorine – 1 mg/l
   (Or any other standard stipulated by SPCB/PCC in their consent order)

20.7 Siting of Industry

Facilities for processing of hydro-fluoro-silicic acid should preferably be located in a notified industrial area or industrial park/estate/cluster.

20.8 Efficiency of utilisation

The plant shall produce about 1.25 tonnes of sodium silico fluoride from 1 Tonne of hydro fluoro silicic acid. Consumption of sodium chloride/sodium sulphate shall not exceed 0.75 tonnes per tonne of spent hydro fluoro silicic acid.

20.9 On-line detectors / Alarms / Analysers

Online detectors/alarms/analysers shall be installed in case of continuous process operations for acid mist (HCl/H_2SO_4) and total fluoride emissions.

20.10 Checklist of Minimal Requisite Facilities

Sl. No	Particulars
1.	Storage shed(s) (constructed above the ground) for storage of hydro fluoro silicic acid in lined tankers or HDPE drums only under cool, dry, well-ventilated covered storage shed(s) within premises.
2.	Storage tank (s) should be of such size/capacity that it can store at least two weeks requirement of the aforesaid waste.
3.	Covered hazardous waste storage area to store residues generated from ETP, scrubber residues, MEE salt, waste silica, product spillages etc. in HDPE bags/drums.
4.	Lined tank for storage of hydro fluoro silicic acid.
5.	Acid proof flooring in process area including the areas of reception, storage and handling of hydro-fluoro-silicic acid.
6.	Chemical pumps for transfer of acidic liquids and slurry pump (optional) for transfer of reaction mass from reaction vessel.
7.	Tank for preparation of sodium chloride/ sodium sulphate solution.
8.	Use chemical pumps – for transfer of clear H_2FSi_6 solution and sodium chloride/ sodium sulphate solution - no manual handling of hydro fluoro silicic acid.
9.	Reactions vessels - should be covered with FRP (or any suitable acid proof) lid.
10.	Fume / dust extraction system with suction ducts connected to reaction vessels, dryers and pulverizer. The scrubber unit should have common ducting with isolation vales connected to ID fan attached to stack of height 30 meters.
11.	Centrifuge for recovery and washing of sodium silico fluoride precipitate.
12.	Drying unit (hot air dryer of adequate size attached with dust extraction system).
13.	Alarm system in dryer to ensure temperature does not exceed beyond 100°C.
14.	Separate collection tank for Spent mother liquor containing HCl.
15.	Multi effect evaporator (MEE) for treatment of neutralised mother liquor containing HCl.
16.	Pulveriser /grinding machine – with mechanical screens and dust enclosures. If required, this unit may be connected to fume extraction system.
17.	Effluent treatment plant comprising of collection tank, neutralization, coagulation & sedimentation and sludge handling unit (Filter/Centrifuge/ Sludge drying bed etc.)

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