

**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**



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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**

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**Utilization of Hydro Fluoro-Silicic Acid:**

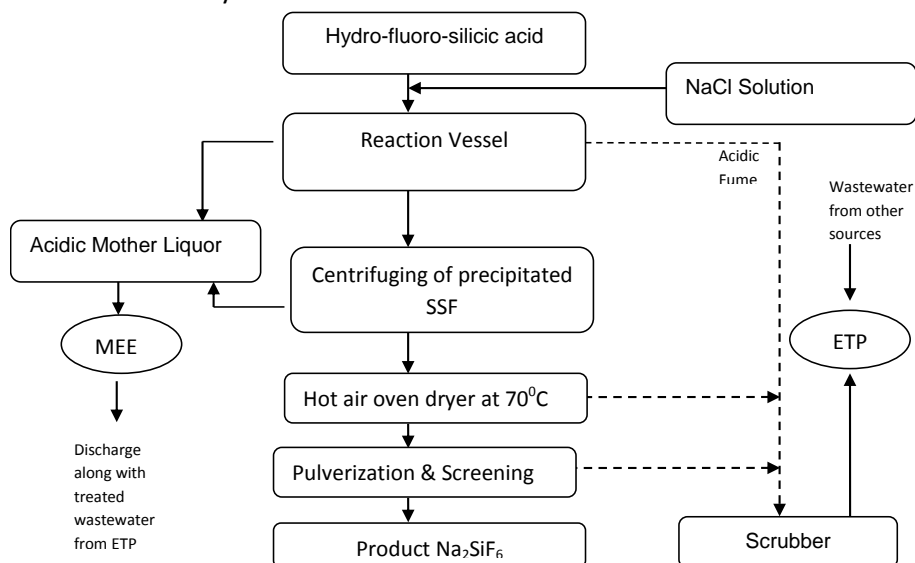
Type of HW	Source of generation	Recovery/Product
Hydro fluoro silicic acid – Acidic scrubber solution. Category C2 of schedule-II of HOWM Rules, 2016	Single Super Phosphate manufacturing industry	Sodium Silico Fluoride (Sodium fluorosilicate) $\text{Na}_2\text{SiF}_6$

**20.1 Source of Waste**

Hydrofluoro-silicic acid is generated during the manufacturing of single super phosphate. It is generated during scrubbing of HF,  $\text{H}_2\text{SiF}_6$  vapours,  $\text{SiF}_4$  and  $\text{SiO}_2$  emanated during reaction of Phosphate rock with sulphuric acid in reaction den. The spent hydrofluoro-silicic acid is an acidic scrubber solution categorised as hazardous waste.

**20.2 Proposed Process**

The utilization process involves reaction of hydro fluoro-silicic acid with sodium chloride resulting into precipitation of the Sodium SilicoFluoride salt, which is centrifuged and washed for recovery of Sodium silico fluoride precipitate from mother liquor. The mother liquor is neutralized with either Sodium hydroxide or calcium hydroxide. The centrifuged precipitate is dried in hot air oven dryer. The centrifuged precipitate is dried in hot air oven dryer.



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**20.3 Product Usage / Utilization**

The recovered Sodium SilicoFluoride can be used in glass 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  $\text{Na}_2\text{SiF}_6$ ) suitable for utilization in glass 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 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 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 solution. And brine solution should be transferred to reaction tank through separate pipeline.
- (9) After completion of reaction between hydro fluoro silicic acid and NaCl solution, the supernatant containing hydrochloric acid shall be pumped out to ETP for treatment,

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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) The material from centrifuge after washing can be transferred to dryer unit manually.
- (11) 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.
- (12) 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.
- (13) Screening of dried product should be done in mechanised sieves with dust enclosures.
- (14) 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 30mtr above the ground level.
- (15) Sources of wastewater from utilization process
  - a) Spent mother liquor containing HCl (high TDS effluent)
  - b) Scrubber bleeds
  - c) Floor washing/reactor wash/vehicle wash/spillages, etc.
  - d) Condensate from MEE
- (16) 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.

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- The unit may discharge only the MEE condensate and treated wastewater from ETP after complying with the standards stipulated by concerned SPCB;
- (17) 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 Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
- (18) 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.
- (19) 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.
- (20) 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.
- (21) 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
- (22) 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 sodium silico-fluoride manufactured, hazardous waste generation and its disposal etc. shall be maintained including analysis report of emission monitoring & effluent discharged, as applicable.
- (23) 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.
- (24) 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

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the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 to concerned SPCB.

- (25) 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.
- (26) 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.

**20.5 Standards**

- (1) Emissions from stack connected to scrubber and dryer units shall comply with PM, acid mist (HCl) and total fluoride emission of 150, 30 and 25 mg/Nm<sup>3</sup>.
- (2) Fugitive emissions in the work zone shall comply with following standards

Hydrochloric acid- 7 mg/m<sup>3</sup> Ceiling limit  
Respirable dust (PM10) - 5000 µg/m<sup>3</sup> TWA  
Fluoride in dust – 2.5 mg/m<sup>3</sup>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.*

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

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**20.6 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.

**20.7 Efficiency of utilisation**

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

**20.8 On-line detectors / Alarms / Analysers**

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

**20.9 Checklist of Minimal Requisite Facilities**

<b>S. No.</b>	<b>Requisite Facilities</b>
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 solution.
8.	Use chemical pumps – for transfer of clear H <sub>2</sub> FSi <sub>6</sub> solution and brine 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

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	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.
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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