

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 Spent Fixer (Hypo) solution Generated From
Photographic / X-Ray Films**



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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 Spent fixer (hypo) solution

Type of HW	Source of generation	Recovery/Product
Spent fixer (hypo) solution. Category A9 of schedule-II of HOWM Rules, 2016	Photography / X-rays films	Silver

19.1 Source of Waste

Spent hypo solution is commonly produced during the photographic film processing, development of X-ray films, etc. In photo/X-ray film processing, silver from photographic/X-ray film leaches into the fixer solution (Sodium Thio-Sulphate) forming Silver Thio-Sulphate complex ions. The fixer is considered exhausted after becoming silver-rich, as it can no longer serve the purpose of fixing the film in an effective manner. Such exhausted fixer is generated as waste (categorized as A9 of schedule-II of HOWM Rules, 2016), that can be processed to recover Silver from it. The typical sources of spent fixer (hypo) solution are Photo studios, health care facilities, etc.

19.2 Proposed Process

The utilization process involves reaction of Spent fixer (hypo) solution with sodium hydroxide and sodium sulphate to neutralize and dissociate silver from the Spent fixer solution which is centrifuged. The material recovered from centrifuge is dried, grinded and melted in a furnace at a temperature of about 1100°C to recover silver metal.

19.3 Product Usage / Utilization

The recovered silver is a pure metal from the melting furnace, which can be used in various applications including jewellery & ornaments.

19.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of Spent fixer (hypo) solution generated from Photography / X-rays films to recover Silver metal (suitable for use in jewellery & ornaments).

- (1) The Spent fixer (hypo) solution shall be procured only in closed tanker/HDPE drums.

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- (2) There should be designated space for unloading/transferring of Spent fixer (hypo) solution from the tankers/drums into a closed storage tank within the unit.
- (3) The receiving storage tank of Spent fixer (hypo) solution shall be placed above the ground and contained with low raise bund wall & acid proof floor with slope to channelize the spillages, if any to a collection pit. Such storage tank shall be provided under covered shed so as to eliminate rain water intrusion.
- (4) There shall be no manual handling of the Spent fixer (hypo) solution. Chemical process pump shall be used for transfer of Spent fixer (hypo) solution through pipelines to the reaction vessel.
- (5) The entire process area shall have leak-proof and acid proof floor tiles with adequate slope to channelize spillages, if any, into a collection pit. The spillages from collection pit shall be transferred to Effluent Treatment Plant (ETP) or reaction vessel, as the cases may be, through chemical process pump.
- (6) The reaction vessel shall have suction hood above it to control fume/vapour liberated from the reaction vessel. The suction hood maintained at sufficient negative pressure so as collect fumes/vapour liberated from the reaction vessel. The suction hood via ducting shall be connected with scrubber where water shall be used as scrubbing medium. The scrubbed gases shall be vented through stack.
- (7) The treated acid fume/vapour shall comply with emission norms and shall be dispersed into atmosphere through stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
- (8) After completion of reaction between Spent fixer (hypo) solution with sodium hydroxide and sodium sulphate, the supernatant shall be pumped out to ETP for treatment/evaporation, while the remaining slurry / suspension (reaction mass) is transferred to centrifuge unit using a suitable slurry pump or other mechanical means with minimal manual intervention.
- (9) The material from centrifuge after sun drying can be grinded (optional operation) and transferred to melting furnace/melting pot manually.
- (10) Fumes/vapors liberated from melting furnace/melting pot during the melting process shall be connected with fume extraction system attached via ducting system to scrubber where water shall be used as scrubbing medium. The scrubbed gases shall be vented through stack.
- (11) The treated fume/vapour of reaction vessels and melting furnace shall comply with shall be dispersed into atmosphere through stack of minimum height of 06 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.

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(12) 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 masks, safety gloves, goggles, safety shoes etc.

(13) Treatment and disposal of waste water:

The following are the sources of wastewater from utilization process;

- a) Spent mother liquor after several cycles of recycling
- b) Scrubber bleed
- c) Floor washing/reactor wash/vehicle wash/spillages, etc.

The above wastewater shall be treated Physico-Chemically by neutralization, coagulation & sedimentation and 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 and the standards stipulated in this SoPs.

In case of zero discharge or no discharge condition has been stipulated in the said Consent or non availability of the Common Effluent Treatment Plant (CETP), zero discharge shall be met by evaporation of the wastewater or treated water.

(14) The hazardous waste (viz. filter cloth, residue from scrubber, ETP sludge, residue from evaporation, as applicable) generated from utilization process shall be collected and temporarily stored in HDPE drums/bags in a dedicated hazardous waste storage area within the unit premises and sent to Common hazardous waste treatment, storage and disposal facility (TSDF) within 90 days from generation of the waste. Such storage area shall be covered with proper ventilation.

(15) The residues generated from ETP, scrubber residues, residue from evaporator etc. shall be disposed as hazardous wastes through common TSDFs as per conditions stipulated under consent/authorization issued by concerned SPCB.

(16) It shall be ensured that the Spent fixer (hypo) solution is procured from the units/hospitals who have valid authorization for the same from the concerned SPCB as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.

(17) 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.

(18) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of Spent fixer (hypo) solution shall be entered:

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- Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of receipt in the premises
- (19) A log book with information on source and date of procurement of the Spent fixer (hypo) solution, quantity, date wise utilization of the same, quantity of other raw material used, quantity of silver metal recovered, hazardous waste generation and its disposal etc. shall be maintained including analysis report of emission monitoring & effluent discharged, as applicable.
- (20) Transportation of Spent fixer (hypo) solution and the residues generated during utilisation process shall be carried out by sender or receiver (utilizer/TSDF operator) as per the authorisation issued by the concerned SPCB under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (21) 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.
- (22) 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.
- (23) 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.

19.5 Standards

- (1) Emissions from stack connected to scrubber of reaction vessel and melting furnace shall comply with the following:

PM	-	150 mg/Nm ³ or as stipulated by concerned SPCB
SO _x	-	200 mg/Nm ³
NO _x	-	400 mg/Nm ³

The monitored values of SO_x & NO_x shall be corrected to 11% O₂ on dry basis.

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- (2) Fugitive emissions in the work zone shall comply with following standards

Silver (metal dust and soluble compounds, as Ag)

Metal Dust: 0.01 mg/m³ TWA*

Soluble compounds: 0.01 mg/m³ TWA*

** Time-weighted average (TWA), Short-term exposure limits (STEL). The Permissible Exposure Limit is 8-hour TWA.*

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

- (4) Waste discharge from the unit shall comply with following parameters in addition to the standards stipulated by SPCB;

Silver – 0.1 mg/l

Sulphide (as S) – 2.0 mg/l

COD – 250 mg/l

Cyanide (as CN) – 0.2 mg/l

19.6 Siting of Industry

Facilities for processing of spent fixer (hypo) solution from Photography / X-rays films should preferably be located in a notified industrial area or industrial park/estate/cluster.

19.7 Size of Plant & Efficiency of utilisation

The plant with processing of about 200 litres of spent fixer (hypo) solution can recover 300 grams of Silver metal. Other raw materials consumed are 1.7 kg of Sodium hydroxide and 200 grams of sodium sulphate. The proposed minimum size of the plant is 200 litres/day. The recycling facility shall achieve > 99.6% recovery efficiency for silver metal.

19.8 On-line detectors / Alarms / Analysers

Online detectors/alarms/analysers are not recommended for batch type processing units. However, in case of continuous process operations, online effluent analysers for COD and Cyanide in treated effluent shall be installed.

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19.9 Checklist of Minimal Requisite Facilities:

S.No	Requisite Facilities
1.	Storage tank (s) for Spent fixer (hypo) solution with acid proof rubber lining having minimum storage capacity of atleast one week requirement
2.	The storage tank shall be placed above the ground and contained with low raised bund wall & acid proof floor with slope to channelize spillages into collection pit.
3.	Chemical process pump to transfer Spent fixer (hypo) solution from tanker to storage tank and then to reaction tank
4.	Leak-proof and acid proof floor tiles in the entire process area with adequate slope to channelize spillages, into collection pit.
5.	Collection pit for collection of spillages from the working and unloading area.
6.	Chemical process pumps to transfer from pit to reaction tank/ETP/ Evaporator, as applicable.
7.	Reaction vessel with suction hood connected via duct to water scrubber and stack
8.	Centrifuge
9.	Grinder (optional)
10.	Melting Furnace/pot furnace with necessary ducting system connected to water scrubber and stack.
11.	The height of stack (s) shall be minimum of 06 m above the roof top or as prescribed by the concerned SPCB, whichever is higher. Stack shall have easy access to port hole for conducting stack monitoring
12.	Evaporator and/or Effluent treatment plant, as applicable, to treat wastewater
13.	Dedicated covered hazardous waste storage area to store filter cloth, residue from scrubber, ETP sludge and residue from evaporation, as applicable.
14.	Online detectors/alarms/analysers are not recommended for batch type processing units. However, in case of continuous process operations, online effluent analysers for COD and Cyanide in treated effluent shall be installed.
