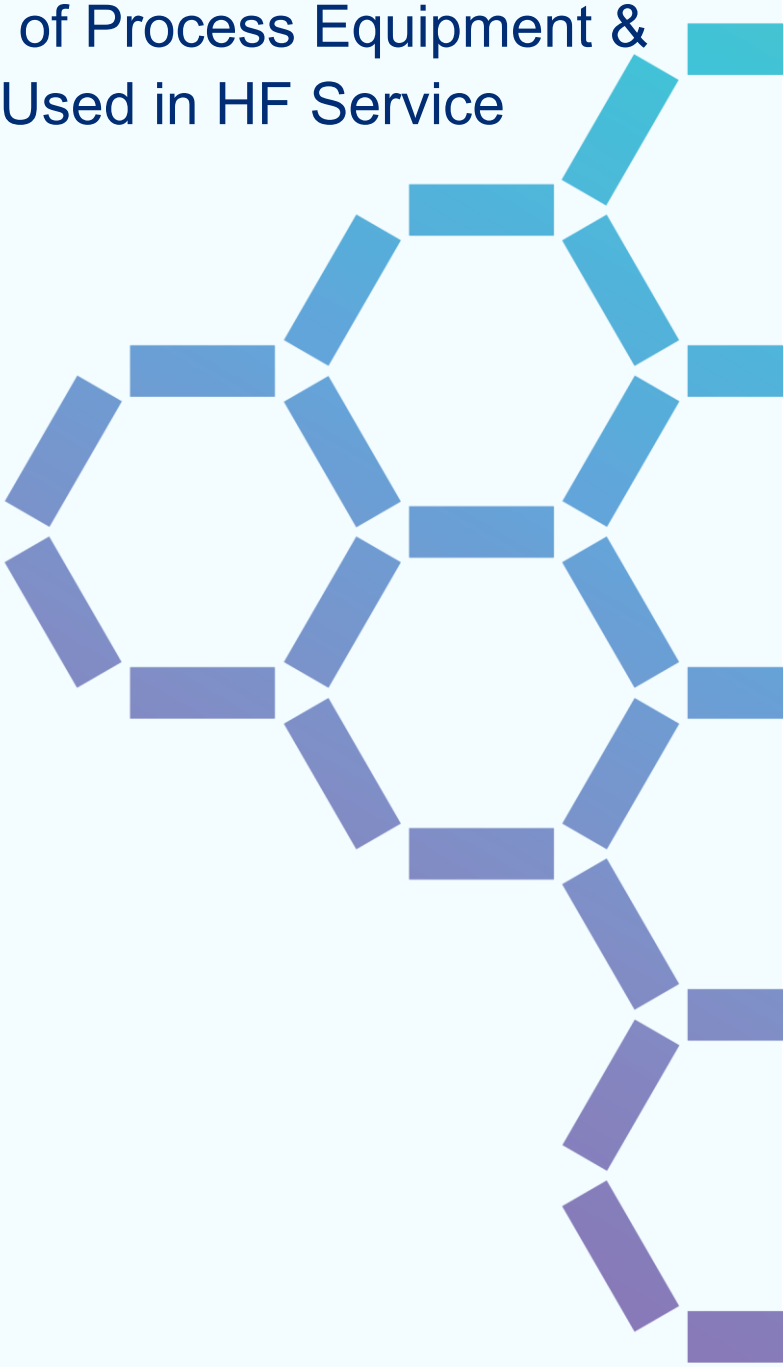
Hydrofluoric Acid Guidance – Section H
Decontamination of Process Equipment & Plant Previously Used in HF Service



Rev. 1 Reviewed by CIA HF Sector Network June 2025

Contents

Chemical Industries Association

Introduction

The Hydrofluoric Acid Sector Network of the Chemical Industries Association (CIA) has developed this Guidance. It is intended to provide a standard to cover the safe practices necessary when undertaking decontamination of process equipment previously used in HF service. The guidance is based upon many years of practical experience.

This guidance reflects the best current practice (at the time of publication) and is recommended for use in conjunction with information from the supplier(s) of HF or HF equipment. It is intended as a recommendation and not as a mandatory standard to which all manufacturers and users of HF must adhere. As the title suggests, it provides guidance on best practice for the decontamination of equipment previously used in HF service only.

The guidance is not to be used as a substitute for any applicable legislation. Whilst all reasonable efforts have been made to ensure the accuracy of the contents and legislative requirements at the time of publication, readers must refer to these themselves to ensure their compliance with current legislation.

Several other relevant HF guidance documents noted will also be relevant to decontamination work, especially **CIA HF Network Guidance Section A – 'Training requirements for HF handling facilities**' and **CIA HF Network Guidance Section B – 'Personal protective equipment in use at HF handling facilities**

Acronyms

AHF	Anhydrous Hydrogen Fluoride
HF	Hydrogen Fluoride / Hydrofluoric Acid
LEV	Local Exhaust Ventilation
PPE	Personal Protective Equipment
RPE	Respiratory Protective Equipment

H1 Scope

The Guidance is intended to apply to process equipment and plant utilised in HF service.

H2 Purpose

To present equipment previously used in HF service in a fit condition for inspection, maintenance or decommissioning by minimising potential exposure to residual acid and metal fluoride deposits.

H3 General

When preparing equipment for maintenance or decommissioning appropriate attention should be paid to the service history of the item.

All personnel, both employees and contractors, undertaking such operations should be suitably qualified and competent to conduct such duties. See **CIA HF Network Guidance Section A – 'Training requirements for HF handling facilities**'.

When equipment is to be removed from plant whilst the process remains operational, appropriate isolation procedures must be applied. Prior to initiating all maintenance/ decommissioning activities a risk assessment should be performed and all subsequent procedures conducted in a manner compliant with the need to control and minimise the associated hazards. This should include the use of appropriate PPE – see **CIA HF Network Guidance Section B – 'Personal protective equipment in use at HF handling facilities** for details of appropriate protective clothing and equipment to be worn when handling items that may be contaminated with HF.

H4 Removal

H4.1 Preparation of HF Service Equipment for Removal

Where possible, all process equipment and plant should be safely freed of acid whilst *in-situ*, thereby reducing the possibility of subsequent uncontrolled releases of significant acid volumes. Consideration should be given to the following practical aspects:

- **Displacement of residual deposits**. If practicable, residual acid deposits may be displaced in a controlled manner by flushing process equipment or plant with an appropriate neutralising wash medium.
- **Heats of reaction/solution**. Due consideration to the heat of solution or heat of reaction following water flushing / neutralising must be taken.
- **Pressure relief.** In addition, suitable and sufficient pressure relief must be considered for water flushing or neutralising operations.
- **Vacuum generation risk**. Spraying water into a vessel containing HF vapours could result in vacuum conditions being created.
- Neutralising with carbonate or bicarbonate solutions will result in CO_2 generation and positive pressure conditions being created.
- **Gas Purging of AHF**. For equipment in Anhydrous Hydrogen Fluoride (AHF) service where flushing processes may be deemed undesirable, purging with a stream of dry air or nitrogen may be considered, and with effluent gases being directed to an HF relief/scrubbing system where available. This may be accompanied by the external application of trace heating or steam to promote vaporisation of acid deposits.
- **Neutralisation and wash media**. It should be recognized that different practices exist for neutralisation and wash media between different process parameters and concentrations of HF – for example between AHF in high pressure / high temperature use such as refinery alkylation, where ammonia, hydrochloric acid (HCl) or citric acid based solutions may be used for whole Unit decontamination; and aqueous HF acid at ambient temperature and pressure where water or water and soda ash or sodium bicarbonate is sometimes used.
- **Extraction and pressure relief from CO_2**. Suitable and sufficient extraction and pressure relief should be provided when utilising soda ash or bicarbonate due to the associated evolution of carbon dioxide that could result in splashing of HF liquors.
- **Initial water flush before any neutralising**. It is also good practice to complete at least one initial water flush before any neutralising flush to reduce the quantity of HF beforehand, thus reducing the reaction thermal and pressure effects. Above all, users should ensure the wash medium is appropriate for the duty.
- **Washing & purging.** The extent of washing & purging deemed necessary, and the purge medium used, will be dependent upon the design of process equipment/ plant involved and the concentration of acid present. The effectiveness of water washing may be determined by analysis of the effluent generated. Examples of analysis include titration to determine HF concentration or a Fluoride Ion Selective Electrode. The use of pH may not be practical as a very small concentration of HF will show up as a low pH and removal of all traces of HF might be difficult.
- **HF permeation of polymeric linings**. Particular care should be exercised when dealing with items of equipment that included polymeric linings, due to the possibility of acid permeation having occurred while in service. Under such circumstances complete removal of residual acid deposits may not be readily achievable and due care must be exercised in subsequent handling. Locations that use internally lined equipment, e.g. piping, valves, vessels and pumps, should consider having specific written procedures outlining the steps that need to be taken during decontamination of equipment.
- **Competency of personnel**. All personnel involved in the decontamination of equipment containing HF acid should be trained and competent in the decontamination procedures.
- **Safe disposal of effluent.** Consideration must also be given to the environmentally safe disposal of any neutralising effluents generated during the decontamination of HF contaminated equipment/plant.

H4.2 Identification of Removed Items

Indication of decontamination status. Once detached from the process all items of equipment or plant should be clearly identified to confirm their status of decontamination. This is particularly important in instances where the maintenance activity is not to be conducted immediately after removal of the item. Identification may be achieved by labelling or tagging – though in some circumstances labelling and tagging may not be required, for example where equipment has been removed, decontaminated and taken immediately to a site workshop by personnel involved in that removal and its subsequent stripdown activity.

Labelling and tagging. When labelling and tagging is necessary, labels should be durable and securely attached to the item, with all information recorded being legible and relevant. Details recorded should include:

- Item identification number or coding.
- Origin.
- Date removed from process
- Point of contact, name, position and telephone number.
- Status of decontamination: a) HF free, b) May contain trace HF or c) HF contaminated
- Recommended minimum PPE requirements for handling specified equipment (per **CIA HF Network Guidance Section B**).
- Subsequent intended action – e.g. maintenance or disposal.

Traffic Light Status. A colour labelling system may be used to show decontamination status of equipment: **Red** (not decontaminated, do not remove), **Amber** (partial decontamination, handle with caution) and **Green** (fully decontaminated, OK to handle).

H4.3 Post-Removal Decontamination

Further Decontamination. Once detached from the process the item may require further decontamination before maintenance or disposal.

PPE. All personnel performing tasks to decontaminate HF equipment must wear appropriate PPE, see **CIA HF Network Guidance Section B**.

Storage Area. Items requiring further decontamination for maintenance or disposal at a later date should be stored in an area dedicated for this purpose. The storage area should be clearly identified as containing items that may be contaminated with acid and access restricted to authorised personnel wearing appropriate personal protective equipment. Storage area should be well ventilated to prevent accumulation of HF vapours that may arise due to release of permeated HF. If suitable ventilation cannot be provided (for example if storage is inside a building) consideration of HF monitoring in storage areas should be given to provide warning of the build-up of HF vapours. Smaller items may be placed in special containers while in storage awaiting further decontamination; however, caution must be exercised against the practice of bagging equipment for sending off site due to the potential for HF fumes to be generated over time and trapped. This would be of particular concern for non-metal items such as plastic where migration of HF out of the material is likely.

Decontamination Method. The method of decontamination should be appropriate to the scale and design of the item involved. In the case of large items this may involve steam or high-pressure water jetting being applied to surfaces that have been exposed to acid in the course of process operations. Smaller items may be subject to immersion in an agitated water bath. Where appropriate a neutralising agent, such as sodium bicarbonate, should be introduced to aid the process. Additionally, heating may be applied to improve the neutralising process.

Effluent. In all cases, it is likely that the effluent generated from further decontamination processes will contain a fluoride component. Where significant levels of fluoride are present the effluent should be adequately treated before disposed of as waste.

Complex equipment. Where complex items such as valves or pumps are involved, it will be necessary to break down these items to their component parts before decontamination is attempted. In such instances appropriate precautions must be taken to avoid possible exposure to residual acid deposits that may have eluded previous decontamination efforts. Equipment should be regarded as likely to contain residual HF, with use of appropriate PPE, and equipment treated as hazardous waste for disposal.

Note: **Plug or ball valves** that have been in HF service and removed from the process must NOT be stripped down whilst in the closed position as they could contain a significant amount of HF acid in the valve's port chamber. Ideally valves should be in the open position and safely freed of acid whilst still connected to the process. If a valve has been removed in the closed position, then it should be submerged in a bath of neutralising solution and opened in a controlled manner and in a controlled environment. Persons carrying out the above task must wear appropriate PPE for a **High-Risk** activity per **CIA HF Network Guidance Section B**.

Oil and Grease Lubricants and synthetic materials used in Seals and Gaskets. Particular care should be exercised when dealing with components that are lubricated with oil or grease. Due to the solubility and permeability characteristics of HF some equipment and material of construction items may contain appreciable levels of acid that may not be effectively removed by an aqueous washing medium. Similar precautions should be taken with synthetic materials utilised in seals and gaskets that may be susceptible to acid permeation.

Updating Decontamination Status Labels. Where post-removal decontamination procedures are performed by personnel other than the individual that will subsequently and immediately conduct the necessary maintenance activity, confirmation of the present decontamination status of each item must be made by revision of the label details/tagging format. See section H7 below for maintenance activities involving third parties.

Hazardous Waste. In the event of components being routinely discarded as part of the maintenance process, disposal should be conducted as hazardous rather than general waste. Such items should be stored in an area remote from that used for the retention of process equipment and plant awaiting decontamination.

H5 Exposure Risk from Metal Fluoride Deposits or from Contaminated Polymeric Materials

Metal fluorides. When in contact with HF, many metals readily form fluorides that may accumulate as a scale deposit on exposed surfaces. When general handling or maintenance activities result in the disturbance of dry fluoride deposits, appreciable levels of dust may be generated. As airborne fluoride in the form of fine dust is considered to be hazardous and detrimental to health, this should be duly considered in any risk assessment conducted prior to commencing the task. Appropriate precautions must be taken to limit dust generation, which may include local extraction or keeping the equipment wetted.

A suitable form of respiratory protection appropriate to the risk assessment should be defined in such instances where exposure to airborne fluoride is possible. As stated above, all personnel performing tasks to decontaminate HF equipment must wear appropriate PPE, see **CIA HF Network Guidance Section B**.

Contaminated Polymeric Materials. General handling or maintenance activities on polymeric materials containing permeated HF can result in the release of HF, including for example plastic welding releasing HF vapours. Therefore, consideration to Respiratory Protective Equipment RPE and Local Exhaust Ventilation LEV for such activities must be included in the risk assessments.

H6 Disposal of Decontaminated Equipment and Plant

Unless equipment or plant destined for disposal can be clearly demonstrated as being free from any hazard arising from its previous service, it must be treated as a hazardous rather than general waste and this should be reflected in the chosen mechanism of disposal. Stripping down equipment to component parts and use of indicator papers or fluids or other indicators may help, but many users still dispose of all equipment that has been in HF service as hazardous waste.

H7 Maintenance Activities Conducted by Third Parties

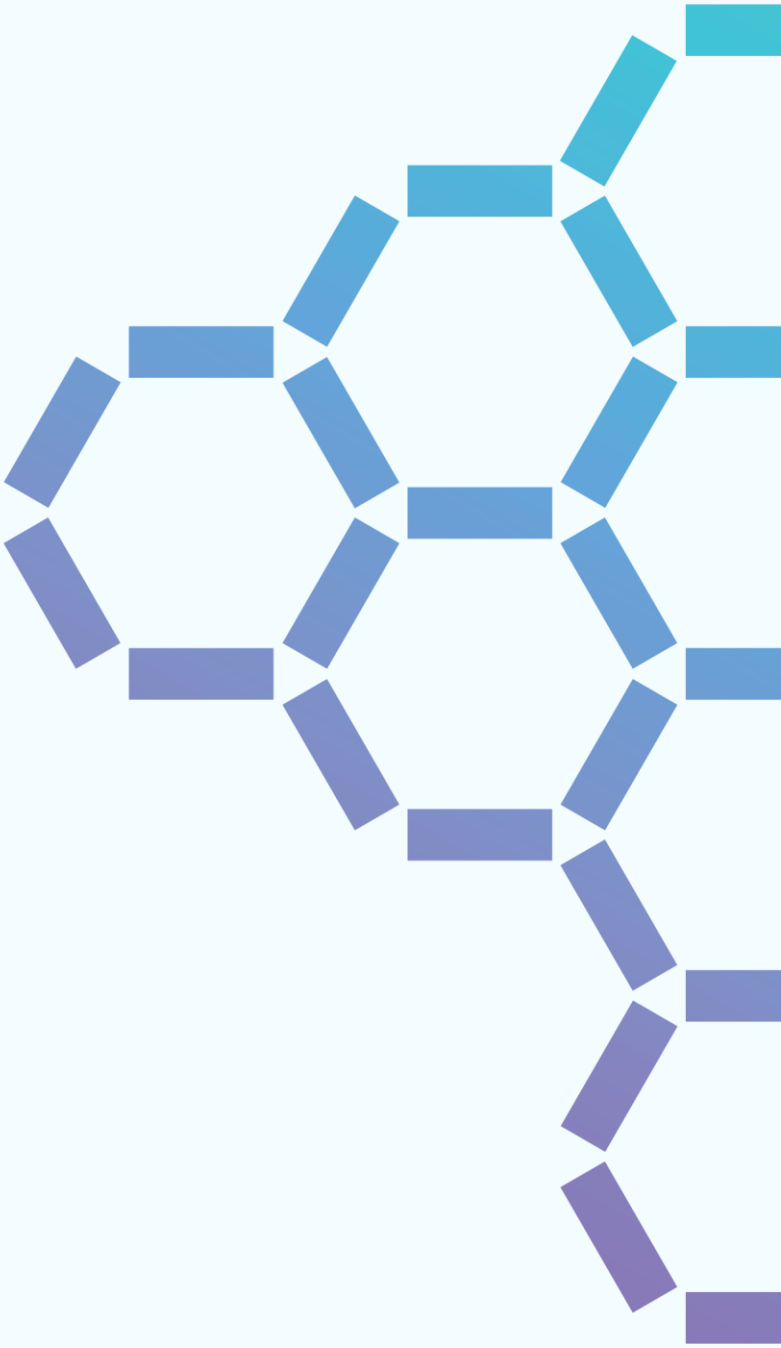
In the event of equipment or plant having to be dispatched from site for maintenance by approved third parties, as may be the case where specialist knowledge or equipment is deemed necessary, all items must be thoroughly decontaminated where possible prior to release from site. When items cannot be fully decontaminated then special agreement and approved procedures between the sending site and the third party must be complied with. This will involve a Duty of Care Audit by the sending site to ensure that all the necessary safety mitigation(s) are in place at the third-party premises to safely deal with a potential release of HF Acid liquid/vapour on the premises. Special focus must be given to ensuring that the third-party facility has a very good knowledge of the hazards of HF Acid and that all the persons handling or working on potentially HF contaminated equipment know of and understand the hazards of exposure to HF Acid and have received HF First Aid training. See **CIA HF Network Guidance – Section I – Medical First Aid**

The third party should be informed of the service history of the item and be aware of the possible hazards that this may present. These shall be clearly identified on the ‘Equipment Transfer Documentation’. These hazards must include any residual pressure that may potentially be present. Additionally, recommendations of levels of PPE required to handle equipment must be clearly written on the document. Additional good practice for equipment being sent to third parties is to include with the Decontamination Certificate a copy of the HF Safety Data Sheet, suitable gloves for handling, and a tube of calcium gluconate gel. Competence to undertake the work – both on site and off site – is paramount, as referenced above.

Where appropriate, specific hazard awareness and First Aid training should be provided for personnel who are expected to come into direct contact with the item as part of their normal working duties.

It is essential that adequate labelling/tagging is maintained to promote identification of the item while off-site activities are conducted.

CHEMICAL INDUSTRIES ASSOCIATION



WWW.CIA.ORG.UK

@SEE_CHEM_BUS

RESPONSIBLE CARE

Kings Buildings, Smith Square, London, SW1P 3JJ
Telephone: 020 7834 3399 | Email: enquiries@cia.org.uk | www.cia.org.uk