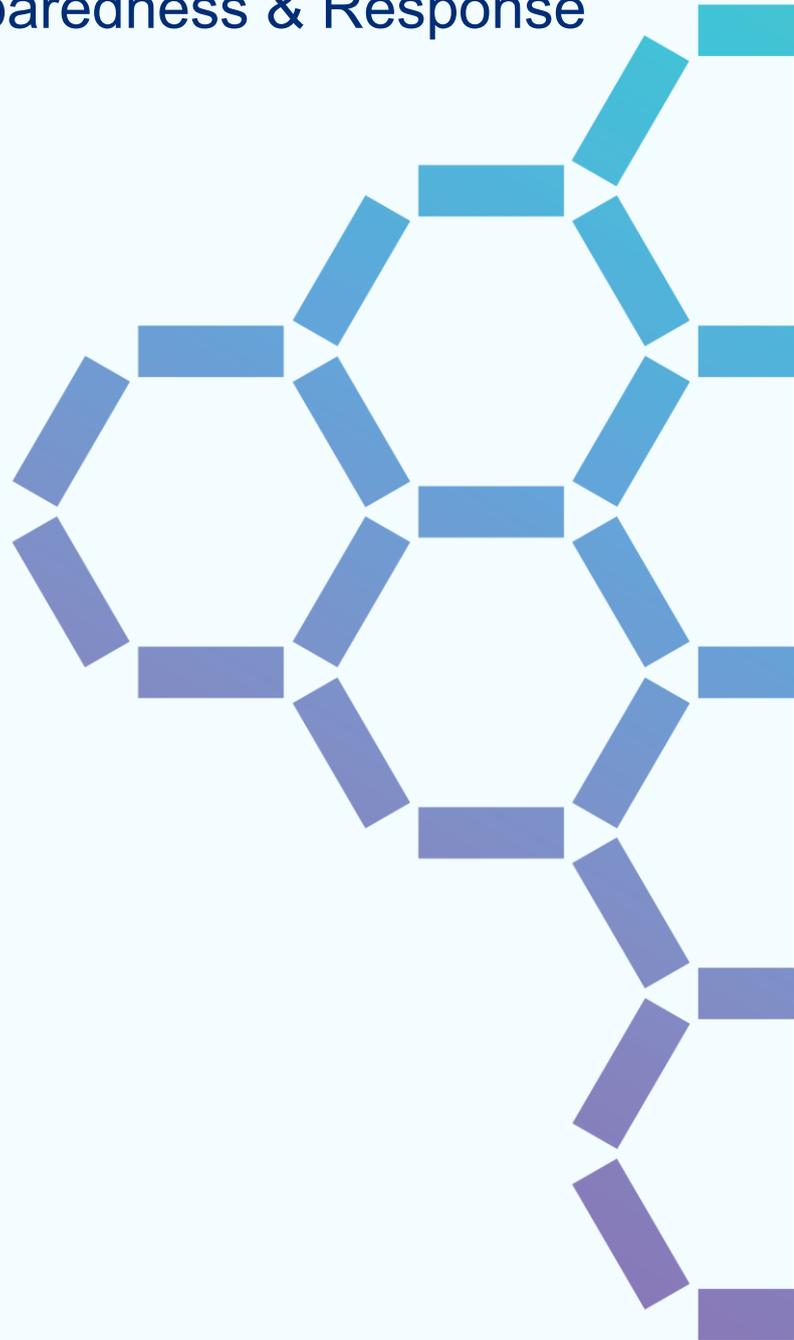


Hydrofluoric Acid Guidance – Section F Emergency Preparedness & Response



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Introduction

The Hydrofluoric Acid Sector Network of the Chemical Industries Association (CIA) has developed this Guidance. It is intended to outline the key elements of an operator's recommended response during an emergency involving HF. The Guidance reflects the current best practice (at the time of publication) and is recommended for use in conjunction with Guidance from the supplier(s) of HF for emergency planning for incidents on sites using HF. Because the nature of businesses using HF is very diverse, ranging from relatively small-scale use of dilute HF to HF manufacture and large-scale refinery use, some interpretation may be necessary about applicability of some of the technical recommendations, though the general principles of good emergency preparedness and response apply to all users.

The Guidance is not to be used as a substitute for any applicable specific legislative requirement. 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 legal duties.

This Guidance draws on experience from within the HF Sector Network, and also emergency response Guidance issued by the Comité Technique Européen du Fluor (CTEF-Eurofluor) which is the European equivalent to the CIA HF Sector Network. In this regard the Guidance is intended to achieve consistency and alignment of Guidance across Europe. In preparing this document, reference has also been made to the American Petroleum Institute Recommended Practice **API RP751, Safe Operation of Hydrofluoric Acid Alkylation Units**.

Acronyms

API	American Petroleum Institute	NRW	Natural Resources Wales
CTEF-Eurofluor	Comité Technique Européen du Fluor	PA	Public Address
COMAH	Control of Major Accident Hazards Regulations	PAM	Polyacrylamide
EA	Environment Agency	PE	Polyethylene
FMEA	Failure Mode Effects Analysis	PPE	Personal Protective Equipment
HAZOP	Hazard and Operability Study	ppm	Parts Per Million
HAZAN	Hazard Analysis	PTFE	Polytetrafluoroethylene
HAZID	Hazard Identification	RATS	Rapid Acid Transfer System
HF	Hydrogen Fluoride, Hydrofluoric Acid	SEPA	Scottish Environment Protection Agency.
MAPP	Major Accident Prevention Policy		

F1. General Overview

When acceptable practices have been followed during design, construction, operation and maintenance of a plant handling Hydrofluoric Acid (HF) the probability of a serious incident is low. However, experience over many years and across storage and use of many hazardous substances has shown that occasionally serious incidents leading to major accidents do occur. For these situations it is essential that emergency procedures are prepared which identify all reasonably foreseeable emergency scenarios arising out of credible incidents and detail the appropriate response.

The **Management of Health and Safety at Work Regulations 1992** requires employers and the self-employed to identify the hazards arising from their activities and make suitable arrangements to ensure that they are properly controlled. In addition, the **Control of Major Accident Hazards Regulations 2015** (COMAH 2015) require operators of sites subject to the Regulations to prepare and keep up-to-date internal (on-site) emergency plans and to supply necessary information to their local authority, who are required to prepare an external (off-site) emergency plan.

Emergency procedures should be periodically tested by conducting emergency drills and exercises. All emergency equipment provided should be maintained in a fit working state and should be tested regularly.

These requirements apply to all hazardous substances that may give rise to a major accident. This document provides best practice Guidance for responding to incidents specifically involving HF. The Guidance does not provide detailed information on all aspects of the content and format of emergency plans, the assumption being that this task has been completed, but it does contain some of the key considerations when implementing emergency plans.

F2. Objectives of Emergency Plans

The COMAH 2015 Regulations require that Operators ensure that **all measures necessary** are taken to prevent major accidents and limit their consequences for human health and the environment.

In planning for an emergency response, the objectives of internal and external emergency plans given in COMAH are as follows:

1. **Containing and controlling incidents so as to minimise the consequences, and to limit damage to human health, the environment and property**
2. **Implementing the necessary measures to protect human health and the environment from the consequences of major accidents**
3. **Communicating the necessary information to the public and to the [appropriate emergency] services or authorities concerned in the area and**
4. **Providing for the restoration and clean-up of the environment following a major accident.**

An HF emergency at a site concerns an actual or possible release of HF as liquid and/or gas, which may endanger the environment and/or people inside and outside the site boundary. Each site will have terminology in their emergency plans to describe the level or escalation of an emergency e.g. local/building emergency, site emergency, off site emergency/ major accident.

Emergency plans should cover an operator's response to an incident involving the release of HF. As no two releases are the same the plan should be flexible, allowing it to be used for all potential release scenarios. Plans should also cover the concept of extendibility (beyond reasonably foreseeable), domino effects (i.e. accidents in neighbouring establishments) and indirect causes of HF releases e.g. utilities failure, fire.

The site emergency plan must also detail how assistance from external emergency services will be summoned, should the incident escalate, and how the site will provide assistance with external mitigatory action.

F3. What Emergency Plans Need to Cover

Emergency Plans will need to cover:

- high consequence/ low probability events and
- low consequence/ high probability events.

In preparing an internal emergency response plan the full range of likely HF incidents that can be realistically anticipated, and resources needed to respond to such events, must be considered. The plan must cover all realistic events of all sizes, from those that can be dealt with directly by plant team, to major accidents that will need the assistance from the local emergency services and local authority. The internal and external plans should be based on all reasonably foreseeable emergency scenarios arising out of credible major hazard

incidents. For Upper Tier sites these should be identified in the COMAH Safety Report, or in the Major Accident Prevention Plan (MAPP) for Lower Tier sites.

The plans should show that the operator has considered and analysed a representative set of major accidents and identified the plant, equipment, resources and procedures required for mitigation. There should be a clear link between the Safety Report or MAPP and the scenarios covered in the plan. The identification of foreseeable scenarios should be through a structured formal process safety assessment approach using tools such as HAZOP, HAZID, HAZAN and FMEA.

For each event considered in the plan there must be an assessment of the typical defects and failures that can lead to the events, the size of the release, the timescales involved (duration of release) and the options for minimising the consequence through mitigating action.

Emergencies at sites can originate from leaks or spills from a range of sources, including:

- Road tankers during loading or off-loading operations
- Transfer equipment (e.g. flexible hoses)
- Process storage vessels
- Process equipment (columns, reactors, oven, and so on)
- Valves, joints and process pipework.

F4. Emergency Responders

Maintaining control in an emergency is complex and clear allocation of responsibilities with appropriate delegated authority is critical if plans are to be deployed successfully.

Emergency plans should identify a clear chain of command to deal with emergency situations at all times.

Emergency role holders should be clear about their responsibilities and the tasks that they may be required to undertake. Checklists and emergency response procedures must be prepared to ensure safe, reliable and consistent actions from responders. This is particularly important if a site runs a shift system where personnel cover for each other. An Incident Controller must know that regardless of which shift team he or she is leading in an emergency, the response will be consistent across shifts and similarly for operators who are acting as part of the remedial team.

When planning the response to foreseeable emergencies the numbers of trained and competent staff required to respond to the emergency at any time must be determined.

Deputising arrangements and call-out rotas should be clearly identified and the provisions made for handling situations that may arise in silent hours.

All personnel with emergency roles must be trained and competent and take part in exercises on a regular basis. The level and type of training will be appropriate to the role that they hold, taking into account their knowledge and experience. Training and participation in exercises should be recorded. For further information refer to **CIA HF Sector Network Guidance Section A – ‘Training Requirements for Facilities Handling HF’**.

The plan should identify key personnel with an emergency response function and how they will be mobilised.

The Emergency Response Team for a large site is typically composed of:

- Site Incident Controller
- Control Room Operator
- Remedial teams - usually plant operators
- Fire and Rescue Service
- Site Main Controller
- Site medical team

There will be other roles depending on the incident and the organisational structure e.g. Technical Advisers, Public Relations Officers and Loggists. The site emergency plan must also detail how assistance from external emergency services will be summoned, should the incident escalate.

F5. Emergency Equipment

The Emergency Team, when entering the incident scene, must be provided with appropriate personal protective equipment (PPE) and with the equipment and resources needed to take appropriate prompt action to manage the emergency. This is especially important for emergency response to substances such as HF that have particular properties that require specialist PPE or other equipment, as detailed below. (For specific information on PPE refer to separate **CIA HF Sector Network Guidance Section B on PPE for use with HF**).

Operators must verify that plant, equipment and consumables are suitable for the task and are placed on an appropriate inspection and maintenance schedule so that they can be certain that adequate stocks are held, equipment remains in good repair and is available on demand. The plan should identify vulnerable critical emergency response resources, and contingency arrangements on or off site should be put in place in the event of failure of these resources.

The site exercise and drill schedule should ensure that emergency responders are familiar with how to use equipment and PPE in various conditions, e.g. using equipment in bad weather or other exceptional conditions. There is no point having lots of equipment available if it remains in its original box and no one on site has ever tried to use it. The day of the emergency should not be the first time that responders have seen or used equipment or donned PPE.

Apart from the general emergency equipment, specific HF emergency equipment should be provided at suitable, well known and well signed locations, e.g.:

- Local to where releases could occur but ensure that equipment will still be accessible in an emergency.
- Assembly points
- Emergency Response Team vehicles or headquarters
- Works medical centre.

The Emergency Equipment list will vary depending on the nature of the HF facility and should be aligned to mitigate the potential release scenarios identified by each establishment. Each site should consider provision of the following:

- Water showers with eye-washer or baths, preferably heated
- Hoods with airline breathing sets
- Full protective suits with airline
- Other protective clothing
- Self-contained breathing apparatus
- Groundwater monitors
- HF monitors and detectors
- Absorbent materials
- Drain bunds
- Emergency tool kits
- Bungs, sealing paste and tape – (see **F7.4 Leaks** when use of these may **not** be appropriate)
- First Aid kits
- Portable communication equipment e.g. radios

If operators are to rely on the emergency services as part of their response it is important that any inter-operability or compatibility issues surrounding equipment and deployment of resources (including people) are ironed out during site familiarisation visits and exercises.

F6. Mechanisms Involved in HF Releases

If a liquid HF leak occurs, the release will usually be emitted from the source in two phases. As well as the liquid, three potential contributions to the overall release must be taken into account in differing proportions according to the source and environmental conditions as follows:

F6.1 Gaseous Emission (Flash Contribution)

Due to the change in HF temperature and pressure conditions, part of the emission is in the gaseous phase. The higher the source temperature and pressure, the higher the gas fraction generated through “thermodynamic flash.”

F6.2 Aerosols

If the release results in a high pressure drop, i.e. high emission velocity and mechanical stress on the liquid, aerosol formation is unavoidable. This contribution can be very important in increasing the size of the resulting plume as the fine liquid droplets tend to evaporate quickly due to the large and exposed surface area.

F6.3 Pool Evaporation

The residual liquid part of the leak that does not evaporate during flash falls on the ground, where it forms a pool which evaporates. The mass evaporation rate strongly depends on liquid and ground/soil temperatures, wind velocity, but mainly on the kind of substrate and on the exposed surface area of the pool, which has to be reduced by any suitable means.

F7. Emergency Actions

Along with the Guidance given below, examples of typical actions for different scenarios are given in Appendix A. This list is not exhaustive and does not replace risk assessment and identification of operator specific emergency procedures and equipment and the training and exercising of responders.

F7.1 Evacuation of Non-Intervention Personnel

Procedures should be put in place to evacuate and roll-call non-intervention personnel in the event of alarm. Employees, visitors and contractors should be provided with information so that they know what to do in the event of an alarm. It is good practice to provide a map detailing the location of the assembly point. Assembly points should be identified as part of the Occupied Buildings Risk Assessment and be located upwind (using prevailing wind direction) in a designated area equipped with means of communication, e.g. Public Address (PA) system or telephone. Wherever possible, alternative locations should be planned to cover wind directions that differ from the prevailing wind direction.

F7.2 Plumes

A hydrogen fluoride plume will spread according to the wind conditions and other local factors (buildings, plant structures, hills, and so on). Action must be taken to abate the plume before it becomes a danger to site personnel, the neighbouring community and the environment. HF plume modelling can be employed to predict and map the size and direction of travel of the cloud based on size of release and prevailing weather conditions.

If installed in the area where the leakage has originated, powerful water curtains are effective to contain or knock down a HF plume. The residual fog which results from the HF reacting with atmospheric moisture can then be removed by spraying finely divided water from hydrants, ground monitors or fire appliances. Sprayed water should be directed from a point upwind of the leakage. The downwind areas should be cleared of people. Action should be taken to contain water curtain run-off and prevent it entering drains and water courses.

Although the molecular weight of HF is less than air it will not always rise, as HF also forms dimers and trimers which are heavier than air. The water must not be sprayed directly onto the source of the leak but only onto the plume, to avoid increasing both the size of the leak by corrosion (weak HF acid is highly corrosive to normal steels) and the gaseous HF emission due to the heat of dilution – however it should be noted that wetting of a leakage plume, when applying water, will almost certainly wet the source of the leak.

F7.3 Spills

When a large quantity of hydrogen fluoride is spilled, it largely remains as liquid but at the same time a large volume of dense acidic fume tends to be released. HF pool evaporation must be stopped or at least reduced by any suitable means as quickly as possible. Actions can be taken to:

- Reduce the HF concentration in the pool and therefore its vapour pressure. This strongly reduces driving force to the evaporation mass flow rate
- Reduce the surface area of the pool as the evaporation mass flow rate is proportional to the air-exposed pool surface

- Create a barrier or screen to entrap the vapour and help prevent it leaving the pool.

When water is added to effect dilution or alkali is used to effect neutralisation, vigorous exothermic reactions can take place and fume may form. The resulting strong heat generation promotes further evaporation if the dilution is not sufficient. Therefore, sufficient quantities of water or neutralising agents must be used so that a greatly increased vapour cloud does not result.

For small pools of liquid HF, water should be added only when it can be applied at a rate very much higher than the HF leakage rate so that it will very rapidly dilute the HF and suppress most of the vapour released. To negate the thermal effect coming from the dilution heat emission, the liquid HF must be rapidly diluted to a concentration less than 2% by weight. Typically, a 50:1 ratio of water applied to Anhydrous HF acid released is required for a 90% knockdown/absorption of the acid. The amount of water required for even a modest leak of liquid HF will be significant. As with Plumes, water should be directed from a point upwind of the leakage and the downwind area should be cleared of people and action taken to contain water run-off.

For large pools of liquid HF, it is unlikely that sufficient dilution could be achieved in which case immediate action should be taken to contain the spillage and reduce the evaporation rate of the pool. Retention walls and underground pools are able to contain the spillage and to reduce the evaporation surface area. If such systems have not been installed in plant operating areas, temporary bunds can be created using earth, polyacrylamide powder (PAM) or other suitable material (**Note: HF can react vigorously with silica in sand, hence sand is not recommended**). When the spillage can be run off at a controlled rate, dilution of the stream with water may commence. The materials used should be evaluated at the emergency planning phase to ensure compatibility.

Pool evaporation in liquid systems can be reduced or removed by using absorbents such as PAM. The pool must be completely covered with PAM and added in the ratio of 1 part of powder to 2 parts of HF. This treatment is easier for a limited surface area within permanent or temporary bunds. The PAM forms a gel which can be treated with water or soda ash solutions. Any untreated PAM which comes into contact with water will give rise to a slipping hazard. After application, the residual solid or gelatinous waste must be neutralised, for example using slaked lime to give an insoluble calcium fluoride. Neutralisation must be carried out very cautiously and slowly because of the potential for an exothermic reaction which may cause the mass temperature to increase and the generation once more of HF. The neutralised solid mass must be finally disposed of in specialised landfills. The method of disposal and environmental considerations of any end product must be evaluated as part of development of the emergency procedures.

- Sawdust is not recommended as it is hydrophilic and then likely to be quite wet. When dispersed on an HF pool it provides such poor dilution that can result in the mass temperature rising even leading to auto-ignition. Other absorbents are available, and the absorption end products differ according to their nature and physical form; advice from the manufacturer should be sought.
- Water based protein foams are not effective to hinder HF evaporation. Their application is in fact equivalent to the addition of water at a low rate resulting in the evolution of hydrogen fluoride vapour which rapidly breaks down the foam layer.
- If the spillages of HF are bunded, evaporation can be reduced by covering the pool with cold mineral oil (oil thickness must be greater than 20 cm). This ensures higher thermal inertia and reduces the exposed evaporation surface. However, issues regarding the post incident clean-up of oily residue need to be considered as part of the planning phase.
- Using the principle of reducing the exposed surface area, evaporation from HF pools can also be depressed by covering the pool with polyethylene sheets but again disposal issues need to be considered. Polyethylene balls are not recommended because they increase the evaporation surface area due to rotation of the balls.

F7.4 Leaks

Each facility should have an ongoing program to closely monitor plant and equipment for early signs of minor leakage, including a good culture of operator awareness and vigilance.

Early identification of minor leaks can prevent potential rapid escalation to a major emergency. Routine mechanical inspection by qualified/certified inspectors is also necessary to identify potential leak locations, especially in pipework, and fixed equipment such as vessels. Leaks can result from external, as well as internal, corrosion of equipment, especially from under thermal insulation which gets wet, water or steam leaking onto equipment, or under paint blisters due to poorly applied or damaged paintwork.

Screwed connections are prone to leakage and have been the cause of numerous serious incidents. Screwed nipples can be affected by internal corrosion, potential stress corrosion cracking of the threads, and fatigue if there is local vibration. Each site should have a procedure for suitable monitoring of screwed connections for signs of potential leakage.

Depending on the process, leakage of HF is often accompanied by other entrained materials which can be extremely volatile, toxic, flammable, and explosive, such as hydrocarbons in oil refining processes. This also needs to be taken into account in determining emergency procedures. When a vessel or a pipe or any other component of a HF plant starts leaking, the most urgent task is to stop the leakage.

In the meantime, any other suitable action to mitigate the effects of an HF release must be carried out e.g. isolating/ shutting down the damaged section, deployment of water curtains, sprayed water and so on. as described above. Some larger facilities such as refineries with Alkylation Units where there is a large inventory of HF will usually have a Rapid Acid Transfer System (RATS) to quickly move HF out of process to safe storage.

The intervention required to stop the leak can range from relatively easy and quick actions (retighten a bolt, a flange or a packed gland)

to more difficult and hazardous actions (to transfer contents of a tank, to vent a system, and so on). A thorough and well-informed risk assessment should always be undertaken before such measures – for example tightening bolts can be extremely dangerous, as the HF attacks the bolt and may result in stress corrosion cracking failure. Clamps must be used to secure the joint before any repair is attempted, and bolt replacement is recommended—this applies equally to valve bonnet studs, gland studs, bolting of line flanges, pump casings, heat exchangers and so on. In a complex, well-designed and multi-structured unit where safety devices are available, the best operating procedure for leaks is:

- To isolate the leaking element from the rest of the unit (best through remote control devices); in the case of, for example, a leaking pipe this could be sufficient to stop the leakage in a short time.
- To evacuate the liquid content of the damaged system into another capacity (typically: an emergency blow-down tank): this makes the leak, if liquid, after a while change from liquid to gas phase.
- To reduce the process pressure, venting the gas phase into a dynamical washing system (see below) which efficiently absorbs the HF; ideally the pressure should be reduced only slightly below the atmospheric pressure to minimise the moisture inlet.
- Plugging a leak may be an option depending on the plant configuration and materials of construction – however it should be appreciated that for metal pipework systems a leak hole could rapidly become enlarged, and the leak situation made worse.

If the accident involves movable drums or tanks or if sophisticated emergency equipment is not available for example in small facilities or where the HF inventory is small, plugging the leak may be the only option. Whatever measures are taken, all materials used must be assessed for compatibility and effectiveness as part of the emergency planning process.

The activities mentioned above and in the following paragraphs should be carried out only under the supervision of specialist personnel; suitable protective clothing must be worn, and the proper tool kit and equipment must be provided. People undertaking activities to stem leaks should be specifically trained, and the training should be refreshed at least once per year.

F7.4.1 Containment of Leaks

Depending on the source of the leak, different actions can be carried out. Each proposed action is much easier to be carried out when the leak is in the gaseous phase, therefore, if possible, the evacuation of the vessel or pipework where the leak has originated is highly recommended. Containment of a leak means to enclose the leaking source such that it prevents HF from being dispersed.

Devices to collect a gaseous leak are:

- Gas-tight boxes
- Vented boxes. For systems operating at pressure, suitable containment devices capable of withstanding the internal process pressure/temperature must always be properly engineered and manufactured by a suitable leak sealing specialist company.
- When an engineered clamp/box has been installed, this is considered to be a temporary repair only, and the clamp/ box should be removed, and the leaking component repaired/replaced at the earliest opportunity. The suitability of the chosen device must be justified as part of the emergency planning risk assessment and depends on many factors such as the:
 - Shape of the source (pipes, valves, flanges, and so on.)
 - Size, dimension of leaking element
 - Residual releasing pressure
 - The quantity likely to be released
 - Nature of the leak (liquid, gaseous).

Use of containment may require that a vent abatement system and suitable means of connection be available, as the leaking HF must be continuously drawn out. Liquid/Gas- tight boxes must be designed for full line design pressure/ temperature that the equipment is likely to see. To improve the seal of any box (vented or gas-tight) soft material can be applied as a thin under-layer between the contacting surface (expanded PTFE, fluorinated rubbers, and so on.).

F7.4.2 Plugging Leaks

As discussed above, this may not be appropriate for leaks in metallic pipework systems. Pipelines and equipment can be internally corroded, and the walls can be extremely thin locally to the leak which could make effective plugging impossible. Again, a thorough risk assessment should be carried out.

Where plugging or taping a small leak is deemed to be a safe short-term option, special devices must be available. Suitable options may include:

- Pipe clips (metallic collar, enveloped in a rubber sleeve, suitable for small diameter pipes)
- Wrap-round straps with under-layers

- Bandages with under-layers
- Plastic plugs.

The wrap-round straps and the bandages have to be coupled with under-layers consisting of soft, HF resistant materials that are able to adhere to the surface and ensure a good seal. Suitable materials for under-layers are usually:

- Plasticized PVC
- Fluorinated elastomers (e.g.: Viton™, expanded PTFE)
- Natural rubber
- Lead (lead wool)
- Polyethylene wedges. Plugs can be made from:
 - PTFE
 - Fluorinated elastomers
 - Polyethylene
 - Wood or mastics (only to plug gaseous leaks)
 - Pastes and carbon or PTFE filled resins to be polymerized inside a sealing.

If the emergency response procedures considered before an event have indicated that leak plugging is an option, a suitable kit, in addition to the mechanical tool kit, should be readily available for the emergency response team. The composition of the kit includes the following:

- Inflatable cushions (example: Vetter type)
- Belts with belts idlers
- Inflation kit for cushions
- Air bottle or cylinder for inflation
- Wooden, PTFE polyethylene plugs of various diameters
- Absorbents (e.g. PAM)
- Polyethylene sheets
- Calcium carbonate
- pH paper
- Pot of mastic
- 1 pot of tar
- 1 lead plate
- 1m of soft PTFE
- 1m of PTFE cord
- 2 metallic strapping rolls (large size).

F7.5 Gaseous HF Absorption Systems

Absorption systems for HF-bearing vent gases are indispensable in plants in which HF is handled. Gaseous fluorides vented from storage systems or process must be conveyed to an absorption system to prevent atmospheric pollution. Hydrogen fluoride is readily soluble in water, so wet scrubbers are used afterwards.

The most commonly used HF removal systems are:

- Spray towers
- Venturi scrubbers
- Wet cyclones
- Impingement towers
- Packed beds/tray towers.

Different systems are often arranged in a double-stage absorption unit. Due to the need to ensure the low-pressure service to vent confined leaks, Venturi scrubbers are often preferred, normally followed by a second conventional system.

An absorption system is normally designed to handle gaseous and not liquid HF. Where it is used for the relief of liquid HF systems or when the gas and entrained liquid may not be excluded when venting a leaking source, it must be protected by a knock-out pot (equipped with a level alarm) where liquid HF can vaporise off at an acceptable rate before entering the scrubber or can be drained carefully. Care must be taken that no moisture from the absorber can flow back to the dry or liquid HF area.

It should be stressed that an HF absorption system should be always available even, and above all, under emergency situations. It is recommended that emergency power and water supplies are provided in case of a general power failure and that these are tested on a

regular basis. The scrubbing acidic solution is then neutralised, usually with slaked lime (CaOH_2) (often referred to as *milk of lime*) to remove the fluoride ion as insoluble calcium fluoride. Potassium hydroxide scrubbers or caustic soda are also used although water can be used effectively. If a dilute (5 to 10%) caustic medium is used for scrubbing, it may be treated with slaked lime (CaOH_2) to precipitate calcium fluoride.

Note: if NaOH is used, then do not exceed 5wt%, otherwise insoluble NaF will precipitate out and can cause plugging of equipment.

F7.6 Transfer of HF

For some accidents, the required course of action is to transfer the contents of a tank or vessel to a receipt tank prior to carrying out remedial action. As the transfer of the contents can be a difficult and hazardous operation, transfer procedures must be developed in advance and a dynamic risk assessment must be carried out before transfer takes place. The transfer must be made with great care and only when absolutely necessary (e.g. a major leak or severe mechanical damage makes movement of the tank or vessel impossible). Should the contents have to be transferred at the scene of the incident, suitable equipment will need to be available, e.g. pump, flexible hoses of sufficient length, connectors and a replacement container. The transfer process will depend on the nature of the container contents and can be carried out:

- By pump, if the liquid is an aqueous HF solution (<75%)
- By pressure, in case of anhydrous HF (ensure that maximum pressure is below 1 barg) once the leakage is stopped.

The materials of construction of the receipt vessel should be compatible with the HF to be transferred. The containers to be filled should be vented by a pipe connected to a water spray jet. If necessary, the ventilation pipe can be run into a polyethylene drum filled with water or any neutralisation agent, although in this case care should be taken to ensure that no water is sucked back up the pipe.

F8. Decontamination

All personal protective equipment after use on plant must be assumed to be contaminated with HF and treated with appropriate care. Care should also be exercised during the removal of all personal protective equipment. In particular, where others provide assistance, the risk assessment should have identified suitable personal protective equipment for the assistants.

Primary decontamination should take place immediately on leaving the area, for example, by use of a shower. Secondary systems to ensure complete decontamination by neutralisation should be available for use by the operating teams.

After decontamination, all personal protective equipment should be tested for integrity prior to being stored again within the HF facility and then routinely maintained by trained personnel in accordance with the manufacturer's recommendations. Defective equipment must be removed from use and disposed of through appropriate channels.

For further information reference should be made to **CIA HF Sector Network Guidance Section H on 'Decontamination'**.

F9. Remediation & Recovery

When the acute phase of an emergency has been completed, further actions to initiate remediation and recovery begin.

Operators should have procedures for recovery in place as part of their emergency planning activities. An HF release potentially will involve pollution of the air, soil and water courses including sewage treatment facilities.

Operators should consult with their:

- national environment agency - Environment Agency (EA, England), Natural Resources Wales (NRW, Wales) or Scottish Environment Protection Agency (SEPA, Scotland)
- utility companies and
- waste carriers and receivers as part of the recovery process.

F9.1 Soil Remediation

The spilled acid (diluted or not) as well as the sprayed water used to abate the HF clouds are likely to have soaked the soil. Tests must be carried out to determine how deeply the acid has penetrated into it. The easiest way is to use pH paper.

Neutralisation is best carried out with slaked lime (CaOH_2 , calcium hydroxide, or its saturated solution - milk of lime). Testing for the residual acid content in the various soil layers should be repeated several times after repeated neutralisation. If neutralisation has not been fully successful and/or agricultural areas have been affected, consideration must be given to excavating the soil to physically remove the contaminated layers. Excavation of the soil may also be necessary if the soil has ceased to produce an acid reaction but the calcium fluoride, CaF_2 , content is thought likely to cause difficulties later on. The excavated soil must be transferred to a suitable waste handling facility. Care should be taken in this operation to ensure that, after removal, any remaining acid is neutralised with slaked lime.

F9.2 Discharge of Liquid Wastes

Acid wastes should never be discharged to sewage treatment facilities or into water courses without previous neutralisation treatment because of the:

- Corrosive effects of fluorides in solution on collecting system: Wastes containing diluted HF or fluorides in solution may be extremely corrosive to ceramic materials and to ferrous metals,
- Adverse effects on biological treatment systems,
- Possible interaction with other industrial wastes to produce toxic gases such as hydrogen sulphide (H_2S) or hydrogen cyanide (HCN) or chlorine (Cl_2),
- Adverse effects on aquatic life.

Emergency lagoons can be useful to segregate the acidic waste and liquids to be neutralised before being sent to the final wastewater treatment unit. As mentioned earlier, neutralisation is a highly exothermic reaction so that cooling or strong dilution is often necessary to dissipate the heat.

Small quantities of waste acid may be added slowly to a larger volume of agitated solution of soda ash (sodium carbonate, Na_2CO_3) or slaked lime. This neutralised solution is then added to excess running water prior to final disposal.

Most regulatory agencies require the pH of the effluent to be in the range of 6 to 9 and the fluorides concentration to be down to few parts per million (ppm). Care must be exercised in the disposal of all neutralised wastes containing soluble fluorides to ensure that any environmental permit and other requirements for discharge into water courses are not breached.

Usually, targets are easily achieved by neutralising hydrofluoric acid wastes with lime, which precipitates the fluoride ion as insoluble calcium fluoride.

Limestone is not normally used because the calcium fluoride precipitate coats its surface, reducing its effectiveness even if finely dispersed and thus increasing the treatment and waste- solids disposal costs. Some other neutralising agents, such as waste alkali streams, dolomite, caustic potash, caustic soda and soda ash have also been used successfully; however, the preferred neutralising agent remains lime, since soda ash or caustic produce sodium fluoride which is highly soluble and toxic to animals and some aquatic organisms.

Appendix

Equipment concerned	Nature of incident	Probable cause of incident	Typical equivalent hole size	Emergency procedures
1. Valves	1.1 Leak from a packed gland and/or bellow	Inadequate tightening. Packing has become oval. Deformation of spindle and so on.	Limited by the construction. Accepted as being equivalent to the leakage on a gasket from a tongue and groove flange (see below).	Re-tighten if safe to do so; clamps are likely to be necessary as temporary repair. Open valve fully to use the back-seating arrangement. A leaking bellows will require a valve replacement. If venting down is possible: Repack the gland. Change the valve bonnet. If venting down is not possible: Use suitable containment methods Call for specialist support.
	1.2 Gasket leak	Defect in the gasket or the flange face of the body or bonnet joint, or on the inlet and outlet flanges. Human factors e.g. poor fitting, misalignment, dirty faces, loose bolts.	For flat faced flanges the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50mm ² . On a tongue and groove flange assume a failure of the gasket over a width of 1mm with bearing in mind the engineering tolerances of the tongue and groove flange.	Carefully re-tighten the joint if safe to do so; clamps are likely to be necessary as temporary repair. Use suitable containment methods. Call for specialist support.
	1.3 Leakage from a bolted flange	Defect in joint or the flange face. Human factors e.g. poor fitting, misalignment, dirty faces, loose bolts.	For flat faced flanges the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50mm ² . On a tongue and groove flange assume a failure of the gasket over a width of 1mm with bearing in mind the engineering tolerances of the tongue and groove flange.	Re-tighten if safe to do so; clamps are likely to be necessary as temporary repair. Use suitable containment methods. Call for specialist resource.
	1.4 Porosity in the valve body or bonnet	Concerns particularly a cast valve: foundry defect.	Assume a hole size of 1.0mm diameter.	The valve must be removed and replaced

Equipment concerned	Nature of incident	Probable cause of incident	Typical equivalent hole size	Emergency procedures
2. Piping	2.1 Leakage from a bolted flange	Defect of the gasket or the flange faces. Human factors e.g. poor fitting, misalignment, dirty faces, loose bolts.	For flat faced flanges the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50mm ² . On a tongue and groove flange assume a failure of the gasket over a width of 1mm with bearing in mind the engineering tolerances of the tongue and groove flange.	Re-tighten if safe to do so; clamps are likely to be necessary as temporary repair. Use suitable containment methods. Call for specialist support.
	2.2 A hole in the pipework wall	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion.	This could be equivalent to a hole size of 2mm diameter possibly increasing to 3mm by erosion/corrosion.	Pipe replacement is required.
	2.3 A leakage on a connection by failure of the flange or rupture of the pipe work.	Expansion of liquid trapped between two closed valves. Human factors e.g. poor fitting, misalignment, dirty faces, loose bolts.	Depends on the overall arrangement of flange gasket and bolting. If deformation of the flange is not possible and there is rupture of the pipe work, assess on the basis of effective instantaneous loss of contents, except for piping of increased lengths for which a study needs to be done of the time taken to vent down and lose all of the contents.	Isolate the section of pipe work. Leakage of this type requires full de-pressurisation to effect a permanent repair.
	2.4 Rupture due to lack of flexibility.	Defect at the design stage or e.g. installation of supports or additional anchor points during maintenance operations.	Full pipe diameter. (Take into account in the calculation the loss of liquid from the two sections of pipe).	Isolate the defective section. Take out of service—then review design, or redesign as appropriate.
	2.5 Rupture due to external impact.	Impact by a crane or some other maintenance equipment or vehicle.	50% of the cross section. Full pipe diameter (Taking into account both ends of the fractured pipe).	Isolate the defective section. Take out of service—then review design, or redesign as appropriate.
	2.6 Piping failure at a hot point on liquid line	Excessive external heat, exit of a compressor, internal reaction, and so on.	Leakage equivalent to full pipe diameter (taking into account both ends).	Isolate, and depressurise the fault section, in particular from any storage system. Take out of service—then review design, or redesign as appropriate.

Equipment concerned	Nature of incident	Probable cause of incident	Typical equivalent hole size	Emergency procedures
	2.7 Damage to instrument connection	External impact	Diameter of the connection	Isolate, and depressurise the fault section, in particular from any storage system.

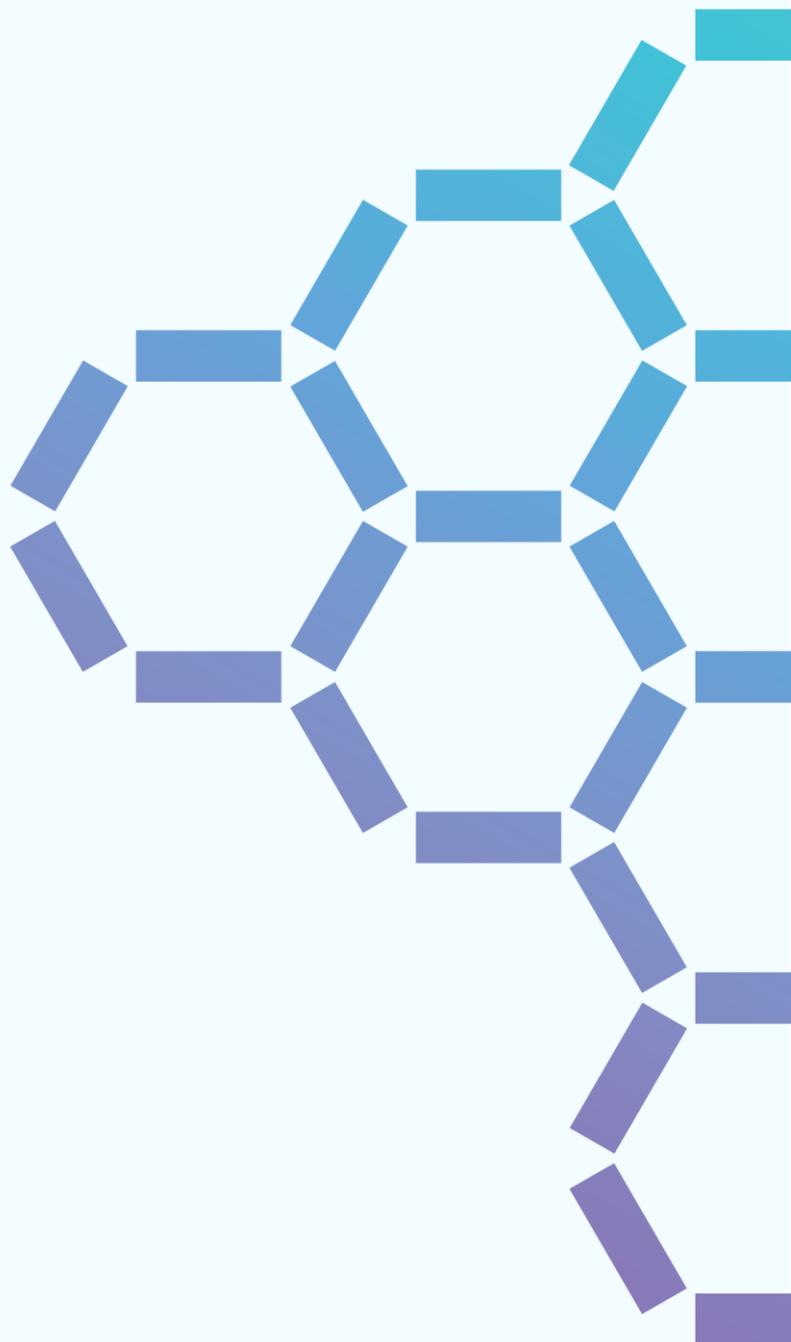
3. Storage vessels (and on-site transport containers)

In general, when a leak occurs in a vessel or structural element of a vessel, transfer of any liquid should be carried out as quickly as possible in order to minimise the amount of HF released. After transfer, depending on the scenario, proceed as follows:

	3.1 Leakage at the gasket on the flanges of the branches.	Defect in the gasket or on the flange face. Human factors e.g. poor fitting, misalignment, dirty faces, loose bolts.	For flat faced flanges the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50mm ² . On a tongue and groove flange assume a failure of the gasket over a width of 1mm with bearing in mind the engineering tolerances of the tongue and groove flange.	Re-tighten if safe to do so; clamps are likely to be necessary as temporary repair. Use suitable method of containment. Call for specialist support.
	3.2 Failure of a branch.	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion.	For the design case assume a hole size equivalent to 2mm diameter possibly increasing to 3mm with corrosion/erosion effects.	Isolate, and depressurise, then renew section. Take out of service—then review design, or redesign as appropriate.
	3.3 A hole in the vessel wall	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion.	For the design case assume a hole size equivalent to 2mm diameter possibly increasing to 3mm with corrosion/erosion effects.	Transfer the contents as rapidly as possible and lower the pressure. Make a fully engineered repair. Take out of service—then review design, or redesign as appropriate.
	3.4 Vessel failure due to reaction with water.	Contamination with water.	To be studied case by case.	Transfer and isolate the vessel as rapidly as possible. Full inspection required to determine appropriate repair.

4. Transfer Equipment	4.1 Leakage on a joint or a bolted flange.	Defect in the joint or the flange face. Human factors e.g. poor fitting, misalignment, dirty faces, loose bolts.	For flat faced flanges the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50mm ² . On a tongue and groove flange assume a failure of the gasket over a width of 1mm with bearing in mind the engineering tolerances of the tongue and groove flange.	Stop the HF transfer. Depressurise and drain.
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Equipment concerned	Nature of incident	Probable cause of incident	Typical equivalent hole size	Emergency procedures
	4.2 Leakage in the pipe wall	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion.	Assume a hole size equivalent to 2mm diameter possibly increasing to 3mm by erosion/corrosion.	<p>Isolate the section of defective equipment or piping which is providing the means of transfer.</p> <p>Vent down the transfer equipment to an absorption system.</p> <p>Purge with nitrogen or dry air.</p>
	4.3 Rupture	Due to abnormal stress or movement of the transport container.	Full pipe diameter.	Isolate as rapidly as possible.
5. Rotating Machinery	5.1. Leakage at the gland on the pump rotor, casing flange, small bore connections.	Deterioration in the sealing arrangement or loss of fluid in the seal.	To be studied case by case	<p>Stop the machine and isolate. Depressurise and drain.</p> <p>Take out of service—then review design, or redesign of seal or seal medium as appropriate.</p>
	5.2 Leakage in the pipe wall	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion.	Assume a hole size equivalent to 2mm diameter possibly increasing to 3mm by erosion/corrosion.	<p>Isolate the section of defective equipment or piping which is providing the means of transfer.</p> <p>Vent down the transfer equipment to an absorption system.</p> <p>Purge with nitrogen or dry air.</p>



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