Comité Technique Européen du Fluor (CTEF)

Working Group on Storage, Transport and Safety (STS)

Group 6

RECOMMENDATION ON EMERGENCY RESPONSE (ON SITE) FOR HANDLING OF ANHYDROUS HYDROGEN FLUORIDE (AHF) AND HYDROFLUORIC ACID SOLUTIONS (HF)

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PREFACE

Anhydrous hydrogen fluoride/ hydrofluoric acid (AHF/HF) is essential in the chemical industry and there is a need for HF to be produced, transported, stored and used.

The AHF/HF industry has a very good safety record; nevertheless, the European AHF/HF producers, acting within Eurofluor (previously CTEF) have drawn up this document to promote continuous improvement in the standards of safety associated with AHF/HF handling.

This Recommendation is based on the various measures taken by member companies of Eurofluor.

Each company, based on its individual decision-making process, may decide to apply the present recommendation partly or in full.

It is in no way intended to be a substitute for various national or international regulations, which must be respected in an integral manner.

It results from the understanding and many years of experience of AHF/HF producers in their respective countries at the date of issue of this particular document.

Established in good faith, this recommendation should not be used as a standard or a comprehensive specification, but rather as a guide, which should, in each particular case, be adapted and utilised in consultation with an AHF/HF manufacturer, supplier or user, or other expert in the field.

It has been assumed in the preparation of this publication that the user will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance it has been prepared.

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The contents of this recommendation are based on the most authoritative information available at the time of writing and on good engineering practice, but it is essential to take account of appropriate subsequent technical developments or legislative changes. It is the intent of Eurofluor that this guideline be periodically reviewed and updated to reflect developments in industry practices and evolution of technology. Users of this guideline are urged to use the most recent edition of it, and to consult with an AHF/HF manufacturer before implementing it in detail.

This edition of the document has been drawn up by the Working Group on "Storage, Transport and Safety" to whom all suggestions concerning possible revision should be addressed via the offices of Eurofluor. It must not be reproduced in whole or in part without the authorisation of Eurofluor or member companies.

AHF is an acronym for anhydrous hydrogen fluoride.

HF is an acronym for hydrofluoric acid solutions of any concentration below 100%.

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INTRODUCTION

This guideline has been developed by the Storage, Transport and Safety Group of the Comité Technique Européen du Fluor (CTEF) now named Eurofluor. It is intended to offer recommendations on emergency response (on-site) for handling of anhydrous hydrogen fluoride or hydrofluoric acid solutions at ambient temperatures (from -10°C to +50°C), unless stated otherwise.

All materials of construction, which are mentioned in this document should be double-checked and there should be a search for more information on materials, in our "Recommendation on materials of construction for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions" available from Eurofluor publication webpage www.eurofluor.org.

1 Definition of an AHF/HF emergency

An AHF/HF emergency at a site concerns an actual or possible release of AHF/HF as liquid and/or gas, which may endanger environment and/or people inside and outside the works boundary.

Emergencies at an industrial site can be originated by leakages or spillages from:

- railway tanks or tankers during operations in loading/unloading stations;
- transfer equipment (e.g. flexible hoses in loading/unloading stations);
- process storages;
- process apparatuses (columns, reactors, oven, etc);
- valves and process piping.

For these specific situations actions must be taken in order to:

- minimize the probability of an AHF/HF release;
- monitor effectively the environmental conditions, to ensure a quick detection of AHF/HF presence;
- ensure safe, efficient and effective behaviour on behalf of the people present at the site;
- minimize the AHF/HF release by applying right, effective and well tested operative counter-measures;
- minimize the AHF/HF release environmental impact during and after the incident.

Whereas the first and the second topics are typical of a good engineering phase and maintenance reliable practices, requiring proper design of the whole plant and periodical checks to keep at the top the necessary safety standards, the other parts must be carefully planned being the core of the emergency response in the event of a major accident.

2 Prediction of emergency situations

Careful consideration should be given to what major emergencies such as tank or line breakage, overpressure etc. can be reasonably foreseen in the production units, the storage and during transport on the location.

Also emergencies which can lead indirectly to an AHF/HF release, such as power failure, utilities failure, fire or explosion in neighbouring plants (domino effect), etc., should be taken into consideration.

Failure modes and chains of events that can lead to an AHF/HF emergency can be identified and properly highlighted through HAZOP analysis sessions, a powerful method of prevention when carried on with open-minded attitude and deep faith by really experienced and well committed people.

3 Emergency plan

For predicted potential emergencies, Emergency plans and procedures should be set:

- to prevent a potential AHF/HF release;
- to stop as fast as possible AHF/HF release (shut down procedures included);
- to mitigate the effects of an AHF/HF release, during and after the event itself.

An incident that occurs inside the boundary of a site can be normally dealt with by an internal Emergency Team, made of an adequate number of experienced and trained people and provided with adequate fighting and protective means. Main aim of an Internal Emergency Team is to minimize the danger both for the inside workers and for the surroundings.

Depending on the potential magnitude of the incident, the Emergency Team Responsible defines if information should also be given to the external emergency services (fire brigade, health services, police, etc.) and their intervention required.

External assistance must be requested whenever an AHF/HF emergency cannot be safely and effectively managed only by internal forces.

The Eurofluor (CTEF) members have set up an organization to take account of any accident in which AHF/HF is involved. Members of this organization have an emergency team and equipment available for going out to the scene of an accident. Personnel are specifically trained in dealing with such emergencies and are available at the request of local authorities within their zone of operation.

To take full benefit of this aid scheme, it is necessary that all responsible Authorities (police, fire brigade, civil protection...) continue to be aware of the organization of these emergency plans in order to be able to call for their application as soon as an accident or incident involving AHF/HF occurs.

The Emergency Plan should define at least:

- the most likely scenarios and how to deal with them;
- procedures for the evacuation of the works personnel not involved in the emergency management;
- the composition of the Emergency Team: members, responsible;
- tasks of the members of the Emergency Team;
- conditions to require external assistance;
- intervention equipment, composition and location;
- emergency phone numbers to be called

3.1 The most likely scenarios and how to deal with them

A list of the most likely scenarios should be prepared.

- For each scenario, the actions to be immediately taken in the unit to stop or to minimize the AHF/HF release.
- relate to plant specific instructions, e.g., to shut off a reactor or to blow down a tank or to insulate a leaking vessel.

An example of list of actions, sorted per kind of leak, is given in Appendix a-09-xy. Such list cannot be exhaustive of all possible events, thus a periodical training in plant emergency stop procedures remains mandatory.

3.2 Evacuation of works personnel and visitors

After the alarm has been activated, the visitors and the personnel of the plant not involved in the Emergency Team should leave immediately the work place. Escape ways and emergency exits must be kept free, marked and well illuminated, even in cases of power failure.

When visitors enter the industrial site, a training module should be attended so that they get informed about the safety rules and the emergency procedures in force. A map detailing the assembly point location should be made available too.

After evacuation the personnel should go directly to the assembly point located upwind or to the designated room and stay waiting for further instructions. An appropriate number of windsleeves should be installed in high positions so to be well seen from far.

Updated additional information about the event in progress should then be given as quickly as possible, e.g. through a loudspeakers network, also in order to suggest the best assembling point and further behaviours to be adopted whether the situation is evolving in unexpected ways.

3.3 The composition of the Emergency Team

The Emergency Team is composed at least of

- Shift Foreman;
- Control Room Operator.

Other members, if available in the site, can be:

- Plant external operator;
- Operator(s) from other plants, trained as internal fire-fighting and/or emergency service member(s).

The Emergency Plan should also define who is the Emergency Team Responsible.

3.4 Conditions to call for external assistance

External assistance must be always called for under the following conditions:

- heavy AHF/HF injuries to one or more workers;

- threats for the population due to AHF/HF clouds coming out from the site boundaries;
- threats for the environment;
- internal resources unable to face effectively the incident.

External authorities activate the External Emergency Plan for the population.

EMERGENCY RESPONSE ON SITE

The Emergency Team, when entering the incident scene, must be provided with Personal Protection Equipment and with the Emergency Tool Kit needed to promptly operate on the leak.

4 Emergency equipment

Apart from the general emergency equipment, specific AHF/HF emergency equipment shall be provided at suitable, well known and well indicated points, e.g.:

- areas where significant escapes could occur;
- assembly points;
- residence of the Emergency Team;
- works medical centre.

The Emergency Equipment should include the following:

- water showers with eye-washer or baths, preferably heated;
- hoods with air-line breathing sets;
- full protective suits with airline;
- self-contained breathing apparatus;
- other protective clothing;
- emergency tool kits;
- first aid kits;
- special medical AHF/HF kits (see First Aid Brochure on www.eurofluor.org);
- portable communication equipment.

Emergency equipment should be checked on a regular basis.

4.1 Personal protective equipment

Four potential 'Levels' of personal protective equipment (PPE) have been identified for use on AHF/HF handling facilities.

The Risk Assessment will clearly identify the PPE required for each task:

- Level Alpha (α): Emergency Response
- Level Beta (β): Operational Equipment for Increased Risk Activities
- Level Gamma (γ): Routine Operational Equipment
- Level Delta (δ): Standard on-plant Equipment

When an emergency is in progress, levels Alpha PPE will be adopted to operate under AHF/HF contacting risk.

For further information regarding the PPE, see Eurofluor "Recommendation on safety management for handling of Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions" available from Eurofluor publication webpage www.eurofluor.org.

4.2 PPE decontamination

All personal protective equipment after use on plant must be assumed to be contaminated with AHF/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.

Where protective equipment is not issued to individuals as equipment for their personal use, care must be taken to ensure that hygiene issues are adequately addressed (biological risks).

After decontamination, all personal protective equipment should be tested for integrity prior to be stored again within the AHF/HF facility and then routinely maintained by trained personnel in accordance with the manufacturers recommendations.

Defective material must be wasted and untested equipment must not be used within the AHF/HF facility.

5 Mitigation

If a liquid AHF/HF-above 60% leak occurs, a two-phase flow will happen. Below 60% HF, only liquid spillage will occur.

Three contributions to the overall emission must be usually taken into account:

- First gaseous emission (potential flash contribution);
- Aerosol emission;
- Evaporation from pool.

Flash contribution

Part of the emission is in gaseous phase, due to the change of the AHF/HF temperature and pressure conditions: the higher the source temperature and pressure are, the higher the gas fraction generated through the so-called “thermodynamic flash” is.

Aerosols

Under high pressure drop, that means high emission velocity and mechanical stress on the liquid, aerosol formation is unavoidable: this contribution can be very important to increase the cloud dimension as the fine liquid drips tend to evaporate quickly due to the high exposed surface.

Evaporation from pool

The residual liquid part of the leakage, that has not evaporated during flash, falls on the ground, where it forms a pool which evaporates; the mass evaporation rates strongly depend on liquid and soil temperatures, wind velocity, but mainly on the kind of substrate and on the exposed surface area of the pool, which have to be reduced by any suitable mean.

The three terms always contribute to the cloud formation, even if with different weights according to the actual conditions of the leakage source.

The foggy look of the AHF/HF clouds is due to the gaseous AHF/HF reacting with atmospheric moisture.

5.1 Treatment of clouds

The hydrogen fluoride vapour cloud will spread according to the wind conditions and other local factors (buildings, plant structures, hills, etc.).

The cloud must be abated before it becomes a real danger for the inside workers, the outside community and the environment.

If installed in the area where the leakage has originated, powerful water curtains are remarkably effective to contain the clouds.

The residual fog then can be destroyed by spraying fine divided water from hydrants or/and from fire trucks.

Sprayed water should be directed from a point upwind of the leakage.

The downwind areas shall be cleared of people.

Although the molecular weight of gas phase is less than the air, be aware that it will not always rise and may remain at ground level.

The water must not be sprayed onto the leak source but only onto the cloud, to avoid increasing both the leak source equivalent size (by corrosion) and the gaseous emission due to heat of dilution (see following paragraph).

5.2 Treatment of spillages

When AHF/HF is spilled, it largely remains as liquid but at the same time a large volume of dense acidic fume tends to be released, as said before.

As fast as possible the AHF/HF pool evaporation must be stopped or at least reduced by any suitable mean.

Actions can be taken in order to:

- Reduce the AHF/HF concentration in the pool and therefore its vapour pressure: this strongly reduces driving force to the evaporation mass flow rate;
- Reduce the surface of the pool: evaporation mass flow rate is proportional to the air-exposed pool surface;
- Create a sort of barrier or screen to entrap the vapour leaving from the pool.

5.2.1 Use of water

When water is added to effect dilution or alkali is used to effect neutralisation, vigorously exothermic reactions take place. The resulting strong heat generation promotes further evaporation, if the dilution is not sufficient.

From these actions, if not properly carried out, a greatly increased vapour cloud will result, so the use of water must then take high care of this fact to prevent fumes formation.

5.2.1.1 Small pools of liquid hydrogen fluoride

Water can be added only when it can be applied at a rate very much higher than the leakage rate so that it will very rapidly dilute the AHF/HF and suppress most of the vapour released.

To make negligible the thermal effect coming from the dilution heat emission, the liquid AHF/HF must be rapidly diluted to a concentration less than 2% by weight by huge amount of water. Diluted HF solutions have also a very low vapour pressure.

Water should be directed from a point upwind of the leakage and the downwind area shall be cleared of people before action is taken.

5.2.1.2 Large pools of liquid hydrogen fluoride

Under these circumstances water should not be applied at once but the spillage should be contained as far as possible.

Retention walls and underground pools should be highly recommended just in order to convey the spillage and to reduce the evaporation surface.

If such systems have not been installed in plant operating areas, temporary bunds with earth, solid absorbents, limestone or other suitable material (attention, some material could be reactive with AHF/HF) may be arranged; only when the spillage can be run off at a controlled rate, dilution water may start to be fed to that stream, according to the prescriptions given above.

Please see as well AHF/HF Neutralization Table in appendix B.

5.2.2 Pool evaporation reduction: use of solid absorbents

Liquid AHF/HF can also be efficiently removed through absorption by solid absorbents like polyacrylamide (PAM) and others which are suitable.

The pool must be completely covered with the absorbent.

This treatment is easier for a limited surface within permanent or temporary bunds.

The absorption end products are differently treated according to their nature and physical form.

For instance, PAM gives as a final product a gel which can be treated with water or soda ash solutions. Any untreated polyacrylamide which comes into contact with water will give rise to a slipping hazard.

5.2.3 Pool evaporation reduction: use of foams

Not to be used.

Water based protein foams <u>are not effective</u> to hinder AHF/HF evaporation.

Their application is in fact equivalent to the addition of water at a low rate: much hydrogen fluoride vapour evolves and it rapidly breaks down the foam layer.

5.2.4 Pool evaporation reduction: use of mineral oil and PE sheets

If the spillages of AHF/HF are bunded, the emission of clouds can be reduced by covering the pool with cold mineral oil (oil thickness must be greater than 20 centimetres): this ensures higher thermal inertia and reduces the exposed evaporation surface.

Starting from the principle to reduce the exposed surface, evaporation from AHF/HF pools can also be depressed by covering the pool with polyethylene sheets.

Polyethylene balls are not recommended because they increase the evaporation surface due to rotation of the balls.

6 Leak confinement and plugging

6.1 General

When a vessel or a pipe or any other component of a AHF/HF treating plant starts leaking, the most urgent task is to stop the leakage.

Meanwhile, any suitable action to mitigate the effects of an AHF/HF release must be carried out (water curtains, sprayed water and so on, see chapter *5 Mitigation*).

The intervention required to stop the leak can range from easy and quick actions (retighten a bolt, a flange or a packed gland) to very difficult and dangerous actions (to transfer a tank, to vent a system, etc.).

In a complex, well designed and multi-structured unit where safety devices are available, the best operating procedure is:

- To insulate the leaking element from the rest of the unit (best through remote control devices); in case of, e.g., 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 AHF/HF; ideally the pressure should be reduced only slightly below the atmospheric pressure to minimise the moisture inlet;
- immediately plug the leak with suitable means.

Unfortunately the accident may involve also movable drums, movable tanks and railway tanks outside the unit boundary and, moreover, such a complex emergency apparatus, as described before, may not be available in small facilities or where AHF/HF is of marginal use.

So the immediate plugging of the leak becomes mandatory.

The activities mentioned in the following should be carried out only under the supervision of specialist personnel; suitable protective clothing must be worn and the proper tool kit must be provided.

People likely to be in charge with these activities in event of leak should be specifically trained, and the training should be refreshed at least once per year, in each part of the emergency intervention.

6.2 Evaluation of the transfer

In these events, it must be decided whether the content must be transferred or not before plugging the leak.

As the transfer of the contents is a difficult and hazardous operation which must be made with great care and only when absolutely necessary (major leak, severe mechanical damages making further operations difficult)

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 transport container.

The transfer process will depend on the nature of the container contents and can be carried out for instance:

- 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 replacement container should be chosen according to the following criteria:

- made of steel or stainless steel, for anhydrous HF and aqueous HF solutions more than 70%;
- rubber coated or polyethylene containers with a wall thickness of at least 6 mm, for HF solutions less than 70%;
- best if the replacement container is devoted to the transport of AHF/HF.

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 neutralization agent, although in this case care should be taken to ensure that no water is sucked back up the pipe.

6.3 Confinement of leaks

Depending on the kind of leak source, different actions can be carried out.

Obviously each proposed action is much easier to be carried out when the leak is in gas phase: therefore the evacuation of the capacity where the leak has originated, if possible, is highly recommendable.

Confinement of a leak means to enclose the leaking source in a suitable capacity that avoids the AHF/HF to be dispersed.

Suitable devices to collect a gaseous leak are:

- gas-tight boxes;
- vented boxes.

The choice of the best solution depends on many factors:

- shape of the source (pipes, valves, flanges, etc);
- size, dimension of leaking element;
- residual releasing pressure;
- nature of the leak (liquid, gaseous).

Vented boxes require that a vent abatement system is available, as the leaking AHF/HF must be continuously drawn out to avoid pressure built up that could even make them to burst.

These leak confining devices should then be connected to the vent abatement system by suitable hoses (PTFE lined hoses, e.g.): a venting service network strategically distributed in the plant is thus highly recommendable in order to ensure ease of connection and intervention.

Also small liquid fractions can be treated through this system but then a liquid trap must be installed on the vent line before the stream enters the scrubber.

Gas-tight boxes can tolerate moderate pressure.

To improve the seal of the box (vented of gas-tight) soft material can be applied as a thin under-layer between the contacting surfaces (expanded PTFE, fluorinated rubbers, etc.)

6.4 Plugging of leaks

Apart from the easiest cases where to re-tighten a bolt succeeds into remove the leak, special devices must be available to effectively put a stop to the leak.

Plugging a leak may be an option depending on the plant configuration and materials of construction. However, it should be appreciated that for metal pipe work systems, a leak hole could rapidly become enlarged and the leak situation made worse.

Pipelines and equipment can be internally corroded and the walls can be extremely thin locally to the leak which could make effective plug in impossible. 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 (they have to adhere to the external surface as well as possible) and AHF/HF resistant materials, able to ensure a good sealing.

Suitable materials for under-layers are usually:

- fluorinated elastomers (e.g.: Viton™, expanded PTFE);
- natural rubber;
- lead (lead wool);
- polyethylene wedges.
- plasticized PVC;

Plugs can be made by:

- 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 box built around the leaking element.

6.5 Kit to plug leaks

A Leakage Plugging Kit, in addition to the mechanical tool kit, should be made always readily available for the Emergency Team.

The composition of the kit is the following:

- inflatable cushions
- belts with belts idlers
- inflation kit for cushions
- air bottle or cylinder for inflation
- wooden, PTFE polyethylene plugs of various diameters
- Absorbents (PAM, e.g.)
- polyethylene sheets
- calcium carbonate
- pH paper
- pot of mastic
- 1 pot of tar
- 1 lead plate
- 1 m of soft PTFE
- 1 m of PTFE cord,
- 2 metallic strapping rolls (large size)

After the use the content must be restored.

What can be recovered must be accurately decontaminated through neutralization to remove any trace of AHF/HF.

6.6 Intervention procedures

A list of possible leakage and of the most proper ways to deal with them is given in the following. Consider calling a specialist.

6.6.1 Valves

A) Leak from a packed gland and/or a bellow

- Re-tighten
- Open the valve fully to use the back-seating arrangement.

If venting down is possible:

- Repack the packed gland;
- Change the valve bonnet.

If venting down is not possible rapidly:

- Apply a suitable device.

B) Leakage on a bolted flange

- Carefully re-tighten the joint;
- Apply a gas-tight box or
- Apply a vented box;

C) Porosity in the valve body or bonnet

- Drive in a plug
- Cast in cement
- Apply a self-tapping screw

6.6.2 Piping

A) Leakage from a bolted flange

- Tighten the joint with care
- Apply a gas-tight box or
- Apply a vented box;

B) A hole in the pipe work wall

Isolate the section of pipe work and then:

- Install a pipe clip,
- Apply graphite cement or
- Apply a sealed box or
- Apply self-tapping screw or use plug driven in

C) A leakage on a connection by failure of the flange or rupture of the pipe work

- Isolate the section of pipe work.
- Re-tighten the flanges with care.
- Apply a sealed box.

D) Rupture due to lack of flexibility or external impact

- Attempt at all costs to isolate the defective section.

- Trap the leakage between two clamps or collars.

E) Piping failure at a hot point on liquid line

- Attempt to isolate the fault section, in particular from the storage.

G) Damage to instrument connection

- It can be dealt with as in point D.

6.6.3 Storage Vessels and on-site transport containers.

In general, when a leakage involves a vessel or a structural element of it, the transfer of the liquid must be carried out as rapidly as possible in order to minimise to amount of AHF/HF released.

After transfer (see 7.2) operate as follows.

A) Leakage at the gasket on the flanges of the branches

- Tighten the joint with care.
- Apply a sealed box.
- Apply a vented box.

B) Failure of a branch.

- Pipe clip.

C) A hole in the vessel wall.

- Lower the pressure.
- Clamp the leakage with the use of a screwed clamp of shaped pad.

D) Vessel failure due to reaction with water.

- Isolate the vessel as rapidly as possible.
- Then use a conical wedge.

6.6.4 Transfer Equipment

A) Leakage on a joint or a bolted flange or a pipe wall.

- Stop the AHF/HF transfer.
- Depressurise and drain.
- Isolate the section of defective equipment or piping which is providing the means of transfer.
- Vent down the transfer equipment to an absorption system.
- Purge with nitrogen or dry air.

B) Rupture

- Isolate as rapidly as possible

6.6.5 Rotating Machinery

A) Leakage at the gland on the pump rotor

- Stop the machine and isolate.
- Depressurise and drain

7 Remediation

When the most critical phases of an emergency have been overcome, further actions may start, being aimed to minimize potential additional damages to the environment and heal the actual ones.

An AHF/HF release potentially involve, apart from the air pollution:

- Soil
- Sewage

7.1 Soil remediation

The spilled acid as well as the sprayed water used to abate the 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.

Neutralization

Neutralization is best carried out with milk of lime.

Testing for the residual acid content in the various soil layers should be repeated several times after repeated neutralization.

Excavation

If neutralization 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.

The excavated soil must be conferred and deposited at an approved dump.

Care should be taken in this operation to ensure that, after removal, any remaining acid is neutralized with slaked lime (calcium hydroxide).

7.2 Sewage

Acid wastes should never be discharged to sewage treatment facilities without previous neutralization treatment because of:

- 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 H_2S or HCN or chlorine.

Emergency basins can be useful to and segregate the acidic waste liquids to be neutralized before being sent to the final waste water treatment unit.

As already said neutralization 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 or slaked lime.

This neutralized solution is then added to excess running water prior to final disposal.

Environmental constraints

Most regulatory agencies require the pH of the effluent to be in the range of 6 to 9 and the fluorides concentration to be of few ppm.

So care must be exercised in the disposal of all neutralized wastes containing soluble fluorides to ensure that local and National requirements for discharge into water courses are met.

Usually both targets are easily achieved neutralizing 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 neutralizing agents, such as waste alkali streams, dolomite caustic potash, caustic soda and soda ash, have also been successfully used, even if the preferred neutralizing agent remains lime since soda ash or caustic produce sodium fluoride which is highly soluble and toxic to animals and some aquatic organisms.

8 Absorbents

8.1 Absorbents for liquid AHF/HF

During the emergency and in the following remediation steps, the need to remove liquid HF from the ground or to inhibit its evaporation often arises.

The aim may be achieved spreading on the pool suitable materials that work capturing the free HF and catching it through chemical or physical interactions.

The best material for liquid AHF/HF absorption is:

Polyacrylamide powders (PAM)

- it must be added in the ratio of 1 part of powder to 2 parts of AHF/HF;
- it forms, after absorption, a gel that can cause slipping hazards;

Sawdust is not recommended as it is hydrophilic and then likely to be quite wet: when dispersed on an AHF/HF pool it provides a kind of poor dilution that can result in a strong mass temperature rising even leading to auto-ignition phenomena.

Disposal

After application, the residual solid or gelatinous waste must be neutralized, best using slaked lime (see REMEDIATION) that gives insoluble calcium fluoride.

Neutralization must be carried out very cautiously and slowly: because of the exothermal reactions, the mass temperature tends to increase and clouds may originate again.

The neutralizing agent addition must go on until pH is 6-9 (tested by pH paper).

The neutralized solid mass must be finally disposed in specialised landfills.

8.2 Gaseous AHF/HF absorption systems

Absorption systems for AHF/HF bearing vent gases are indispensable in plants in which AHF/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.

Most commonly used AHF/HF removal systems are:

- spray towers,
- Venturi scrubbers,
- wet cyclones,
- impingement towers,
- packed beds.

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 AHF/HF. Where it is used for relief's of liquid AHF/HF systems or when the presence of gas-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 AHF/HF can vaporize off at an acceptable rate before entering the scrubber or can be drained carefully.

On the other hand, care must be taken that no moisture from the absorber can flow back to the dry or liquid AHF/HF area.

Utilities failure

What should be however stressed is that an AHF/HF absorption system should be always available even, and above all, under emergency situations.

It becomes therefore highly recommendable that emergency power and water supplies are provided in case of general power failure.

Disposal of the scrubbing solution

The scrubbing acidic solution is then neutralized, usually with 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 milk of lime to precipitate calcium fluoride.

For deeper technical information on the design, see Eurofluor “Recommendation on storage, loading and unloading of Anhydrous Hydrogen Fluoride” available from Eurofluor publication webpage www.eurofluor.org.

APPENDICES

APPENDIX A: ACCIDENT SITUATIONS IN AHF/HF PRODUCING OR CONSUMING FACTORIES: CORRECTIVE MEASURES

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 a bellow	▪ Inadequate tightening ▪ packing has become oval ▪ deformation of spindle etc.	Limited by the construction. Accepted as being equivalent to the leakage on a gasket from a tongue and groove flange (cf. 1.2)	▪ Re-tighten where it is safe to do so ▪ Open the valve fully to use the back-seating arrangement ▪ If venting down is possible: ○ Repack the packed gland ○ Change the valve bonnet

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
	1.2 Gasket leak Leakage on a bolted flange	Defect in the gasket or the flange face of the body or bonnet joint, or on the inlet and outlet flanges	For flat faced flanges, the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50 mm^2. On a tongue and groove flange, one should take in consideration a crack of the gasket leading to an average of 1 mm gap depending on the tolerance of the tongue and groove flange. For instance, gasket thickness of 2 mm will lead to a leak of $2mm^2$.	▪ Carefully re-tighten the joint where safe to do so ▪ Gas tight box ▪ Vented box
	1.3 Porosity in the valve body or bonnet	Concerns particularly a cast valve: foundry defect	This is equivalent to a hole size of 1.0 mm diameter	▪ Drive in plug ▪ Cast in cement ▪ Use of self-tapping screw

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	For flat faced flanges, the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50 mm^2. On a tongue and groove flange, one should take a failure of the gasket over a width of 1 mm with bearing in mind the engineering tolerances of the tongue and groove flange.	▪ Tighten the joint with care where safe to do so ▪ Gas tight box ▪ Vented box

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
	2.2 A hole in the pipe work wall	▪ Defect in the material or at a weld ▪ Internal corrosion or erosion ▪ External corrosion	This could be equivalent to a hole size of 2 mm dia[1]. possibly increasing to 3 mm by erosion/corrosion.	Isolate the section of pipe work and then: Pipe clip, graphite cement, sealed box, apply self-tapping screw or use plug driven in

[1] Based on consolidated industry experience, confirmed also by recent discussions (May 2019).

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
	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	Depends on the overall arrangement of flange gasket and bolting	▪ Isolate the section of pipe work ▪ Re-tighten the flanges with care where safe to do so ▪ Sealed box
	2.4 Rupture due to lack of flexibility	Defect at the design stage. Installation of supports or additional anchor points during maintenance operations for example	Full pipe diameter (take into account in the calculation the loss of liquid from the two sections of pipe)	▪ Attempt at all costs to isolate the defective section ▪ Trap the leakage between two clamps or collars
	2.5 Rupture due to external impact	Impact by a crane or some other maintenance equipment or for example a tipper lorry in the upright position etc.	50% of the cross section Full pipe diameter (taking into account both ends of the fractured pipe)	▪ Attempt at all costs to isolate the defective section. ▪ Trap the leakage between two clamps or collars
	2.6 Piping failure at a hot point on liquid line	Excessive external heat, exit of a compressor, internal reaction, etc.	Leakage equivalent to full pipe diameter (taking into account both ends)	Attempt at all costs to isolate the fault section, in particular from the storage
	2.7 Damage to instrument connection	External impact	Diameter of the connection	Attempt at all costs to isolate the fault section, in particular from the storage

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
3. Storage vessels (and on-site transport containers)	3.1 Leakage at the gasket on the flanges of the branches	Defect in the gasket or on the flange face	For flat faced flanges, the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50 mm^2. On a tongue and groove flange, one should take a failure of the gasket over a width of 1 mm with bearing in mind the engineering tolerances of the tongue and groove flange.	▪ Carefully re-tighten the joint where safe to do so ▪ Gas tight box ▪ Vented box ▪ Call specialist resource

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
	3.2 Failure of a branch	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion	For the design case one assumes a hole size equivalent to 2 mm dia[2].	▪ Transfer the contents as rapidly as possible ▪ Drive in plug ▪ Pipe clip

[2] See footnote 1

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
	3.3 A hole in the vessel wall	Defect in the material or at a weld. Internal corrosion or erosion. External corrosion	possibly increasing to 3 mm with corrosion / erosion effects	▪ Transfer the contents as rapidly as possible. ▪ Lower the pressure ▪ Clamp the leakage with the use of a screwed clamp of shaped pad
	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 ▪ Then use a conical wedge
4. Transfer Equipment	4.1 Leakage on a joint or a bolted flange	Defect in the joint or the flange face	For flat faced flanges, the equivalent section for the thickness of joint displaced between two adjacent bolts can be taken up to 50 mm^2. On a tongue and groove flange, one should take a failure of the gasket over a width of 1 mm with bearing in mind the engineering tolerances of the tongue and groove flange.	▪ Stop the AHF/HF transfer ▪ Depressurise and drain

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.	One can assume a hole size equivalent to 2mm dia[3], possibly increasing to 3 mm by erosion / corrosion.	▪ Isolate the section of defective equipment or piping which is providing the means of transfer ▪ Vent down the transfer equipment to an absorption system ▪ Purge with nitrogen or dry air

[3] See footnote 1

EQUIPMENT CONCERNED	NATURE OF INCIDENT	PROBABLE CAUSE OF INCIDENT	TYPICAL EQUIVALENT HOLE SIZE	EMERGENCY PROCEDURES
	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	Deterioration in the sealing arrangement or loss of fluid in the seal	To be studied case by case	▪ Stop the machine and isolate. Depressurise and drain

APPENDIX B: AHF/HF NEUTRALIZATION TABLE

NOTES TO NEUTRALIZATION CHART

1. Any alkaline material may be used for HF neutralization. The chart above lists those most commonly used to mitigate spills. Others, such as Ammonium Hydroxide (NH4OH) may be used but may have inherent deterrent factors (e.g. odor).

2. The common neutralizing materials are listed alphabetically (Column 1). The emergency responder must consider many factors when choosing the appropriate alkaline material including:
    - Cost
    - Availability and Ease of Acquisition
    - Physical Form and Ease of Handling
    - Ultimate Disposal of the Neutral Salt or Salt Solution (Column 6)

        - Calcium based materials yield non-hazardous but very insoluble Calcium Fluoride
        - Materials yielding salts, which may be classified as POISON but with high water solubility, may be preferable for scrubbing applications

3. The amount of alkaline material required for neutralization (Column 5) is based on Kg of equivalent 100% Alkali per Kg of 100% HF. The factor will have to be adjusted based on the Alkaline form used (Column 3)

4. Responders must take care to control the chemical reactions. For example, to better control the Heat of Neutralization, the HF Spill and Neutralizing Alkaline Solution should be diluted as much as practical, considering the need to contain and control all effluents.

5. When using carbonates (e.g. Soda Ash), the rate of Carbon Dioxide gas evolution must be controlled from upwind of the containment area.

TYPICAL ALKALINE MATERIALS (BASES) FOR NEUTRALIZATION OF HF

ALKALINE MATERIAL	COMMON NAMES	FORM AVAILABLE	HAZARDS + REACTION	Kg.100% BASE per Kg. 100% HF	SALT PROPERTIES
CALCIUM CARBONATE ($CaCO_3$)	LIMESTONE	PEBBLES	Slow reaction Slow evolution of carbon dioxide gas (CO_2) Pebble surface can become passivated	2.50 Kg / Kg HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%
CALCIUM HYDROXIDE [$Ca(OH)_2$]	HYDRATED LIME	DRY POWDER SLURRY IN WATER	High heat of neutralization Slippery when wet	1.85 Kg / Kg HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%
CALCIUM OXIDE (CaO)	QUICKLIME	DRY POWDER	Danger / UNO: -- / 1910 Very high heat of hydration & neutralization	1.40 Kg / Kg HF	Calcium Fluoride (CaF2) Non-hazardous Sol. In Water = 0.004%
POTASSIUM HYDROXIDE (KOH)	CAUSTIC POTASH	85% SOLID BEADS or FLAKE <45 % SOLUTION	Danger / UNO: 80 / 1813 Danger / UNO: 80 / 1814 Very high heat of hydration & neutralization	2.80 Kg / Kg HF	Potassium Fluoride (KF) Danger / UNO: 60 / 1812 Sol. in Water >40%
SODIUM BICARBONATE ($NaHCO_3$)	BICARB BAKING SODA	DRY POWDER	Rapid evolution of carbon dioxide gas (CO_2)	4.20 Kg / Kg HF	Sodium Fluoride (NaF) Danger / UNO: 60 / 1690 Sol. in Water = 4.0%
SODIUM CARBONATE (Na_2CO_3)	SODA ASH	DRY POWDER	Rapid evolution of carbon dioxide gas (CO_2)	2.65 Kg / Kg HF	Sodium Fluoride (NaF) Danger / UNO: 60 / 1690 Sol. in Water = 4.0%
SODIUM HYDROXIDE (NaOH)	CAUSTIC SODA	100% SOLID BEADS or FLAKE <50% SOLUTION	Danger / UNO: 80 / 1823 Danger / UNO: 80 / 1824 Very high heat of hydration & neutralization	2.00 Kg / Kg HF	Sodium Fluoride (NaF) Danger / UNO: 60 / 1690 Sol. in Water = 4.0%

TABLE OF DECISION FOR NEUTRALIZATION OF HF

ALKALINE MATERIAL / SITUATION	$CaCO_3$ pebbles	$Ca(OH)_2$ powder	KOH	$NaHCO_3$	Na_2CO_3	NaOH	water	comments
Contaminated PPE					Spray or wash with solution		Flush with large quantities	Carefully inspect PPE after rinsing, search for potential damage
Contaminated pipes, tools, valves, …				Soaked In tank			Flush with large quantities	
Contaminated railcar or road tank	Avoid (not efficient)	Fill the tank with water and add lime – stir with air	Fill the tank with water	Be careful with CO2 generation	Be careful with CO2 generation	Fill the tank with water		1. Fill with water at least twice (pay attention to the temperature rise!). Beware of the risks of diluted HF solutions 2. Then use neutralizing agent 3. Repeat until pH paper indicates no remaining acidity
Continuous leak	Dyke around the leak							Other adsorbent products can be used
Traces of HF on the ground		Spread powder on the contaminated areas						Other adsorbent products can be used
Small pool of HF (<0,5 m²)	Dyke around the leak							1. Contain HF by dyking with solid agent 2. Then spread very slowly any neutralizing agent (beware the reaction with water)
Large pool of HF (>0,5 m²)	Dyke around the leak							1. Contain HF by dyking with solid agent 2. Then cover the pool by using polyacrylamide foam to stop HF evaporation 3. Ask for advice of HF specialist to recover or to neutralize residual HF
Spillage of HF to river / lake / pond / sewers								Warn the local authorities to stop all the pumping stations and prevent any public access to the river in the concerned area