Comité Technique Européen du Fluor (CTEF)

Working Group on Storage, Transport and Safety (STS)

Group 3

RECOMMENDATION STORAGE, LOADING AND UNLOADING 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%.

Summary

Introduction

This guideline has been developed by the Storage, Transport and Safety Group of Eurofluor, the European Technical Committee for Fluorine (previously named CTEF). It is intended to offer recommendations for the storage, the loading and the unloading of anhydrous hydrogen fluoride (AHF) 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. STORAGE

1.1 Definition

This paragraph concerns the bulk storage of anhydrous HF (AHF) having a volume of more than 10 cubic meters and functioning at ambient temperature (-10°C to +50°C).

Note: HF solutions of more than 85% concentration can be handled as AHF

1.2 Capacity

Technical considerations and risk assessment are the only reason for limiting capacity. Beyond a certain size it can become difficult to fulfil the technical conditions indicated in the present recommendation.

In order to provide the desired storage capacity, a compromise is required between the individual unit capacities and the number of stock tanks. One should note that increasing the number of vessels leads to a proportional increase in the number of accessories, with its various risks of mal-operation which follow from that. On the other hand, having too big storage tanks may result in bigger risks in case of leakage on them

One should also take into consideration the need for internal inspection of the tanks without interrupting the operation of the associated processes

At least, the capacity of the individual tank should never be less than the one of bulk delivery quantity (a ratio of minimum 1.5 is recommended)

Therefore one should attempt to find the better compromise according to its individual situation

1.3 Design and construction of storages

1.3.1. Isolation distance of storage area for hydrofluoric acid

The major part of the risk to environmental safety depends on the unit volume and not on the number of tanks constituting the storage.

Thus, the separation to be imposed is to be chosen in respect of the unit volume of the largest stock tank in the storage area. Nevertheless, it should be noted, as already stated, that a multiplication of tanks requires a proportionate increase in accessories with the risks of faulty manipulation which could occur. Multiplication should therefore be carefully studied.

- The location of the storage shall protect the vessel from other risks (corrosion - fire - explosion - impact (from vehicles, crane operation ...)).
- Storage facilities shall be enclosed in restricted areas where work is controlled by suitable procedures e.g. permit to work.
- Vessels shall be protected against mechanical damage and impact.

1.3.2. Space between adjacent tanks

There should be sufficient space between adjacent tanks to ensure accessibility for the purpose of operation or maintenance of the tanks.

The need for future inspection and maintenance activities in and around the AHF facilities should be taken into account. Sufficient space around the tanks has to be provided taking into account the personal protective equipment that the people will have to wear.

1.3.3. Bunds

Placing of bunds underneath stock tanks is recommended. In every case, the surface area of the bund should be limited to reduce the rate of evaporation of the acid in case of leakage.

Note that concrete is not AHF resistant. Specific lining is required if the AHF remains in the bund.

1.3.4. Buildings

1.3.4.1. Considerations regarding installation of a building

The main advantages of outside operations are:

- Access to the installation is easy, permitting rapid intervention in case of incidents as the leakage is more safely accessible from upwind without heavy equipment.
- The installation is always under visual control even in case of leaks.
- Identification of the point of leakage is easy.
- Access for routine inspections, checking, is good. Safety of operators requires fewer precautions.

The main disadvantages of outside operations are:

- When the storage is not under continuous manning early leakage detection may be difficult.
- The gas leaks are more difficult to confine and to absorb.

The main advantages of inside operations are:

- Easy leak detection even in case of unmanned installations.
- The installation is protected from accidental mechanical damage from outside (provided the building is made in a resistant material)
- Controlled ventilation permitting absorption of the leaks.

The main disadvantages of inside operation are:

- Necessary heavy protection equipment for intervention could bring additional delay for intervention.
- Access and visual control of the installation is not easy, particularly in case of leak. Identification of the point of leak may be difficult.
- Access for routine inspection and checking requires more precautions

1.3.4.2. Requirements arising from the above considerations

Outside installations

To compensate the disadvantages listed in Section *1.3.4.1. Considerations regarding installation of a building* the following measures have to be considered:

To compensate the difficulty of early leakages detection, if the plant is not under continuous manning, additional leak detections should be provided with alarms.

These alarms have to be periodically checked to ensure adequate reliability.

Regarding the difficulty of confinement and absorption of the leaks, compensation measures can be applied by:

- Quick isolation of the leaking parts,
- Depressurizing or emptying the leaking parts,
- Applying water curtains
- Applying suction of the leak with flexible hoses going to an absorption unit.

Eurofluor has developed design and recommendation for shut off valves for quick isolation. See specific recommendation of Eurofluor about it.

Inside installations

To compensate the disadvantages listed in Section *1.3.4.1. Considerations regarding installation of a building*, the following measures have to be considered:

- Sufficient self-contained breathing apparatus must be provided and the operators must be well trained to use this equipment in a short response.
- Emergency procedures must be developed for entering to the building.
- Building and equipment design should provide easy access for operators wearing such equipment.
- To compensate the difficulty of identification of the point of leak the following can apply:
  - Quick and remote isolation of the all system
  - Quick response to the early alarm obtained with the detectors
  - Procedures have to be developed for this situation.

1.3.4.3. Conclusions

There is no unique position for that topic. One should clearly analyse the pro and cons of each solution taking into account its individual situation

1.3.5. Operating pressure

Depending on the way the AHF is transferred from the tank to the process unit or to the loading station, the tank can either operate at atmospheric pressure (or slight vacuum) or under pressure.

As both solutions have their own advantages and disadvantages, consider them carefully according to the local situation to make the best choice.

1.3.5.1. Tank operating at atmospheric pressure

In that case, there are two main solutions for emptying the tank:

- To pump with a pump located below the tank. This solution requires a nozzle on the bottom of the tank. Due to the risks that are linked to the potential damage of this nozzle, this solution must be avoided.

- To pump with an immerged pump. In that case, the main constraints are :
  - to find a pump with a good tightness (to avoid the leaks)
  - to find a pump with a good reliability to reduce the frequency of maintenance operations. In fact, as the pumps are located inside the AHF tank, the removal of the pump from the tank is a tight operation.

The main advantages of tanks operating at atmospheric pressure is that in case of a leak, once the pump is stopped, there is no more leak (provided, there is no nozzle on low point).

Moreover, there is no risk of liquid backflow through the inlet pipe (filling pipe) of the tank in case of damage on it.

1.3.5.2. Tank operating under pressure

The main disadvantage of this tank is that in case of rupture of a liquid pipe (liquid inlet or outlet of the pump), AHF can come out the tank.

The main advantage is that maintenance is much easier and that there is no need for a nozzle at the bottom of the tank.

Two solutions can be used to transfer the liquid:

<u>Pressurization of the tank with an inert gas</u>

In that case, the main advantage is the absence of a pump.

Depending on the level of pressure, the trouble is that it becomes necessary to have a higher pressure in the lines that feed the tanks (unloading tank and unloading pipe in particular)

<u>By a pump located outside the tank</u>

Main advantage is an easy maintenance (the tank does not have to be opened for maintenance of the pump) and more choices are available in the technology of the pump.

In that case, one should take care to have the optimum pressure in the tank: not too much to avoid generating to big hazard area in case of leaking, not too less to avoid cavitations in the pump.

Operating temperature

It can be useful to consider refrigerating the tank to reduce the vapour pressure of AHF.

It can be particularly interesting in the case of the pump located outside the tank because it allows reducing the operating pressure of the tank.

One should take care of the insulation and corrosion associated if one decides to refrigerate its storage.

1.4 Construction of tanks

Tanks construction will be done in accordance with European or national norms derived from it. Consider European rules for tanks under pressure 97/23/CE (or national rules derived from it) as well, if applicable.

The tank should be done according to international recognized codes and respect local regulations. The aim of this paragraph is:

- to list the complementary requirements that should apply to the construction of AHF tanks
- to list the particular risks associated with AHF tank that can influence its design
- to freeze some options where the code proposes different options

1.4.1. Design pressure and minimum temperature limits

When the upper and lower design pressures are chosen, all situations must be considered so that the upper pressure cannot be exceeded on any occasion in the course of working and the lower pressure does not fall under these limits. For example, if a dry gas is utilized for transferring the liquid, the design pressure must be chosen in accordance with the maximum possible pressure of the dry gas utilized and the vapour pressure of the liquid.

If not possible, consider installing a pressure relief valve on the tank (associated with a scrubbing system)

Storage tanks must be designed to withstand unloading pressure as well as vacuum in the event internal pressure drops below atmospheric pressure when the acid gets colder.

The design minimum temperature limit should be chosen as a function of operating or climatic conditions and every effort must be made to ensure that temperature do not fall below this limit. When the tank temperature is controlled by ambient conditions, it is recommended that the minimum design temperature shall not exceed the lowest daily temperature, e.g. in Western Europe -20° C.

If the tank is refrigerated by means of a cooling agent, the minimum temperature of the cooling agent should be taken as design temperature.

1.4.2. Corrosion and erosion allowance minimum thickness

A corrosion allowance of 2 mm (for carbon-steel tanks) is considered as a minimum requirement. Higher corrosion allowance should be considered depending on AHF temperature and specific risks depending on the application. Operating procedures should be defined to avoid any entrance of moisture into the storage tank. It is also necessary to provide corrosion and erosion allowance for the branch connections or nozzles on the storage tank, as some erosion may happen on that nozzles, due to the liquid circulation at high velocity.

In addition, the thickness of the nozzles must take care of some stress coming from the connected pipe work.

Self-reinforced nozzles are recommended to reduce the stresses on the tank.

For example (further information in our “Recommendation on materials of construction for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions” available from the publication webpage of www.eurofluor.org), for continuous liquid flow, the size of nozzles will be designed to have velocities under 1.5 m/s (room temperature) if normal steel is used. For gas flow, the speed should be limited to 10 m/s.

1.4.3. Materials of construction

1.4.3.1. Steel plate

Materials shall fulfil the requirements of international standards for pressure vessel manufacturing and delivered with inspection certificate 3.2 according EN 10 204.

Welded carbon manganese steels shall be supplied with an equivalent carbon = 0.43% max on heat analysis, and 0.45% product analysis.

C.E. shall be determined by the complete formula (and not by a simplified one)

These values guarantee good weld ability.

These values could be reduced to C < 0.23 to reduce the risk of blistering.

Plates shall be supplied in normalized condition.

The steel chosen for the construction of AHF storage tanks should be of fine grain steel.

To avoid any risk of brittle fracture at minimum design temperature a test (impact Charpy-V-notch test for example) has to be conducted at the right temperature to guarantee the resilience of the material.

Storage tanks can be subject in hydrogen blistering.

Consequently, the choice of the grade of steel and the additional requirements to specify by the manufacturer, will have to take into account, strictly, recommendations published on the matter (To see for example CODAP MA3)

The maximum dimensions shall be used in order to minimize the length of circumferential and longitudinal welds.

In any case, the steel sheets should be checked ultrasonically to ensure the steel is lamination free. The maximum size of defect that can be accepted should be specified. No defect at all should be tolerated in the nozzle area.

All reinforcements welded on the steel sheet must be provided with vents.

Blistering could appear in stresses concentration area. All the stresses on the nozzles should be carefully taken into consideration.

The hardness of the steel should be limited to avoid cracking. The welding procedure must guarantee the hardness.

1.4.3.2. Welding

Arc welding process shall be used.

Shielded metal arc welding 111 (SMAW) and submerged arc welding 121 (SAW) are acceptable.

As hardness is limited, Gas Tungsten Arc welding (GTAW) or Flux Cored Arc Welding 136 (FAW) can also be accepted.

MIG/MAG welding with solid electrodes is only allowed for non-pressurized fillet welds.

Permanent backing rings or strips are not permitted.

All nozzles shall be set in type.

All joints on the envelope shall be butt welded with back gouging where possible, and shall be full penetrated.

Performance qualification for welding shall be in accordance with the requirement of the regulation and the code.

The hardness shall not exceed Vickers 244 (HRC 22).

WPAR shall include impact test.

1.4.4. Stress relieving

Stress relieving is recommended and should be carried out in accord with the quality of steel used and with the method of welding. It is especially recommended for the larger wall thickness. (>25mm)

Mechanical characteristics shall be guaranteed for all body parts on the base metal and as well as on weld deposit

1.4.5. Inspection and testing

1.4.5.1. Inspection of raw materials

Raw material should be provided with certificate 3.2.

After forming, the side part steel plate of the tank must be normalized.

1.4.5.2. Inspection during fabrication

The inspection procedure during the construction of the liquid AHF storage system should be according to the codes being applied, particularly in respect of the following aspects:

- 100% radiography of welds;
- Thickness control and detection of cracks or laminations by ultrasonic means ; (concerns the inspection of steel plate)
- Certification of the welders and of their welding methods ;
- Inspection to determine gas tightness, e.g. by the use of dye penetrate testing;

1.5 Auxiliary equipment

1.5.1. Branch connections in the liquid phase

All nozzles of the tank should be installed on the top of the tank. Although not recommended, when a bottom nozzle is used, the size should be minimized and the flanges, gaskets and valves shall be carefully selected in order to prevent failure.

In any case, if there is a risk to lose the content of the storage tank in case of pipe failure, a remote pneumatic shut off valve shall be installed on the line as near as possible to the flange of the tank, the latter followed by a manual valve.

In all cases, one must minimize the number of openings on the tank to reduce hazards.

1.5.2. Pressure relief valves

If a pressure relief valve is made necessary by the service conditions of the tank, it should be protected from the atmosphere of the tank in such way it would remain in perfect working order and free from leakages for example by use of a rupture disc.

The off gas from the valve must be contained in a suitable installation: an empty storage tank, a guaranteed usage or an absorption system. A protection from the back side by the way of a rupture disk is recommended.

One should take into account the back pressure in the discharge line for choosing the right pressure relief valve.

1.5.3. Loading factor

The stock tank should be filled and operated in such a manner that in no case does the loading factor exceed 95% of the total volume at the maximum operating temperature of storage tank, normally taken as 50° C.

1.5.4. Recommended equipment for storage

The storage tank must be fitted with a weight indicator (weighbridge or load cells) or level gauge properly developed for AHF duty. It must also be fitted with a pressure indicator, except if the tank can be only operated under atmospheric pressure conditions.

It is recommended to have a high level alarm, or maximum load alarm, to ensure that the loading factor indicated in *1.5.3. Loading factor* is not exceeded. This alarm should be independent of the normal level gauge.

If the tank is refrigerated, a temperature measurement is also recommended.

Automatic shut off valve must be installed wherever a pipe failure could lead to the emptying of the tank.

Storage and handling facilities should be equipped with appropriate alarms, interlocks, remote operated valves and emergency shutdown buttons of easy access even in case of spillage. Such equipment should work even in case of normal power failure.

1.5.5. Maximum size of branch connections

A diameter of 150 mm should be considered as the maximum for direct branch connections into an AHF stock tank. This would be satisfactory for producers or tanks on large customer's premises and should be reduced for stock tanks at smaller premises. Manholes and branches for level measurements are not considered in this context. These must be placed in the gas phase of the storage tank.

1.5.6. Connections between the storage and loading area

Connections from fixed installations to road or rail tanks can be made with the aid of flexible hoses or articulated arms or flexible copper or steel pipes. This pipe should be equipped with a device to stop the feeding in case of pipe failure.

1.5.7. Separation between the storage and loading area

A remote controlled device to stop acid flow between the storage and loading point is recommended. The remote control should be placed at sufficient distance from the storage and loading areas to enable it to be used in case of emergency.

1.5.8. Recommended specification for pipe work associated with storage

The pipe work used for service on AHF should be designed to have an adequate wall thickness and should be a quality of steel which corresponds to the temperature and pressure of operation. As far as possible, it is recommended that 100% radiography of welds should be carried out. In situations where radiography is not possible, the welds should be inspected by a form of dye penetrate test. Bends and accessories (tee and reducers) must have at least the same thickness as the tubes.

1.5.9. Valves and isolation

Valves used on the storage tanks should be of a type especially developed for AHF duty. If possible, do not use plug and ball valves as a primary liquid isolation of a AHF storage tank but prefer internal check valves. But note that these valves have higher pressure drop that could results in over sizing the nozzles and so the best choice depends on the local situation.

The material of construction of these valves should correspond to the intended operating temperatures and pressures. It is necessary to provide on the filling and emptying pipe work of the stock tank valves which enable it to be isolated rapidly. They should therefore be installed in a way to provide easy access if they are manually operated or should be remotely operable.

1.5.10. Utilities

Direct utility connections to acid containing equipment and piping should be avoided but where absolutely necessary safeguards should be incorporated to prevent the possibility of inadvertent backflow of AHF liquid or HF vapours into the utility systems which could have various consequences. Experience indicates that extreme care should be exercised on the specification, installation and maintenance of the equipment to prevent backflow. Similarly, it is essential to avoid accidentally contaminating the AHF with any of the utilities; especially water or moist air as this may lead to extremely severe reactivity, possible equipment pressure surges and corrosion problems.

1.6 Operation and protection of the storage system

1.6.1. Periodic inspection

Periodic inspections of the storage tank are necessary. A minimization of internal inspections or a precise preparation of the inspection should be considered as every internal inspection could lead to corrosion. Between two internal inspections, it is advisable to carry out thickness testing using ultrasonic techniques from the outside, for example every two years.

1.6.2. Recommendations concerning the means of protection and warning

on the anhydrous HF storage tank

It is recommended as a minimum that the following equipment is provided:

- The top of the tank should be accessible with stairways (and not ladder) at least from two different points (in case of emergency situation, the personnel could have to access the storage area wearing full personal protective equipment)
- Emergency lighting shall be provided.
- The emergency plan and alarm system should be written down and all personnel trained in its operation ;
- The operator (or the fire brigade if any) should be able to bring into operation rapidly a mobile water curtain to restrict the spread of vapour from a leak ;
- At each internal inspection of the tank, as a protective measure, the AHF tank user should overhaul equipment which is most susceptible to damage, such as valves and pipe connections leading to filling or emptying installations (especially in the liquid phase). As a general principle, equipment should be replaced before there is a significant risk of its failure ;
- Gas mask, self-contained breathing equipment together with protective suits suitable for AHF duty should be provided for the operator in a suitable cabinet near to the storage area, but in such a way, that it will always be accessible in case of an emergency ;
- Emergency equipment should be available locally on the plant. A list of this equipment is contained here below :
    - Self-contained breathing equipment
    - Showers and eye wash equipment(protected against freezing and regularly tested)
    - Bath equipped with neutralizing solutions
    - Jackets - Acid resistant overalls
    - Gas proof suits (plastic)
    - Spare compressed air cylinders
    - Hose (30 m long) for air cylinder and "extra hours" connection + canister masks
    - Canister masks
    - Chemical goggles
    - Gauntlet gloves
    - Rubber footwear
    - Water guns with spray nozzles
    - Lamps warning lights
    - Warning signs
- This emergency equipment list should be considered as the minimum requirement.
    - A means of indicating wind direction should be installed so that the personnel involved can determine the direction of dispersion of the leak in case of emergency
    - Special personnel should be trained in the method of dealing with leakages a periodic training exercise carried out ;
    - Personnel working in the plant must be correctly instructed in the important

aspects of handling hydrofluoric acid and particularly :

- hazards linked to the product,
- hazards linked to the units when improper handling,
- clean up procedures,
- maintenance procedures,
- emergency procedures,
- use of personal protective equipment.

1.6.3. Recommendations concerning maintenance

Storage tanks should be inspected and tested on a regular basis (ultra sonic or others...) Pipe work - including valves, supports, flexible and fittings - should also be subject to regular inspections in order to ensure that the design standards are maintained.

Heavy maintenance work - e.g. work involving the use of cranes and/or motor vehicles - should only be allowed after full assessment of the hazard involved. It is preferable that the relevant storage tanks are empty.

1.6.4. Quick emptying of a tank

It is strongly recommended to allow a possibility of quick emptying of the contents of any storage tank in case of emergency (for example when a big leak is developing).

Two solutions may be considered:

- Limit the degree of filling of each AHF tank in order to be able to empty and distribute the volume of the biggest AHF tank in all the others in case of emergency ; or
- Install an "empty tank" able to receive the contents of the biggest of the existing AHF tanks. In particular, this solution is the only possible one when there is only one AHF tank.

1.6.5. Consideration concerning water curtains

AHF is well absorbed in water.

With 40 times the amount of water per amount of HF evaporated, it is considered that 90% of the HF must be absorbed (reference : EPA - hydrogen fluoride study - Report to congress - Section 112(n)(6) - Clean air act as amended).

One should take care to the exothermic reaction between water and AHF in sizing and positioning its water curtains.

1.6.6. Consideration concerning the use of foam

Water free foam can be used to reduce the evaporation of the AHF.

To avoid exothermic reaction between the water contained in the foam and the AHF high expansion water free foam should be used.

The foam has to be AHF compatible.

For example foam of Polyacrylamide can be used.

1.6.7. Consideration concerning HF sensor and camera

One should consider putting HF sensor in AHF building and also near strategic points where a leak can occur (near pumps for example).

In case HF is detected (with a specific logic between the sensors if there are several sensors), there should be automatic shut down.

If automatic shutdown is not installed, one should consider adding television camera linked with the HF sensor. In that situation in case of alarm on a sensor, the operator should be able determine the gravity of the leak with his camera and push an emergency button at his disposal.

2. FILLING AND UNLOADING STATIONS FOR ANHYDROUS HYDROFLUORIC ACID

2.1 Introduction

The purpose of this section which is based on the experience of all members of Eurofluor is to achieve the safe design of filling and unloading stations for anhydrous hydrofluoric acid.

2.2 Layout

Any movement of the road or rail tanker must be avoided during the operations of filling, unloading and venting

This can be accomplished by the use of brakes, line blocks, wheel, chains, etc...

Any approach of another rail tank to a mobile tank connected to the system must be avoided by the use of a lockable switch block or barrier.

The use of the rail line should be limited to serving the filling station. Any gravity movement of the rail tank must be avoided and the slope of the line should not exceed 1/400. When road tanks are in place, the landing legs must be efficiently locked in position.

Warning notices or flags or lights must be used to indicate that operations at the station are in progress.

Sufficient clearance must be provided between the mobile tank and the fixed structure and pipe lines to avoid any collision.

The filling station should be sufficiently isolated from the normal traffic flow and the storage vessels to provide the necessary accessibility to the equipment in case of leakage.

For example, plastic chains and warning notices should be used to indicate that entry to the filling station area is restricted to authorized personnel.

The parking of unauthorized vehicles or the storages of flammable materials must not be allowed within the area of the filling station.

The loading platform which should be provided with access stairs should be designed to give a good accessibility to the valves and enable a worker wearing protective clothing and self-contained breathing equipment to move about easily in his duties.

2.3 Design

2.3.1. Connections

2.3.1.1. Generalities

The connections between the mobile tank and the fixed pipe work are the most vulnerable points of the station and have to be carefully designed on the basis of experience.

The connections to the liquid phase of the mobile tank should be made of steel pipes, PTFE flexible hoses or articulated arms, all confirmed by experience. A maximum pipe diameter of 50 mm is recommended for the liquid phase connection. Corrugated metallic hoses without internal lining are not recommended because they do not drain fully. Hoses made of stainless steel, Monel, Inconel, or Hastelloy lined with PTFE can be used but care must be taken for the porosity of the PTFE lining. Therefore permanent use is not recommended and for intermittent uses periodic checks or changes (twice a year) are necessary.

2.3.1.2. Flexible steel pipes

Definition

This pipe work enables a flexible connection to be made between the fixed pipes of a filling or unloading point and a road or rail vehicle or iso-container. This connection must be retained without abnormal tension during the entire duration of the operations of filling or unloading for vertical movements of the tank due to the loose of weight.

The design, materials and method of operation of the connections must, in a general way, conform to this requirement for the conditions detailed below.

This paragraph only determines the minimum conditions of construction for flexible steel pipes.

Conditions of use

The pipes must connect hermetically to the tank for the following conditions of temperature and pressure:

- Minimum temperature : -20°C
- Maximum temperature : +50°C
- Minimum working pressure : 0,20 bar absolute
- Maximum working pressure : 11 bars absolute

Functions

In order to absorb the abnormal tension caused by relative movements between the mobile tank and the fixed installation, the connection must comprise:

- Steel pipes long enough to ensure sufficient elasticity in the total connection. If the distance between the fixed installation and the mobile tank is too short, a coil type construction should be used ;
- Connecting flanges specially designed for the duty and entirely tight to AHF;
- An elastic system of suspension for the whole, intended to ensure support, especially when the connection is not in use, and in such position that it cannot be damaged by the moving tank car.

Materials

Refer to the STS document about material of construction

Couplings

Couplings, if there are any, must be manufactured of forged steel exclusively. The seal between two couplings must be ensured by a flat joint. Most generally, with small bottles and containers, screwed type couplings are used without any gasket.

Gaskets

Refer to the STS document about material of construction

Controls and tests

Control by 100% radiography of welds

Hydrostatic tests with a minimum pressure of 16 bar absolute

Periodical inspections

At least every 12 months, the user must carry out an external inspection and the flexible pipe must be replaced before there is a significant risk of failure.

2.3.1.3. Flexible PTFE hoses

Definition

The hoses enable to have flexible connections between the fixed pipes of the filling and/or unloading station and the road or railcar, which is to be filled or unloaded.

The hoses must be of sufficient length to avoid abnormal tension during the filling and/or unloading operations.

Minimal technical specifications

Material

PTFE hoses with a stainless steel wire braid.

PTFE hoses designed for general industrial use for conveying liquids and gases are suitable for the service of filling and unloading AHF provided the conditions set forth hereafter are met.

Protective armor may further be used where hose lines are subject to excessive abrasion or to help prevent kinking damage.

The diameter of the hose will be limited to 50 mm.

Pressure and temperature specifications

Design pressure of the hose: minimum 20 bar effective

Working pressure: maximum 11 bar effective

Note: this is the minimum requirement for the hose assembly including fittings

Minimum temperature: -20°C

Maximum temperature: +50°C

Bursting pressure: minimum 80 bar effective

Fittings

PTFE hoses used in filling and/or unloading service of AHF should be equipped with flange fittings, to ensure leak free connections.

Protective liner

The PTFE protective liner will be required throughout the assembly of the hose including the flanges. The thickness of the liner will be sufficient to prevent porosity, at least for the time of service.

Protective casing

The protective casing and reinforcing wire braids over the casing will be made of stainless steel.

Testing

The manufacturer will perform and certificate a hydrostatic test of the hose at 1.5 times the maximum working pressure.

The bursting pressure will be certificated by the manufacturer;

In case water is used for pressure testing purpose, hoses must be properly dried before application in AHF service.

Precaution of use

All the items of the filling and discharge hoses while awaiting use will be kept in a way which will avoid any deterioration.

The end flanges will be protected against entrance of moisture and against damage.

All the exterior metal parts will be protected in order to avoid external corrosion.

Every time before use, a visual inspection of the hose will take place to verify that no fault is present. The HF will not be allowed to pass through the flexible hose unless no fault has been detected.

All suspect hose will be immediately replaced.

The gaskets of the connecting joints will be replaced before each operation of filling or discharging.

Care must be taken for the porosity of the PTFE lining. Therefore permanent use is not recommended but only intermittent uses can be accepted. On such cases, periodic checks or changes, (at least every six months) are necessary in order to replace the hose before there is a significant risk of failure.

The AHF producers, members of Eurofluor, have equipped all their mobile AHF tanks (wagons, road tanks, ISO - containers) with a remotely actuated shut off valve with internal sealing, which enables the acid flow between the storage and the mobile tank to be stopped by a button, provided another shut off valve is installed on the fixed pipe. This safety device is particularly useful in case of failure of the flexible hose.

2.3.1.4. Articulated arms

Presentation

The arms are intended to provide a flexible connection between the fixed pipe work of a loading or off loading installation and a road or rail tanker vehicle, or an iso-container. They should be capable of providing this connection without any inbuilt stresses during the entire operation of loading or off loading, and should be able to take up, in particular during the course of transfer, the movement of the barrel on its suspension. The design, the materials of construction and the method of operation of the articulated arms should from a general point of view, be able to meet this objective under all the operating conditions indicated below.

General comments

Field of application

This type of connection is often used for the transfer of AHF/HF, that is to say for filling or unloading operations from a railcar/container to/from a storage tank or process.

Minimum design conditions	Liquid/Gaseous AHF	
	Min	Max
Temperature (°C)	-20	+50
Pressure in bars absolute	0,20	15

Design requirements

Principles

In order to be able to take up without stress the relative movement between the fixed installation and the mobile transport vehicle, the articulated arm should include the following:

- The articulated connections should be adequately tested for this service and perfectly gas tight for AHF. The number of flexible couplings should be adequate to absorb without stress all movement in three dimensions.
- The pipe work, elbows and flanges in steel should be welded to the articulated sections. No screw connections should be admitted. With the exception of the swivel joints assembly where screw/bolted connections should be admitted though bolted connections are preferred.
- The possible nitrogen and degassing connections for purging the swivel joint chamber could also be screwed.
- A counter balance system should be provided by the use of a spring or counter weight or an equivalent system.

Design principles to facilitate maintenance

All wearing pieces or areas subjected to permanent wear should be rapidly replaceable with the aid of simple tools. This is particularly important for the joints on the articulations. This maintenance activity should be capable of being carried out by the normal factory maintenance personnel.

Safety aspects

The sealing material in the articulations should be conceived in such a fashion that it can neither flow nor escape. In circumstances where it is subjected to significant stress, it is desirable that it should be protected by a closed system purged by a flow of inert dry gas (oil free air or nitrogen) or with leak detection. The dew point should be less than -40°C. In a design where the alignment of the articulated arm is determined by one ball movement, it is recommended that a bellows seal should protect the jointing area.

But in that case, one could consider doubling the ball bearing.

Compatibility with the components of the mobile container

The dimensions of the articulated arm at the loading extremity should be compatible with the equipment on the mobile container. Connection to the container can either be metal flanged or semi screwed such as using the clamping nut and gasket or equivalent.

Choice of materials of construction

Piping

Seamless drawn steel pipes should be used for the fabrication of the articulated arms, even if they are lined.

Components subjected to stress

All equipment, which is to be subjected to a static or dynamic stress, should be designed in a material which is compatible with AHF, and which has adequate mechanical impact resistance and strength to deal with the recommended temperatures and pressure indicated in this section. This excludes the use of cast iron.

Refer to our "Recommendation on materials of construction for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions" available from the publication webpage of www.eurofluor.org.

Impact strength of metals used

The impact strength of the materials used should be at least equal to those required by international regulations (RID-ADR), for the construction of transport vehicle barrels and as required by recommendation concerning the design and construction of rail tankers and concerning the design and construction of isomodule containers for use in the transport of liquid AHF.

Articulations

If contact with AHF is possible, metallic components in the bearing surfaces of the articulations should preferably be manufactured from material, which is resistant to gaseous and liquid HF, either dry or slightly moist (for more information about materials please refer to our "Recommendation on materials of construction for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions" available from the publication webpage of www.eurofluor.org.

In addition, any metallic component which can be in contact with HF due to seal failure should be preferably made in materials resistant to slightly moist HF or PTFE or PFA lining on steel when possible (when moisture is possible to be found there).

Sealing material

Sealing material of the swivel gasket should be made of pure virgin PTFE (with a captive gasket).

Gaskets should be made of PTFE or with equivalent HF resistance characteristics for metal flanges connections.

It is recommended that a leak detection system should be provided on the swivel joint as well as nitrogen or dry air padding.

Bolting

They should comply with STS recommendation (refer to STS documents on material of construction).

Inspection and testing

At the manufacturers premises

- 100% radiography off all the welds for metal articulated arms; 100% magnetic and penetrate testing of all welds for metal PTFE/PFA lined metal arms.
- Mechanical tests
  There should be a hydrostatic pressure test at a pressure of 22 bars absolute.
  This should last for at least 10 minutes, during which time the pressure should not vary. The pressure test should be followed by dismantling, cleaning, drying, re-assembly and drying in nitrogen.
- Leak testing
  The equipment should be tested with dry gas (air or nitrogen) with a dew point of less than -40°C at least at twice its maximum operating pressure. The equipment should be checked for leaks by the use for example of soapy water, together with movement of the articulations.
  It is recommended to check during a certain time (half an hour) that the pressure in the arm does not decrease to be sure that the arm is really tight.
  After the above pressure tests the articulated arms should be blanked off and put under a dry air or nitrogen atmosphere.

Periodic testing

After the first year of operation or the first one thousand operations, the user of the equipment should carry out an external/internal examination of the articulated arms and subject them to an exhaustive leak test.

After this first visit, the user should plan regular inspection depending on its past experience.

Precautions to be taken on delivery

Articulated arms should be delivered perfectly dry with all traces of grease, oil, etc. removed as well as any solvents used during the course of fabrication, testing or inspection, or any other material which is likely to react with HF. Any components which need to be lubricated should only make use of grease which is compatible with HF (chlorofluorinated grease). Unmachined external surfaces should be treated after receipt with an anti-rust paint, and all traces of mill scale, etc. having been eliminated beforehand by sandblasting. Machined or threaded surfaces should be protected. The flanged orifices should be blanked off and protected by plastic plugs. The diameter of these plugs should be such that the entire jointing surface is adequately protected. All precautions must be taken such that the articulated arms do not undergo any deterioration during their subsequent transport.

Precautions to be taken during use

- Articulated arms before use should be stored in such a way that the flange connections and the articulated joints are not subject to deterioration. All precautions must be taken to avoid the ingress of moisture.
- At the time of installation :
  - A visual examination should be carried out to demonstrate that there is no defect in the articulated arm. The same visual examination should be carried out before each operation of loading or off loading from a container. HF

should never be admitted to the articulated arm when any defect is detected,
  - All suspect articulated arms should immediately be withdrawn from service for maintenance,
  - An isolation valve, suitable for the use with the articulated arm and attached to the discharge end of the arm in order to avoid the entry of air into the arm after operation and the subsequent risk of corrosion is recommended. This valve is required :
    - to ensure a gas tight seal from the atmosphere in the periods when the articulated arm is out of service (this gas tightness should be reinforced by the backup of a blank flange),
    - to permit the venting down of the articulated arm and the depressurization of any connection adaptor.
- One should take care to avoid leaving liquid HF trapped in the articulated arm. At the end of each operation of loading or off loading, the arm should be vented towards an installation for absorption of HF and purged by the use of a dry inert gas.
- During periods when the arm is out of service, the purge gas should be maintained under a small pressure to avoid moisture entrance.
- The gas tightness of the arm should be regularly checked during operation by the user, either by external checks with the use of for example soapy water or ammonia, or by an analysis of the purged gas in the articulated connections when this is used.
- A register, which is always kept up to date, should indicate for each articulated arm the number of operations carried out.
- A gas tightness test at 3 to 6 bar should preferably be performed before each operation.

<u>Identification</u>

The manufacturer should fit a corrosion resistant identity plate to the articulated arm and this should indicate the following characteristics:

- name of the manufacturer,
- code number in the series,
- maximum operating pressure,
- test pressure,
- minimum and maximum operating temperature,
- year of manufacture.

<u>Flanges and gaskets on fixed pipe work</u>

Refer to STS dealing with material of construction

If splash guards fixed over the flanges are used, these guards must be designed to avoid corrosion of the bolts, the flanges and the pipe work.

2.3.2. Valves

Refer to STS document on material of construction

2.3.3. Remote controlled device

A remote control device to enable the acid flow between the storage and loading point to be stopped should be installed. The remote control should be placed at sufficient distance from the storage and loading areas to enable it to be used in case of emergency.

One should take into account the potential risk of backflow from the storage tank (in case of unloading) or from the rail or road tank (in case of loading).

2.3.4. Control of the load

The control of the load can be made, for example by:

- weighting the mobile tank
- measuring the level or the weight of the acid in the storage tank.
- a flow measurement

2.3.5. Filling methods

The filling of the mobile tank can be achieved by the use of:

- the following types of pumps :
  - vertical submerged
  - canned pumps.
- dry inert gas pressure on the storage tank. A dew point of at least -10° C is required.

Precautions must be taken to avoid the back flow of HF into the inert gas system. The pressure of the inert gas to the storage tank must be limited to the maximum working pressure of the storage tank by use of a suitable pressure relief valve or other pressure limiting device.

Before leaving the station, each filled tank will be vented in order to reduce the concentration of inerts and limit the build-up of pressure during transportation.

The choice of the pressure in the tank leaving the plant should also consider the risk of vacuum during transportation.

2.3.6. Unloading methods

The unloading of a tank can be achieved by:

- dry inert gas pressure as indicated in *2.3.5. Filling methods*
- canned pumps connected to the liquid phase of the tank which is padded with dry inert gas.

The pressure of the inert gas in the tank should be limited to the strict minimum.

Before leaving the station, each tank will be vented to limit the pressure build up during transportation.

2.3.7. Purge of the connections

The filling line and particularly the connection should be self-draining. Any liquid acid which remains in the lines should be purged by:

- blowing through with dry inert gas to the tank or storage (or any other device like the absorption unit for example, provided it is protected against liquid arrival)
- external steam heating of the lines

2.3.8. Venting systems

A venting, recovering or scrubbing systems is required if, for example, dry inert gas is used for filling or unloading.

Precautions must be taken to prevent the entrance of moisture into the tank, e.g. a dry inert gas purge or a slight vacuum into the line to the scrubbing system.

2.3.9. Pipe work

The use of pipe work to a controlled specification and thickness is required. Bends and accessories (tees, reducers) must have at least the same thickness as the piping. 100% of the welds in newly constructed pipe work should be radio graphed.

2.4 Operations

2.4.1. Identifications of pipes and valves

Any method for having a clear identification of pipes and valves should be used. For example, use of tapes or pipe colour coding.

2.4.2. Preventive maintenance

Periodically, as a protective measure, the HF loading or unloading station user should overhaul equipment which is most susceptible to damage such as valves, pressure relief valves and pipe connections leading to filling or emptying tank, especially in the liquid phase. As a general principle, equipment should be replaced before there is a significant risk of its failure.

2.4.3. Filling in parallel

If several tanks have to be filled in parallel, the control of each load must be independent.

2.4.4. Control before filling tanks

The following controls should be made on the tank going to be filled:

- Identification and control of the HF services of the tank.
- Comparison between the tank weight and the tare. If the weight exceeds a certain limit above the tare, the contents of the tank should be checked.

Any contaminated tank must be cleaned before filling.

2.4.5. Controls before moving the tank

Confirm that the valves are in the closed position

Confirm that all pipes are disconnected between filling station and tank.

Install blank flanges on the tank car valves.

Secure the protection dome if installed in the closed position.

A check list for all necessary controls will be completed by the operators before the tank may leave the station.

2.4.6. Means of protection and warning

See *1.6.2. Recommendations concerning the means of protection and warning on the anhydrous HF storage tank*

2.5 Buildings

See *1.3.4. Buildings*

3. SAFETY EQUIPMENT FOR THE ABSORPTION OF GASEOUS EFFLUENTS CONTAINING HF

3.1 Objectives of the study

This recommendation provides guidance on the design and operation of HF absorption installations aimed at ensuring a high standard of safety.

3.2 Sources of HF which may be connected to the installation

- Continuous absorption of residual gases containing HF.
- Intermittent absorption of residual gases containing HF.
- Absorption of vent gas arising from start-up and shutdown of HF plants.
- Absorption of vent gases from valves or hydraulic seals or emergency relieves.
- Absorption of vent gases from loading and unloading operations.
- Absorption of vent gases from pressure relief valves.

These vent gases may contain other reagents, which will influence the choice of the absorbent. In the case of dealing with discontinuous emissions, the availability of the neutralizing medium must always be sufficient to handle the maximum gas flows requiring absorption.

The first priority for the design of an absorption system is to specify carefully:

- the total quantity of HF ;
- the composition of the gas stream ;
- the maximum instantaneous flow which has to be absorbed.

It has also to be considered whether it will be used continuously or only intermittently. This specification will influence the size of the unit, the storage capacity for the neutralization agent as well as the necessity for the installation of coolers, back-up systems or emergency supply for electricity and utilities.

3.3 Reagents normally used

- Water is able to absorb the HF content of inert gases efficiently. The efficiency is a function of the inlet concentration of HF in the vents and of the concentration and temperature of the solution.
    - Good efficiency generally involves several steps of scrubbing.
    - In order to avoid calcium fluoride plugging, the water must be low Ca content.
- Caustic soda or Sodium carbonate solution could also be used, provided that the solubility of NaF is not exceeded in the washing solution (40g/litter at ambient temperature).
- Potassium hydroxide solution may also be used. Potassium fluoride is in fact very soluble in the solution.
- Milk of lime should not be used because of the low solubility of CaF_2
- HF could be partially absorbed in sulphuric acid.

3.4 Technical design of absorption systems

Generally the absorption system should generate slight suction which is inherent for ejector scrubbers based on the Venturi principle. This construction is relatively simple, only one pump is needed for liquid circulation and suction. But the ejector has to be designed by an experienced supplier.

Packed columns need a pump for liquid circulation and a blower for suction. This system has a better emergency running behaviour if electricity supply fails, especially when a caustic soda or potash stock is stored in a head tank.

When water is used for HF abatement, several transfer units may be necessary, according to the concentration of the solution. Water must be calcium free to avoid calcium fluoride precipitation.

The volume of water or absorption reagent should be large enough to provide heat removal or a heat exchanger should be used.

Regular monitoring of the scrubber performance is necessary.

An absorption system is designed to handle HF gas and not liquid, usually at ambient pressure. Where it is used for relief's of liquid HF systems it must be protected by a knock out pot (filled with a level alarm) from which liquid HF is allowed to vaporize off at an acceptable rate or to be drained carefully; depending on the conditions and concentrations.

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

The liquid effluent from the scrubber must be treated before disposal. Lime slurry may be used to precipitate calcium fluoride

3.5 Recommendations concerning the pipeline systems for HF vents

- The first priority is to specify very carefully the materials, the composition and the quantities which have to be absorbed from the various vents. This should also include a specification of the maximum and minimum concentrations, the maximum instantaneous flow and the total quantities which need to be absorbed. The gas compositions must be specified. One must also, in particular, take into account the most unfavourable circumstances which will have to be dealt with.
- As far as possible the vent gas mains should form a closed system and all connections to it should be gas tight. In order to avoid accidental emission of HF, for example, due to inadequate suction on the vent gas headers. As a result, it is not advisable to use the same main for decontamination before maintenance and for the process vents. It is also recommended to have a dedicated network collecting the outlets of the safety relief valves.
- The pipe work should also prevent the return of humidity from the absorber system to the dry parts of the unit. This can be achieved, e.g. by a controlled purge system. Alternatively the dry parts of the unit can be manufactured from materials which resist corrosion of wet HF.

Another solution is to have the network made in material resistant to wet HF and to guarantee a permanent suction in the pipe (by means of a fan associated with an anti-vacuum check valve).

Use of rupture disc in network only used for emergency (safety relief valves) can be also an alternative.

- The pipe work headers should be of adequate size so that an emission in any part of the system does not lead to an escape of HF from any other part of the network. This requirement can be met by the use of expansion tanks or buffer capacities. In particular one can install if necessary an expansion tank (behind a pressure relief device) to limit the pressure surge in the network which can result from the operation of the pressure limiting device.
- Connection to the vent gas network from exceptional points of emission (for example relief valves) should be designed to indicate any continuous source of flow. This can be achieved, for example, by the use of a bursting disc before the relief valve and the installation of a leak detector between the bursting disc and the relief valve. It can also be achieved by the installation of a level alarm on a catch pot. In any situation where there is a risk of occasional leakage of liquid HF into the system, one should install liquid/gas separators on the line and these separators can be fitted with a level or weight alarm, which will indicate the presence of liquid HF in the separator. Precautions must be taken to avoid any contact between liquid HF, water and aqueous absorbents.
- The materials of construction of the headers should be designed to take into account the quality, composition and temperature of the vents, under anticipated upset exceptional modes of operation.
- The required gas rates for the maximum throughput should be permanently guaranteed, if necessary, by the installation of a second vent fan and an emergency power system. Where an ejector is used to create the necessary suction, a stand-by suction system should be included. In the design of systems for dealing with accidental intermittent emissions, one should take account of the maximum number of emissions which could occur simultaneously.
- The possible presence of liquid at low points in the network should be considered and necessary drainage systems installed. Branches on the headers should preferably be top connections.

3.6 Recommendations concerning the absorption equipment

- The absorption reactor is generally designed as a packed column or an ejector system also combined units of both are in use.
- Since the equipment must absorb the throughput of gas indicated before, the flow-rate of absorbent which is circulated within the absorption system should be at least equal to that necessary to neutralize or absorb this flow-rate of gas.
- Where individual vents cannot be rigidly controlled, the flow-rate of absorption medium should be permanently maintained.
- The volume of absorption agent immediately available for use should not be less than the equivalent amount required to absorb the maximum quantity of HF, which could occur in the worst case. This required volume of absorption agent can be provided from an emergency head tank.
- The pressure drop in the absorption system should always be compatible with the vent gas collection system. In particular the absorption towers should operate at

a point well away from the point of flooding under the most unfavourable operating conditions. The pressure drop should be checked regularly, and if necessary the airflow to the absorber system should be reduced, in order to ensure that the pressure drop is compatible with the design requirements for the installation.

- If necessary, the absorbent may circulated to the tower via a water cooled heat exchanger
- Depending on the pressure of the source from which the gas is assumed to arise it may be necessary to install a fan after or before the absorber to vent any inerts to the atmosphere
- When water is used as absorbent it may be useful to have 2 towers in series at different HF concentration levels or to add at the top of the column some absorption bubble tray plates fed with pure water at the top
- Except under circumstances where the HF vent rate can be controlled, the services which operate the absorption installation (electric power, instrument air) should be guaranteed as permanently available either by installed spares or by the provision of a stand-by supply.
- For pneumatic valves, the mode of failure of the valves to the closed or open position on failure of the air supply should be compatible with the basic safety requirements of the installation.
- Safety equipment
  - As a minimum the following alarm systems should be installed on the absorption equipment :
    - Low flow of the absorption medium.
    - Failure of the circulating pumps.
    - Low/High pressure alarm
    - Failure of the vent fan
    - In addition all precautions must be taken to avoid back flow of aqueous absorbents to the dry parts of the system.
  - If the overall heat balance on the equipment is important then a cooling system should be incorporated in the absorbent circuit.
  - Because of the risk of overload of the absorption system and subsequent HF emission, care must be taken regarding the location of all air intakes of surrounding buildings ventilation. It is advisable to provide emergency shutdown of the ventilation fans should HF be released to atmosphere.

3.7 Operation

- The pressure drop in each absorption system required to meet the maximum designed throughput should be checked periodically, if necessary by the use of a controlled throughput of air.
- The satisfactory operation of the system, that is circulation of absorbent and throughput of gas, should be checked periodically.
- Regular checks should be carried out to determine the residual absorbent strength or HF concentration in the absorption medium.
- For normal condition of continuous flow, stream water absorption will allow

concentration of HF in the exhaust to be reduced to 5 ppm w/w (in the absence of mist). In emergency situations this result can not be achieved and hence a total design efficiency of 99,5% is used.

- Crane and truck impacts shall be prevented by controlled access. Heavy maintenance work should only be allowed after full assessment of the hazard involved. The unit shall be enclosed in a restricted area where maintenance work is controlled by suitable procedures.

4. A SAFETY AUDIT SCHEME AT HF PRODUCER/CUSTOMER PLANT

4.1 Purpose

The purpose of this scheme is to ensure that adequate equipment, appropriate operating procedures and trained personnel are in place on producer's/customer's premises to permit the safe unloading, storage, and handling of liquid HF.

4.2 Scope

The principal objective is to ensure that the transfer of HF from the delivering vessel to the customer's facilities can be carried out safely.

The visit should also be used to:

- assess that the general policy and procedures in use are adequate,
- obtain customer's comments on the transport operation and equipment being used.

Customers should be instructed to immediately report to the supplier any difficulties which are experienced with the operation of valves. The provision of an information tag on the returning transport equipment identifying the difficulty can be of assistance.

4.3 Conduct of a visit

It is recommended that the relevant checklists are used during the visit as an aid to ensure that all items are considered.

4.4 General summarizing considerations

At the end of the visit what is the general impression of the operation.

- Is the housekeeping correct?
- Is the plant organization satisfactory?
- Is the attitude to safety good?

4.5 AHF unloading

4.5.1. The unloading area

<u>Ease of access especially for road vehicles.</u>

- Is the unloading area situated within the customer's premises, easily and safely accessible?
- Is the unloading area located on a flat ground?

There should be adequate access for vehicular movements without endangering people and equipment. Access roadways should be in good condition such that vehicles can safely enter and depart the unloading area, in the later case, particularly in the event of an emergency.

<u>Separation from other activities</u>

- Is the unloading area sufficiently separated from traffic and from risks of fire and explosion?

Facilities to isolate area and prevent movement of the transport container during unloading

- Are chocks, physical barriers, warning notices, existing and used?

Consideration given to mitigation

- Are there possibilities for mitigation in case of leak? (e.g. water curtain...). Are there provision for spill containment and neutralization?

Waiting tanks

- If the tank cannot be unloaded immediately, is there a suitable area for safe parking?

4.5.2. The unloading facility

Safety of the personnel

- Are easy ways of escape provided?
- Are personnel working on top of transport containers protected against fall?
- Are personnel equipped with adequate respiratory equipment?
- Is self-breathing equipment easily available?

Valves

- Are Eurofluor recommended manual and automatic shut off valves installed and connected?
- Are the manual valves located in accessible position?

Flexible connection

- Are adequate flexible connections or articulated arms stored and maintained in good condition?
- Is the date of commissioning marked so that they can be maintained in due time?
- Is there a possibility of quickly isolating the connections in case of emergency by several activation points?

Gaskets

- Are gaskets, of a recommended type, replaced after each use for each connection? See STS recommendations about material of construction

Bolts

- Are bolts of the recommended type used? See STS recommendations about material of construction

Commodities

- Is sufficient air pressure available for pneumatic valves operations?
- Are several push buttons available, well located in case of emergency, to actuate the shut-off valves?
- Is facility provided for degassing the lines and preventing emission?
- Are precautions taken to prevent liquid HF arrival to the vent system? Is there a liquid trap with alarm on the vent line?

4.5.3. The unloading procedure

Written procedure

- Does a detailed written procedure exist, is it posted up, understood adequate and strictly followed?

Personnel

- Are the off-loading operators well trained?
- Is the operator present during off-loading?

Specific precautions

During unloading:

- Has the receiving tank enough capacity to accept the entire mobile tank load?
- Are all precautions taken to avoid overpressure of the mobile tank?
- Are all precautions taken to prevent back flow and contamination of the mobile tank?

Supervision of the empty transport container

- Are the valves blank-flanged with gaskets and all bolts in place?
- Has any defect (e.g. valve passing) been signalled?
- Is the dome cover fixed?
- Is the labelling complete?

First aid

- Is the medical staff fully aware of the medical treatment of HF burns?
- Is first aid equipment available at the plant?
- Are the special safety facilities (see *1.6.2. Recommendations concerning the means of protection and warning on the anhydrous HF storage tank*) available? (Safety shower, eye wash fountains, eyewash bottles, calcium gluconate gel...).

4.6 Liquid storage

4.6.1. Storage sitting

- Location :
    - is the storage in the open air?
    - under a roof?
    - in a light building?

    - in a closed bunker?
- Is the storage adequately located with no risk of fire, explosion or mechanical impact nearby?
- Is the storage bunded?
    - Without any permanent drain?
    - Does the bund material resist HF?
- Are the access and ways of escape easy?
- Is the storage tank properly anchored even in case of flooding in the bund?

4.6.2. Tank design

- Are the design temperatures and pressures correctly determined (working pressure, maximum operating pressure, test pressure...)?
- Is there a corrosion allowance for the tank and branches?
- Are the materials adequately chosen for hydrogen assisted stress corrosion resistance?
- Is the steel of tank and liquid piping of adequate impact strength at the minimum design and outside temperature chosen?
- Has the tank been stress relieved?
- Have the tank and related pipe work been completely inspected during construction? (100% radiography of welds, ultrasonic tests...).
- Is the tank externally protected against corrosion?
- If any thermal insulation is the material adequate? (incombustible, chemically inert to HF).
- Are the supports adequately designed? (allowing thermal expansion of the tank, preventing excessive stress on the shell and preventing corrosion by accumulation of moisture, allowing hydrogen vent).
- Are all openings in the top of the tank? Are they all necessary?
- If not, is the design satisfactory for safety? (bottom, valve of high quality...).
- Are all nozzles very short and flanged?
- Are the flanges bolts and gaskets as recommended by Eurofluor?

4.6.3. Accessories

- Are the valves for tank isolation directly flanged on the nozzles?
- Are all these valves of a type recommended by Eurofluor?
- Are there remotely operable shut-off valves?
- On the main pipes, are there additional manual valves for routine operation?
- Is there an overpressure protection system? Is the redundancy satisfactory (high pressure alarms)?
- If safety relief valves are used, are they protected from corrosion upstream and downstream?
- If bursting discs are installed upstream of safety valves, is a padding pressure provided in between and a low and high pressure alarms installed to check the tightness of the disc? (covering all cases of pressure in the tank).
- Can the relief valve be isolated in case of necessity?

- Is the relief designed at least for the overflow case?
- Is the system connected to an absorption facility?
- Is a liquid trap of sufficient capacity installed between relief system and absorption facility?
- Is this trap provided with liquid alarm? Weight sensors?
- Is the tank equipped with a weight gauge?
  - Instrumentation (on each tank): see *1.5.4. Recommended equipment for storage*
- Is there an independent high weight or level alarm?
- Is there a level gauge?
- Is there a pressure gauge?
- Are all hydraulic fluids or oils compatible with HF? e.g. in transmitters.

4.6.4. Commissioning

- Have all the following operations been carefully done before normal service? (after construction, maintenance or periodic inspection).
- Visual inspection.
- Mill scale removal.
- Cleaning.
- Degreasing (only HF compatible greases could be used).
- Drying (final dew point < -40°C).
- Leak testing.

4.6.5. Operation

<u>Liquid HF transfer by gas padding</u>

This part of the questionnaire may also be used to complete the unloading check-list.

- If air or nitrogen is used, it must be:
  - pure and oil free
  - dry, dew point lower than -40°C.
- Is there no risk of moisture introduction?
- Is there no risk of reactive material introduction?
- Is there a risk of back flow of HF into the air or nitrogen network?

<u>Liquid HF transfer by a pump</u>

- Is the pump specially designed for HF service? (submerged pump or canned pump, last one must be in full compliance with the STS document equipment for HF handling)

<u>Protection against backflow of water or reactive material</u>

- Between HF tank and process, is a sufficient differential pressure with alarm always maintained and protection against backflow with enough redundancy?
- Is there an automatic shut-off valve?

- Is there also a liquid trap and non-return protection between HF tank and absorption unit?

4.6.6. Emergency procedures

- Is there a possibility of quick depressurization of a tank pressure?
- Is there an empty emergency tank available with possibility of emergency transfer of a storage tank?
- Does an emergency procedure exist?
- Is there an easy access to all valves of the tank (even when wearing full personal protective equipment)

4.6.7. Maintenance and periodic inspection

- Do written codes exist for :
    - The list of all points to be checked?
    - The preparation for internal inspection
    - The entry personnel in the tank?
    - The hydrostatic test procedure?
    - The preparation for service? (cleaning, drying, decommissioning).
    - The dates and frequencies of the different inspections?
- For the tank inspection, are thickness measurements regularly made? (wall and nozzles).
- Are all the valves regularly inspected and operated?
- Are the safety relief devices systematically replaced or overhauled?
- Are all the measuring systems regularly tested?

4.6.8. Safety, methods of protection and alarms

- Are HF detectors or other leak detecting systems installed?
- Is quick isolation of any tank possible?
- Are push-buttons available in various locations for this function?
- Are there possibilities for mitigation in case of leak? (e.g. water curtain...).
- Is there a visible indication of the wind direction?
- Is protective equipment easily available in sufficient quantity and properly maintained? (cartridge respirators, self-contained breathing equipment, protective clothing).

4.7 Piping

- Is the material adequately chosen for the whole range of possible operating conditions?
- Is the mechanical robustness of the system sufficient? (protection against impact, pressure rating, corrosion allowance).
- Are all the pipe diameters of large enough? (1'' or more)
- Are all the pipes diameters not to large (below 150 mm)

- Is the HF velocity in the pipes small enough? (at room temperature, not more than 1.5 m/s for liquids, 10 m/s for pure gas and 4 m/s for gases where liquid entrainment is likely (see our “Recommendation on materials of construction for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions”).
- Is the risk of excess pressure due to liquid HF trapping between valves in a pipe taken into account?
- Are the flanges, bolts and gaskets adequate?
- Do the valves comply with Eurofluor recommendations?
- Is the general lay-out adequate and permitting convenient access?
- Is the pipe supporting adequate?
- Is the corrosion protection adequate?
- Are venting and purging possibilities provided?
- Are the pipes adequately located and labelled?
- If any insulation, is the insulation material suitable? (not easily flammable, chemically inert to HF, gastight, for moisture ingress prevention not corroding the pipe).
- Are there written procedures for construction, commissioning and maintenance?

4.8 Vaporization

When a vaporizer is used:

- Is the design adequate for HF use? (easy drying and maintenance, no risk of plug flow, no dead space).
- Is the material adequate for service at the lowest and highest possible temperatures?
- Does the heating medium avoid undesired overheating?
- Is there a HF super heater zone?
- Is there a liquid trap with alarm to prevent any liquid HF entrainment to the consumer unit?
- If necessary, especially when isolation is possible, is there a safety relief valve or any other pressure limiting device installed, and are the possible vents correctly handled?
- Is there protection (with redundancy) against water or organic materials back flow? (liquid trap, differential pressure valve...).
- Is there a detection of leak in the heating fluid?
- Is there adequate instrumentation (and control system) provided? (e.g. for high pressure or low temperature).
- Is there a written procedure for commissioning?
- Is there a periodic inspection?

4.9 Safety absorption system

- Is there a facility for the treatment of gaseous effluents containing HF?
- Is the system of adequate size such that any HF escape from any part of the network is prevented? Can all the possible sources of HF be collected?
- Is the instantaneous absorption capacity large enough?

- Is the absorption capacity sufficient for the biggest HF total quantity that could be vented?
- Is the absorbent inventory large enough?
- Is the equipment reliability high enough? (E.g. spare electric supply, spare fan, and spare pump).
- Is the system fully protected against liquid HF introduction? (e.g. existence of a liquid trap with alarm).
- Is the pressure drop in the system regularly checked?
- Is the temperature of the absorbent regularly checked?
- Is the concentration of the absorbent regularly checked?
- Is the concentration of HF in the gas discharge checked?
- Are the liquid effluents adequately treated before discharge?

4.10 Commodities

4.10.1. Instrument air

- Is there no possibility of direct connection of the air network with the HF system?

4.10.2. Padding and purging gas

- Is the gas (air, nitrogen) not contaminated by harmful impurities?
- Is the moisture content below dew point of -40° C and regularly checked?
- Is the use of this gas strictly limited to the HF system?
  - If not, is any ingress of HF in the padding and purging gas network adequately prevented? (pressure differential with alarm, automatic shut-off valve, a single check valve is not considered as sufficient).

4.10.3. Sewage systems

- Are there no possibilities of liquid HF introduction into the sewers?

4.11 General considerations and process safety management

4.11.1. Process safety information: Does following information exist?

- Information on materials and products.
- Information on legal and official codes and rules.
- Up-to-date permits and inspection.
- Drawings, PID and logic diagrams complete and up-to-date.
- Process book complete and up-to-date.

4.11.2. Operating procedures and safety instructions

- Are complete written operating procedures and safety instructions for commissioning, start-up, normal operation, shutdown, maintenance, periodic inspection existing. Are they distributed wherever useful and well known?

4.11.3. Equipment integrity

- Are equipments, fabricated maintenance materials, and spare parts suitable for their process application? Are there written procedures to maintain the integrity of these equipments?
- Is the equipment regularly inspected and tested notably all the alarms, and are the deficiencies systematically corrected?

4.11.4. Process hazards analysis

- Have possible incidents been identified? Are their consequences evaluated? Has consideration been given to reduction of the hazard, consequence and/or probability?

4.11.5. Safe work practices

- Is it a special access permit for cranes and heavy vehicles?
- Is a formal authorization to be issued for all work in the HF area and a special hot work permit required on HF systems? Is the work followed up by the operation supervisor?
- Is protective equipment available and adequately used? Is there a reliable communication system? Is there a specific training on its use?

4.11.6. Training

- Does each employee involved in operating the process receive training about the process operating procedures and safe work practice?
- Is refresher training systematically organized?
- Do maintenance personnel and contractor's personnel also receive necessary training?
- Does training include emergency drills?

4.11.7. Management of changes

- Do procedures exist to assure that the technical basis, impact on safety, modification of existing procedures and necessary training are considered before a change is implemented?

4.11.8. Pre start-up safety review

- Is a review conducted prior to start-up to confirm that construction and equipment are in accordance with design specification, that adequate safety procedures are in place and that training has been completed?

4.11.9. Emergency response

- Does the emergency response system include written procedure, formation, and training?
- Have contact with authorities and contact with supplier been considered? Is simulation of incidents included in the training?

4.11.10. Incident investigation

- Is every significant incident followed by a discussion of the measures to be taken, and distribution of the information?

5. HAZARD REVIEWS IN THE HF PLANTS

5.1 General comments

5.1.1. Introduction

Any responsible manufacturer or user of hazardous substances such as HF must be able to satisfy himself, his workforce and his regulatory authority that his process is safeguarded against major loss of containment. To do this he needs to demonstrate that he has identified all foreseeable hazards and is aware of their causes. Against each of these causes, he must be able to show that either their likelihood is remote or that the plant has design standards and operating procedures which give very high confidence that they will not arise. Where the gravity of the possible consequence justifies it, he should be able to point to back-up systems that will reliably intercept and correct deviations should the primary control measures fail. Finally he should be able to show that wherever practicable he has provided emergency procedures and means of mitigating the consequences of spillages if, despite high standards of control and containment, these should occur.

To carry out this review we recommend that a formal audit be undertaken. The purpose of this note therefore is to provide guidance on the range of hazards that should typically be considered, to illustration the extent and type of countermeasures that need to be in place and to show how the review can be presented methodically in tabular form.

5.1.2. Tables

Eurofluor has set up lists of causes of potential hazards for some specific units of HF plants:

- HF storages
- Absorption units
- Loading and unloading stations

For each cause, the table provides preventative measures, corrective measures and emergency measures.

"Preventative" means that the measures are able to prevent the deviation from occurring.

"Corrective" means that the measures are able to limit the extent of the deviation.

"Emergency" means that the measures are able to limit the effects and consequences of the deviation once containment is lost.

These tables are given only as an example and each plant must carry out its own site specific study.

In particular, the preventative, corrective and emergency measures are given only as examples and must be adjusted to the specific case taking in account specific factors such as the size, the location and the activity of the plant. There is also no intention to imply that the measures described are all necessary or adequate: it is a list amongst which measures can be selected, leaving the designer free to choose the best adapted, or use other to fulfil the same purpose.

These tables can also be used for developing training packages e.g. tape slides and video to communicate an understanding on hazards and control measures to operators and supervisors on the plants.

An audit such as that described will not only provide assurance to management, workforce and the authorities but can be referenced as the source of essential supporting argument where safety reports are required under the EEC Seveso Directive 501/82.

5.2 Tank storage area

5.2.1. Hazards: Loss of containment of liquid HF due to vessel failure

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
A Loss of containment of liquid HF due to vessel failure	A/1.1. Severe explosion (domino effect)	1. There are no plants in the near vicinity which represent a serious explosion risk to the tank storage area.		1. HF detectors information, relayed to control room 2. Remotely operated shutdown valves on pump delivery lines 3. Remotely operated shutdown valves on tank bottom run offs with back-up manual operation available locally 4. Pumps can be remotely tripped 5. All stock tanks bunded and bund design has slope which collects liquid HF in small surface area collection pit 6. Facility to transfer liquid HF to vented tanks
	A/1.2. Sabotage, civil commotion, acts of war	1. The site has a security section that carry out routine patrols. (An incident caused by civil commotion may be prevented by the security section). 2. Process operators are in the vicinity of the stock tank area 24 hours per day and have routine inspection tours to make. 3. It is recognized that neither of the above measures can be considered completely effective against a determined saboteur with the necessary technical experience		

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	A/1.3. Subsidence	1. All stock tanks mounted on concrete plinths. 2. Tank storage area is not liable to subsidence.		7. Spare storage capacity in HF stock tanks to accept liquid from any stock tank 8. Plant emergency procedures 9. Works emergency procedures
	A/1.4. Earthquake, High Winds	1. Possible seismic effect considered at design stage. 2. The storage tank structure has been designed to withstand the normal extremes or wind forces experienced in the country		
	A/1.5. Fire, radiant heat	1. Storage area away from major flammable hazards - Flammable liquids wagons and solids flammable storage prohibited at less than minimum distance 2. Insulation material, if any, is chosen to have fire retardant characteristics i.e. it chars rather than melts and therefore protects the tank from external heat for a short period of time 3. Any "hot work" i.e. welding, burning etc is assessed under permit to work procedures with	1. High pressure alarm on stock tanks gives early indication of temperature rise 2. Failure of stock tank bursting discs and / or relief valves at higher pressure initiate second alarm 3. Water spray cooling (fixed or mobile) 4. High temperature alarm	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		stock tanks purged free of HF		
	A/1.6. Accidental damage collision, impact, aircraft	1. Crash barriers where appropriate, are fitted to protect stock tanks and pipe work 2. Supervision of crane and mobile platform operations. Permit to work 3. Because of the small target area presented by the HF storage area, the major accident frequency from aircraft impact is considered negligible except in special cases		
	A/2 Process related causes of vessel failure A/2.1a Over pressurization (vapour padding / inert)	1. Operating principle to maintain stock tank pressure below the maximum allowable pressure 2. Padding gas is not permanently connected (or 4) 3. Operator awareness of isolation of stock tanks with inert present 4. Gas padding pressure less than	1. Regular checks on stock tank pressures by process operators 2. High pressure alarms on stock tanks 3. Bursting discs or/and relief valves	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		maximum allowable working pressure		
	A/2.1b Over pressurization (liquid overfill)	1. Definition of stock tank operating range 2. Unloading pump discharge pressure maximum less than maximum allowable system pressure 3. Design standards of pump, pipe work and vessels 4. Pressure relief inspections 5. Procedure for tank unloading (check of the free volume of storage tank compared to the volume of the railcar or tank car before unloading)	1. Pump trips at high level and/or pressure 2. Two independent level/weight alarms on receiving tank 3. Pressure alarm on receiving tank 4. Pump can be tripped remotely 5. Pressures and levels in tanks monitored regularly by process operator 6. Bursting discs and/or relief valves at appropriate settings	
	A/2.1c Over pressurization (hydraulic thermal liquid expansion)	1. Definition of stock tank operating range 2. Normal operating principles, procedures and operator awareness	1. Pressure alarms (maximum) 2. Two independent overfilling alarms using different physical measurement principles 3. Pressures and levels in tanks monitored regularly by process operator 4. Bursting discs and/or relief	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
			valves 5. Independent weight or level monitoring by supervisor in control room	
	A/2.2 Under pressurization as a result of excessive vacuum from the vents system or pump suction or low temperature	1. Vent suctions cannot exceed the minimum vessel design pressure 2. Operating procedures discourage pumping at tank pressures below 0.5 bar g. 3. Vaporization resulting from heat ingress and temperature into the stock tank compensates for liquid displacement 4. Tank should withstand vacuum	1. Low pressure in stock tank trips pump	
	A/2.3. Internal explosion	No conceivable reasons for a situation resulting in internal explosion		
	(a) Water/HF reactions	1. Maintenance procedures (i.e. all branches to tank physically disconnected before water is introduced. No HF in tank before water is introduced or	1. High alarm on padding gas moisture indicator	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		neutralization performed with soda ash 2. Recommissioning procedures check for water and carry out moisture analysis 3. Padding gas moisture indicators 4. Routine blow down of air receivers and filters to remove any residual moisture 5. Design of vent system prevents moisture ingress from vent absorption unit 6. HF treatment and rectification reduce moisture content in HF less than 0.3%	2. Regular analysis of liquid HF to check moisture content	
	A/2.4 Severe corrosion (internal)	1. All the preventative measures described in water/HF reactions A/2.3 apply	1. All the control measures described in water/HF reactions A/2.3 apply 2. Pressure vessel inspections	
	Severe corrosion (external)	1. Insulation specification to inhibit water ingress and properly maintained 2. All stock tanks operated at sub-zero temperatures are	1. Pressure vessel inspections include selective removal of insulation to permit inspection of external surfaces	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		insulated and freeze/thaw situation is controlled		
	A/2.5 Low temperature thermal stress	1. Carbon steel vessels, welds etc used in the fabrication of the stock tanks have been stress relieved to prevent failure from high induced stresses 2. Prohibit excessive physical force on valves in tank branches 3. Steel resilient for low temperature		
	A/3 Stock tank (at ambient temperature) joint leaks	1. All joints on the storage tanks are located in the vapour space. If bottom branches are used, their number and sizes are limited and the arrangements flange-gasket are Described can be in ▪ tongue and groove arrangement with 100% PTFE gaskets(with care of possible corrosion of the tongue) ▪ flat face flanges with spiral wound metal (e.g. stainless	1. Isolation valve on stock tanks liquid outlets can be closed remotely and manually 2. Isolation valve tested regularly by process operators	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		steel for AHF below 50°C) + graphite gaskets (with careful choice of the metal spiral wound) ▪ flat face flanges with 100% PTFE gaskets (with care of possible cold flow of PTFE) 2. Joint design according to STS recommendations 3. Training of craftsmen to ensure standard joints used and inspection by supervisor 4. All liquid and gas HF joints are gas tested during recommissioning		

5.2.2. Hazards: Loss of containment of liquid HF due to pipe work failure local to stock tank

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
B Loss of containment of liquid HF due to pipe work failure local to stock tank	B/1 Physical damage B/1.1. Impact	1. Protection of pipe bridge supports 2. Crash barriers are fitted where appropriate to protect stock tanks and pipe work 3. Supervision of crane operations 4. Cranes and mobile work platforms are not allowed without permit		
	B/1.2. Fire	1. Storage area away from major flammable hazards		
	B/1.3. Fatigue (liquid hammer, vibration)	1. Shut down valves are slow acting to prevent liquid hammer 2. Manual isolation valves require several turns to close and therefore by their nature are slow closing 3. Pipe work and valves fully supported to avoid overstressing 4. Vibration free pipe work 5. Pipe work flexibility studies are		

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		required		
	B/1.4. Support failure	1. Design standards specify support requirements	1. Pipe work local to stock tanks inspected when stock tanks undergo pressure vessel inspection 2. Regular plant patrols by process operator	
	B/2 Process related causes B/2.1. Trapped liquid HF (flange leak)	1. Process operator awareness 2. Maintenance and operating procedures ensure liquid HF mains are drained after use in batch operations	1. Thermal relieves fitted where two valves are far enough apart to be operated by different operators 2. Thermal relieves fitted between two automatic valves	
	B/2.2. Erosion	1. Maximum liquid HF velocities do not exceed 1.5 m/sec (room temperature) 2. Check of wall thickness		
	B/2.3. Corrosion	1. Insulation specification to inhibit water ingress	1. Pipe work local to stock tanks inspected periodically when stock tanks undergo pressure vessel inspection	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
			2. Regular monitoring of moisture concentrations in liquid HF	
	B/2.4. Maintenance activity	1. Procedures jointly developed by process and maintenance 2. Experienced personnel present during break-ins to liquid HF mains 3. HF mains placed under suction before break-in starts		
	B/2.5. Non conformity with standards (Gasket specification, materials)	1. All liquid HF pipe work according to STS recommendation equipment for HF handling 2. Gaskets according to STS recommendation equipment for HF handling		

5.2.3. Hazards: Loss of containment of liquid HF due to pump failure

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
C Loss of containment of liquid HF due to pump failure	C/1 Specification shortcoming (materials)	Documentation checks prior to pump replacement		
	C/2 Wear out (can failure)	1. Routine plant patrols by process operator to detect abnormalities (e.g. characteristic noise) 2. Pump cavitation prevented by maintaining sufficient NPSH by stock tank level	1. Low recirculation flows in the canned pumps trip pumps 2. Dry trip pump 3. Low lube flow (or equivalent) trips the pumps (for canned pumps) 4. Motor outer casing and cable gland designed to withstand full pump pressure on can failure (for canned pumps) 5. Use of a barrel equipped with leak detection (pressure gauge)	
	C/3 Casing failure (corrosion due to moisture)	1. Pre-commissioning procedure for dry-out	1. Low tube flow (or equivalent) trips the pumps (for canned pumps) 2. High temperature alarm in motor windings	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
			3. Regular monitoring of moisture in HF	
	C/4 Thermal stress	1. Pre-commissioning procedure		

5.2.4. Hazards: Miscellaneous causes of leaks

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
D Miscellaneous causes of leaks	D/1 Liquid HF in vent	1. Operating principles 2. Tank operating range 3. Liquid traps in vents 4. Post maintenance procedures for pump	1. Level alarms on stock tanks	Control and increase venting rate. Drain liquid to vented tanks
	D/2 Contamination of padding gas	1. Under normal operation the padding gas pressure is always higher than the pressures in the pipe work and stock tanks 2. Differential pressure control system on padding gas supply 3.Operator awareness	1. Regular checks on stock tank pressure by process operator 2. High and low pressure alarms on padding gas supply to stock tanks 3. Padding gas HF detector and differential pressure control after air driers 4. Padding gas blow down to absorption unit	
	D/3 Valve leaks	1. Preference for STS approved valves See recommendation STS	1. Key isolation valves exercised frequently or on regular schedule	

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	D/4 Maintenance shortcomings (flexible vent connections)	1. Clearance certificate procedure 2. Process maintenance supervisor role 3. Training 4. Liquid HF gaskets controlled 5. Avoidance of hoses permanently connected to vents. 6. Permanent venting arrangements for maintenance are generally provided where appropriate		
	D/5 Modification shortcomings	1. Hazard and operability studies carried out by multi-disciplinary team 2. Equipment specifications produced by experienced mechanical and chemical engineers 3. Work procedures 4. Safety audits 5. Plant inspections 6. Precommissioning procedures		

HAZARD	CAUSE	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	D/6 Small bore pipe work leaks (e.g. instruments)	1. Avoidance of small bore branches less than 1"	1. All instrument connections backed by process isolation valves	
	D/7 Error in tank unloading	1. HF tank wagons are on dedicated duty with specific connections 2. Standardized layout of valves according STS recommendation 3. Check of wagons on reception (documentation, valves, tightness)		
	D/8 Error of pipe during maintenance	1. Mark HF lines 2. Procedure for work on HF lines		
	D/9 Imperfect repair	1. Checks for quality of repairs 2. Recommissioning of equipment after repair		

5.3 Absorption unit area

5.3.1. Hazards: HF to atmosphere via vent

<table>
<tr><th>HAZARD</th><th>CAUSED BY</th><th>PREVENTATIVE MEASURES</th><th>CORRECTIVE MEASURES</th><th>EMERGENCY MEASURES</th></tr>
<tr><td rowspan="3">A
HF to atmosphere via vent</td><td>A.1.
Gas breakthrough due to excess of HF in vents</td><td>1. Additional water available
2. Control of HF concentration in tanks
3. Alarm in case of relief
4. Two towers in series
5. Design capacity well studied
6. Neutralization agent available</td><td>1. HF solution concentration / alarm</td><td rowspan="3">1. Alarm on HF in vent
2. Reduce load
3. Controlled site shut down
4. Initiate plant gas alarm</td></tr>
<tr><td>A.2.
Gas breakthrough due to loss of tower circulation</td><td>1. Spare pump installed
2. Emergency power supply and automatic change over
3. Reliable electrical supplies
4. Two towers / scrubbers in series
5. Gravity feed / or water guaranteed pressure</td><td>1. Alarms on loss of circulation (flow rate)
2. Alarm indicates pumps stopped
3. Alarm on motor current
4. Alarm on HF breakthrough in vent</td></tr>
<tr><td>A.3.
Gas breakthrough due to inadequate wetting/ distribution</td><td>1. Circulation normally controlled
2. Two towers / scrubbers in series
3. Design of liquid distributor</td><td>1. Alarm on loss of circulation
2. Alarm on HF breakthrough
3. Increase water / liquid supply to towers</td></tr>
</table>

5.3.2. Hazards: HF to atmosphere via blockage or suction failure

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
B Blockage or suction failure	B.1. Loss of fan suction due to : a) Power failure b) Instrument power supply failure c) Direct drive coupling failure	1. One fan in stand by 2. Emergency power supply 3. Reliable power supply 4. Policy on fan maintenance (outage a minimum) 5. Policy re-alternate operation of fans 6. Indication of power supply status	1. Alarm when fan tripped 2. Low suction alarm 3. Start the stand-by fan	
	B.2. Loss of suction due to massive air ingress	1. Operators are alert to consequences 2. Design for high flow of air per fan	1. Low suction alarm	
	B.3. Blockage due to tower flooding	1. Tower designed to absorb maximum expected flow rate	1. Low suction alarm	
	B.4. Blockage due to tower scaling up	1. Low freezing point 2. Choice of soluble neutralizing agent 3. Large tower capacity and circulation flows	1. Routine pressure drop checks 2. Low/High suction alarms depending on the position of the fan	

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		4. Routine shift analysis of salt strength (titration) or pH 5. Periodic wash out		

5.3.3. Hazards: HF to atmosphere due to pipe-work / vessel damage

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
C HF to atmosphere due to pipe-work / vessel damage	C.1. Thermal stress due to liquid carry-over	1. Avoidance of liquid HF in vents (liquid traps) 2. Liquid in vent detectors at vulnerable sources 3. Buffer tank when liquid can be expected in vents	1. Identify and stop liquid carry over at source	
	C.2. Exceeding design temperature due to insufficient liquid irrigation	1. All major relieves initiate absorption liquid at max rate 2. Two towers/scrubbers in series 3. Design of tower operation for maximum expected flow rate (cooling if necessary) 4. Design rating of towers (max 75°C) 5. All measures of section A2 and A3 apply	1. Temperature alarm on liquid tower exit (30°C) 2. Temperature record / alarm on towers (30°C) 3. Increase liquid circulation rates	
	C.3. Physical damage during maintenance (e.g. crane impact)	1. No crane or truck access without permit 2. All crane lifts supervised by process / maintenance personnel 3. Equipment located with ease of		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		safe access for maintenance		
	C.4. Pipe-work damage due to corrosion	1. Proper specifications of pipe-work 2. Avoidance of back flow of wet gas into the dry sections of vent system (B1)		

5.4 Rail loading stations

5.4.1. Hazards: Loss of containment of AHF from a rail barrel

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
A Loss of containment of AHF from a rail barrel	A.1. Barrel overfill	1. Filling sheet procedure 2. Reliable load cell weighing system 3. Reliable painted tares within set tolerances 4. All barrels vented-if customer has not dedicated HF storage, establish a quality insurance protocol 5. Operator diligence 6. Liquid HF in vent detector closes the emergency shutdown valve and alerts the operator 7. Design of filling station ensures rail barrel is positioned correctly 8. Do not ship barrel at pressure more that 2 bar gauge	1. Alarm on barrel overfill weight 2. Two different methods of control (independent) of the load	1. HF detectors alarming at control room 2. Remotely operated shutdown valves at various points in loading storage area 3. Supply pump can be tripped from control room or local to pump 4. Collection pits under weigh-bridges 5. Local emergency procedures and plant communications. Operator carries personal radio 6. Readily available canister masks BA sets and gas suits 7. On site and off site emergency procedures

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	A.2. Barrel over pressurization - during filling - during padding	1. Venting procedure during filling of rail barrel to remove pressure 2. Venting procedure to remove inerts 3. Gas padding supply flowrate is restricted 4. Gas padding pressure lower than maximum allowable pressure in barrel		8. Excess flow valve or remote operated valves in tanker liquid and vent lines
	A.3. Explosion / detonation A.3.1. Hydrogen	1. Hydrogen formation is only possible with long storage period 2. Moisture control of the load		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	A.3.2. HF and water reaction	1. Check tare weight of rail barrel 2. Customer liaison alerts operator to barrel containing contamination 3. Operator diligence 4. Normal moisture level far below the corrosion level 5. Padding gas system has moisture indicators 6. Liquid seals and vessel operating levels prevents back diffusion of moisture from vent system and valves preventing risks from atmosphere 7. Post maintenance checks on rail barrels 8. No backflow of moisture possible from scrubber of vent gas	1. Regular monitoring of moisture concentrations in liquid HF 2. Moisture analysis in line on production unit 3. Alarm to warn of high moisture in padding gas 4. Suction failure alarm in vent gas scrubbing system	

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	A.3.3. HF / Iron hot reaction	1. Any "hot work" to welding, burning etc is assessed under permit to work procedures. All barrels purged free of HF 2. No flammable liquids or materials in the surroundings of loading area		
	A.3.4. Contaminants (oil, organics)	1. Customer liaison alerts operator to barrel containing contamination 2. Check tare weight of rail barrel 3. Maintenance procedures prohibit the use of grease, oil and solvents 4. Physical post maintenance checks 5. Oil free compressors used on padding gas system 6. Filters and receiver vessels on padding gas system (on air)		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	A.4. Collision with other rail traffic / barrels	1. The use of the rail line is limited to the service of the filing station 2. Interlocked rail retarders reduce the risk of runaway rail wagons getting into filling area 3. Loading facility is installed on a single track 4. No rail movements allowed with single main in attendance 5. Loading platform interlocked with retarders to avoid collision during loading activity or spring loaded points 6. Brakes on rail wagons checked before loading every trip 7. Audible alarms linked to the rail retarders (alerts operator to towered position) 8. Rail wagon movements controlled by operator using rail wagon brakes 9. Training of process operators	1. Emergency shut off valves on barrel and supply mains initiated by push buttons	

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	A.5. Severe internal corrosion	1. Cross check tare weight with records 2. Customer liaison alerts process operator to suspected corrosion 3. Scheduled inspections carried out periodically on rail barrels 4. Regular monitoring of moisture concentrations in liquid HF 5. Recognition of abnormal pressure in rail barrel on return from customer 6. Ultrasonic tests every 4 years at least and pressure test every eight years with internal inspection		

5.4.2. Hazards: Loss of containment of HF from the flexible filling pipe

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
B. Loss of containment of HF from the flexible filling pipe	B.1. Severances of flexible filling pipe B.1.1. Collision	1. The preventative measures listed in section A.4. apply to this hazard	1. Shut off valves on both sides or internal excess flow valves on liquid and vent close on severance of flexible filling pipes 2. Control measures listed in section A.4. apply to this hazard	
	B.1.2. Rail barrel movement	1. Rail wagon braked 2. The preventative measures listed in section A.4. apply		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	B.2. Random failure	1. Design standards of filling equipment 2. Support boom for flexible filling pipe 3. Maintenance procedure to replace flexible filling pipe (<u>not</u> repaired) 4. Protective valves or blind flanges enclosing flexible filling pipe prevent wet air ingress 5. Visual inspection of flexible filling pipe by process operator 6. Flexible filling pipes inspected minimum 12 months registration system to record flexible filling pipe changes 7. Flexibles provide adequate tolerance for minor vertical and horizontal movement of barrel (e.g. barrel springs sag during loading)	1. Shut off valves on both sides or internal excess flow valves on liquid (2) and vent (1) close on severance of flexible filling pipe	

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	B.3. Operator error	1. All valves marked 2. Attention to ergonomics at design phase 3. Operating procedures and operator training 4. Eurofluor standard for valve position on barrel		

5.4.3. Hazards: Loss of containment of liquid HF from supply pipe work to rail filling bay

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
C. Loss of containment of liquid HF from supply pipe work to rail filling bay	C.1. Physical damage C.1.1. Impact	1. Layout of pipe work designed to minimize risk from road vehicles and rail wagons 2. Rail filling bay set back or protected from roadway 3. Maintenance procedure and restricted area		
	C.1.2. Fire	1. Rail filling area away from major flammable hazards 2. Any "hot work" i.e. welding, burning, etc is assessed under permit to work procedures (all barrels purged free of HF)		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	C.1.3. Fatigue (liquid hammer, vibration)	1. Shutdown valves are slow acting to prevent liquid hammer on long pipe-lines 2. Manual isolation valves require several turns to close and therefore by their nature are slow closing 3. Pipe-work and valves supported to avoid overstressing 4. Vibration free pipe-work 5. Pipe-work flexibility studies		
	C.1.4. Support failure	1. Design standards specify support requirements 2. Routine plant patrols by process operator		
	C.2. Process related causes C.2.1. Trapped liquid (flange leak)	1. Process operator awareness 2. Operating procedures 3. Maintenance and operating procedures ensure liquid HF hoses and adjoining pipe-work are drained after use		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	C.2.2. Erosion	1. Maximum liquid HF velocities do not exceed 1,5 m/sec (room temperature) 2. Large radius on bends and elbows		
	C.2.3. Corrosion	1. Insulation, if any specification to inhibit water ingress 2. Normal moisture level far below the corrosion level 3. Valves or blind flanges at the end of hoses to minimize moisture ingress 4. Regular monitoring of moisture concentration in liquid HF		
	C.2.4. Maintenance activity/operator error	1. Procedures jointly developed by process and maintenance 2. Experienced personnel present during break-ins to liquid HF mains 3. HF pipe-work purged and depressurized before break-in commences		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	C.2.5. Non conformity with standards	1. All liquid HF pipe-work conforms with Eurofluor recommendation equipment for HF handling		

5.4.4. Hazards: Miscellaneous causes of loss of containment of HF

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
D Miscellaneous causes of loss of containment of HF	D.1. Liquid HF in vent	1. Operation principles 2. Alarm on barrel overfill 3. Loading weight defined 4. Operator awareness	1. Liquid HF in vent detector (alarm/trip) alerts operator 2. Vent flexible of same specification than liquid flexible 3. Liquid HF of vent caused by an error in cross connecting liquid and vent lines is limited by restrictor plate. 4. Eurofluor standard for valves lay-out 5. Liquid trap before the scrubbing system	1. Control and increase venting rate 2. Drain liquid to vented tanks
	D.2. Contamination of padding gas (air or nitrogen)	1. Under normal operation the gas pressure is always higher than the pressure in the HF rail barrel 2. Differential pressure control system on gas supply 3. Operator awareness 4. Restrictor in padding gas supply to barrel 5. Vent barrel after filling to avoid subsequent over	1. High and low pressure alarm on padding gas supply	

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
		pressurization due to warm up		
	D.3. Valve leaks	1. Preference for Eurofluor standard valves 2. Critical isolation exercised frequently on regular schedule		
	D.4. Maintenance shortcoming	1. Clearance certificate procedure 2. Training 3. Special controlled joints for liquid HF lines		
	D.5. Modification shortcoming	1. Hazard and operability studies carried out by multi-disciplinary team 2. Equipment specifications produced by experienced mechanical and chemical engineers 3. Works instruction procedure 4. Safety audits 5. Plant inspections 6. Precommissioning procedures		
	D.6.	1. Avoidance of small bore pipe-		

HAZARD	CAUSED BY	PREVENTATIVE MEASURES	CORRECTIVE MEASURES	EMERGENCY MEASURES
	Small bore pipe-work leaks (e.g. instruments)	work minimum 1" branch size on HF mains 2. Instruments have process isolation valves		