Group 4

RECOMMENDATION ON MATERIALS OF CONSTRUCTION FOR 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

1. INTRODUCTION - GENERAL REMARKS

This recommendation is written to provide general advice on the suitability of various materials for industrial application with both anhydrous hydrogen fluoride (AHF) and hydrofluoric acid solutions (HF) in terms of corrosion resistance concerning new and replacement facilities at temperatures from -10°C to +50°C, unless stated otherwise. It does not attempt to define the various corrosion processes but indicates the conditions under which certain materials can be used or should be avoided. Care must however be taken to consider the possibility of the presence of other constituents in either the AHF/HF or the materials of construction, as the presence of certain trace components can considerably influence the corrosion behaviour. Practical testing under service conditions is therefore the best guide to the suitability of any particular material.

The recommendation does not cover the question of mechanical properties, which are more appropriately dealt with in specific engineering recommendations.

These recommendations, in any case of uncertainty, should not be taken as a firm guide but reference should be made to an AHF/HF manufacturer to confirm the suitability of any material for a given duty.

Hydrogen fluoride is an extremely hazardous material, in the liquid or vapour form. Clearly, great care must be taken in handling any material that has been exposed to AHF/HF.

This document does not include all acceptable materials of construction. Process vessels and piping constructed for AHF/HF service should follow recognized design codes.

In addition to the described corrosion rates, some contaminations of the AHF/HF will occur.

2. MATERIALS

2.1. Metallic materials

When a small AHF leak or diffusion mixes with moisture in the air it forms a highly corrosive aqueous HF acid. This will corrode both carbon steel and stainless steel very fast. The same effect happens with HF leak or diffusion.

Corrosion of metallic materials will increase with temperature.

2.1.1. Non-alloyed carbon steel

The material should be selected carefully based on standards and proven by certificates (according to national legal requirements).

Special care must be taken for construction of AHF/HF vessels and tanks. For instance:

- Steel sheets should be checked ultrasonically to ensure the steel is lamination-free.
- All reinforcements welded on the steel must be provided with vents for hydrogen venting.
- Increased hardness of the steel may increase corrosion by stress cracking, both for the material itself and the welding zones (critical hardness level starts with 22 HRC (Rockwell C hardness) = 238 HB (Brinell hardness).

2.1.1.1. For use with anhydrous HF (AHF)

Carbon steel is the most commonly used material for handling liquid or gaseous AHF. All steel components must be thoroughly cleaned and dried, before coming into contact with AHF. Carbon steel coming the first time in contact with AHF is building an insoluble iron fluoride protecting film. The protective layer may be removed by erosion, by the presence of reactive material or where the metal has a large specific surface area.

Note: the corrosion rate is closely linked to and increases with the velocity of the liquid or gas as well as the temperature. For example:

- At 30°C and velocity of 1.5 m/s, the corrosion rate is in the range of 0.1 - 0.125 mm/y
- At 50°C and velocity of 1.5 m/s, a corrosion rate of 0,25 mm/y can be expected

In order to avoid destruction of the protective layer due to erosion, the linear velocity of liquid AHF at the vessel wall should be limited. The normal practice for pipe work is to limit liquid AHF velocity to 1.5 m/s on average, at room temperature. At higher temperature the velocity of liquid AHF must be reduced. Carbon steel is not recommended for liquid AHF at temperatures above 50°C.

Take care that this protective layer might be destroyed during maintenance (absence of liquid AHF). For gaseous AHF below 200°C, velocity should be limited to 10 m/s (at 1 atmosphere). Entrainment of liquid droplets in AHF gas may greatly accelerate the corrosion.

Forged or cast steel can be used on condition that the mechanical property of the fabricated components have been studied for the range of temperatures and stress which might be encountered. For cast steel, inclusions shall be reduced as far as possible and solidification shrinkage shall be controlled.

2.1.1.2. For use with hydrofluoric acid solutions (HF)

Note: the corrosion of steels in hydrofluoric acid solutions increases with the dilution of the HF solution. Moreover, it can be worse by erosion.

- Between 85% and 100%, corrosion rate remains quite similar and low
- Between 70% and 85%, corrosion rate increases but carbon steel may be used at room temperature
- Below 70%, the corrosion rate will increase dramatically. For example: HF 70 % < 0.5 mm/year; HF 65 % < 1.5 mm/year. The use of carbon steel is not recommended.
- Dilute solutions < 60 % will attack steel rapidly even at low temperatures.

Corrosion of carbon steel in HF will result in hydrogen formation. Therefore, care must be taken to prevent any explosive mixture between hydrogen and air.

Even in concentrations > 85 % and with AHF, some atomic hydrogen migration will occur into the steel sheet. This may cause blistering if the steel sheet is not free of defect of lamination or inclusions.

2.1.2. Cast iron

Its use in AHF/HF is not advisable due to risks of porosity and embrittlement and in some cases corrosion rates much higher than carbon steel or cast steel.

2.1.3. Stainless steels

Austenitic chromium nickel steels do not have a better resistance to AHF/HF than carbon steels, and cannot be used at higher temperatures.

There is no experience with stainless steel, therefore it is not recommended to use it with aqueous HF solutions.

Fluoride ions could promote stress corrosion cracking even at low temperatures. If austenitic stainless steels are used, it is recommended to use only a grade with low carbon content (C < 0.03 %) or Ti or Nb stabilized.

Special attention for cast pieces must be taken with regard to the risk of presence of molding sand inclusions.

Ferritic, martensitic and even DUPLEX stainless steels may increase risks of hydrogen embrittlement.

2.1.4. Nickel and nickel alloys

Nickel alloys have much better resistance than stainless steel but their properties vary according to the grade and type of alloy. See below for specific properties.

Alloy 400 (UNS N04400 = EN 2.4360/2.4366, incl. Monel® 400)

- AHF
  - resistant to at least 120°C in liquid AHF
  - resistant to at least 400°C in gaseous AHF
- Aqueous HF
  - Alloy 400 is one of the most resistant alloy for use with aqueous HF
  - For all concentrations
    - → Resistant at room temperature
    - → Corrosion rate will not exceed 0.5 mm/year up to atmospheric boiling point in air free solutions
  - Special care with regard to oxygen, CuF_2 and generally all types of oxidants contents
    - → corrosion mainly in the vapour phase
    - → stress corrosion cracking, especially if cold formed or if welds are not stress relieved

Alloy C-276 (UNS N10276 = EN 2.4819, incl. Hastelloy® C-276)

- AHF
  - resistant to at least 120°C in liquid AHF
  - resistant to at least 350 °C in gaseous AHF
- Aqueous HF
  - Alloy C-276 is one of the most resistant alloys for use with aqueous HF
  - For all concentrations:
    - → Resistant at room temperature
    - → Maximum allowable temperature will depend on concentration (e.g.: corrosion rate ~ 0.5 mm/year in HF 50 % at 60°C)
  - Stress corrosion cracking possible in case of presence of oxidants such as CuF2 but should be preferred to alloy 400

Alloy 600 (UNS N06600 = EN 2.4816, incl. Inconel 600)

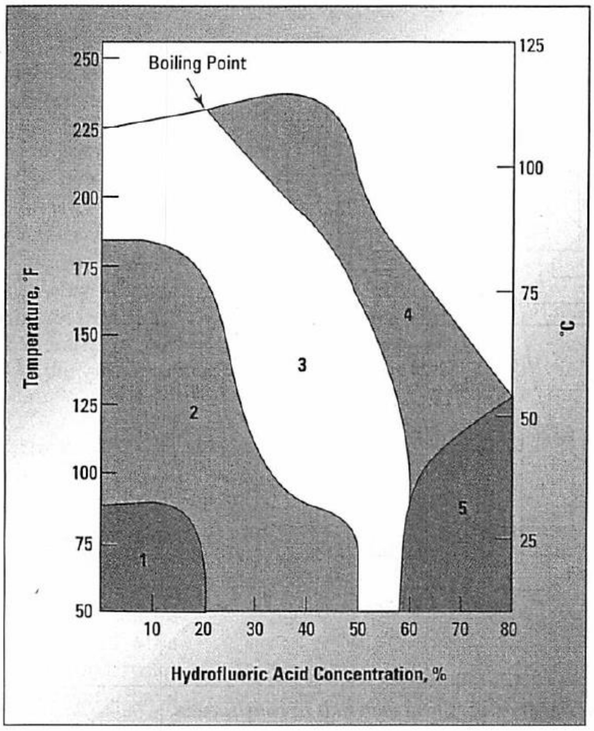
- AHF
  - Alloy 600 is one of the most resistant alloy for use with AHF
  - resistant to at least 120°C in liquid AHF
  - resistant to at least 500°C in gaseous AHF
  - be careful with the welds: avoid Ti, Nb content
  - stress corrosion cracking possible with oxidants such as CuF_2
- Aqueous HF: not recommended

Nickel 200 (UNS N02200 = EN 2.4060/2.4066) and Nickel 201 (UNS N02201 = EN 2.4061 and 2.4068)

- AHF
  - Nickel 200 is normally limited to service at temperature below 315°C. At higher temperature Nickel 200 products can suffer from graphitization which can result in severely compromised properties. For service above 315°C, nickel 201 is preferred.
  - be careful with the welds: avoid Ti, Nb content
  - Stress corrosion cracking possible with oxidants such as CuF_2
- Aqueous HF: not recommended

Oxidising agents and reducing sulphur compounds increase the corrosion rate of all these materials.

Figure 1. Suitable materials of construction for handling HF of various strengths and temperatures.



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[1] Figure 1 and Table 2: Schillmoller C. M., "Select the right alloys for hydrofluoric acid services", Chemical Engineering Progress vol. 94, November 1998, p. 51, republished with kind permission of American Institute of Chemical Engineers Publication, conveyed through Copyright Clearance Center, Inc.

Table 2. Corrosion resistance of materials in Figure 1 to hydrofluoric acid.

		Zone in Figure 1				
		1	2	3	4	5
		Corrosion Rate <0.020 in./yr				
Alloy	**UNS No.**					
Alloy C-276	N10276	X	X	X	X	X
Alloy 400*	N04400	X	X	X	X	X
70-30 Cu-Ni*	C71500	X	X	X	–	–
Alloy 20	N08020	X	X	–	–	–
Nickel 200*	N02200	X	–	–	–	–
Alloy 825	N08825	X	X	–	–	–

*Air-free.

For more information on nickel alloys, please refer to

- Schillmoller C. M., “Select the right alloys for hydrofluoric acid services”, Chemical Engineering Progress vol. 94, November 1998, pp. 49-54
- Herbert S. Jennings, “Materials for hydrofluoric acid service in the new millennium”, NACE International Corrosion 2001, Paper N° 01345, NACE, 2001
- R. B. Rebak, J. R. Dillman, P. Crook, and C. V. V. Shawber, “Corrosion behavior of nickel alloys in wet hydrofluoric acid”, Materials and Corrosion 52, 289-297 (2001)

2.1.5. Copper and copper alloys

Copper has sometimes been used in the range of 60-90 % concentration of HF up to the boiling point with a moderate corrosion rate.

Copper-nickel alloys (with 30 % nickel) are less resistant than Alloy 400 itself.

Bronze has also an acceptable resistance at room temperature and is sometimes used for pump castings in HF solutions. But it is not suitable for higher temperatures.

These materials are subject to embrittlement.

These alloys should be used with great caution in AHF service.

2.1.6. Lead

Chemical lead is fairly resistant to HF solutions up to 40 % at ambient temperature and lead coated steel has been used in the past for metal fluorides fabrications.

Corrosion increases with temperature and oxidising agents.

2.1.7. Titanium, tantalum, zirconium and niobium

Titanium, tantalum, zirconium and niobium are strongly attacked by hydrofluoric acid at all concentrations.

2.1.8. Aluminium, aluminium alloys (without copper), tin, zinc, yellow brass, magnesium

None of these materials should be used with AHF/HF, nor should alloys based on these metals except copper alloys (see section "*2.1.5. Copper and copper alloys*") despite the fact that pure aluminium has some resistance to AHF.

2.1.9. Precious and other metals

Precious and other metals may be used for special applications (e.g. instruments or laboratory uses). Depending on these uses, see report from Herbert S. Jennings, "Materials for hydrofluoric acid service in the new millennium", NACE International Corrosion 2001, Paper N° 01345, NACE, 2001.

2.2. Ceramics, glass – bricks – mineral fibres

All these materials containing silica are strongly attacked by AHF/HF even diluted and at low temperatures and must not be used in AHF/HF service.

2.3. Carbon - graphite or silicon carbide

Graphite equipment can be used in the whole range of concentrations of AHF/HF applications depending on the type of graphite used (nature of impregnation for impermeability).

Silicon carbide equipment can be used in the whole range of concentrations of AHF/HF applications as long as it doesn't contain any free silicon (Si).

Be aware of lower mechanical strength compared to metallic materials (the material is brittle).

2.4. Organic materials

All recommendations in this section need to consider the application and circumstances like temperature, pressure, concentration, presence of impurities, etc.

Possibility of embrittlement with organic material, especially in welding zones, must be considered.

In the presence of AHF/HF diffusion of hydrogen fluoride into material may occur with impact to the mechanical properties.

Diffusion increases with both concentration and temperature.

The following comments deal only with the use of the materials on construction duties or as a lining. Their behaviours when used on specialised duties are dealt with under "*3. Applications*".

Most of these organic materials are slowly attacked and require a schedule of inspection and replacement before they become defective. Many of the plastic materials listed are liable to stress corrosion cracking and the fabrication of components or systems from plastics should be done so as to avoid regions of high stress during manufacture or service.

2.4.1. Rubber

All forms of synthetic or natural rubber lack mechanical strength and are attacked by AHF/HF. The slow rate of attack of rubber in very dilute solutions of HF means that it is however frequently used as a lining material (natural rubber, butyl rubber) for solutions < 40 % and room temperature. Care must be taken of the quality of the filling materials and their resistance to HF.

Soft natural rubber can be used for HF up to 40 % concentration at room temperature, and butyl rubber/ chlorobutyl rubber up to 70 % HF concentration at room temperature.

Nevertheless, prior to choosing for a rubber lining, the manufacturer/applicator of it should always be consulted as composition of the rubbers varies a lot from one supplier to another and application technique (workshop with autoclave curing or prevulcanized on the field) may also have some impact on the corrosion resistance of the lining.

Special care must be taken in case of repairs of the lining.

2.4.2. Polyethylene, polypropylene, PVC

High density polyethylene is resistant to hydrofluoric acid solutions up to 70 % at temperatures up to 60°C.

Polypropylene and PVC are not recommended as single construction material, i.e. without reinforcement by resins-fibres (fibreglass must be avoided for this application).

2.4.3. Fluorinated polymers

Below are listed some of the fluorocarbon plastics that have been used successfully in loose lined pipe, valves and other equipment, and for gaskets and seals in AHF/HF service.

- PTFE polytetrafluoroethylene
- FEP copolymer of TFE (tetrafluoroethylene) and HFP (hexafluoropropylene)
- PFA & MFA & “modified” PTFE copolymers of TFE (tetrafluoroethylene) and a fluorinated ether (the type of final material depending on the nature of the comonomer and of its relative concentration)
- ETFE copolymer of TFE (tetrafluoroethylene) and ethylene
- PVDF polyvinylidene fluoride, also a copolymer of VDF (vinylidene fluoride) with HFP, CTFE chlorotrifluoroethylene
- ECTFE copolymer of CTFE and ethylene

All these fluoroplastics have a good to very good resistance to AHF/HF at quite high temperatures. Special care must be taken regarding permeation of the material (e.g. temperature, pressure, concentration, design, etc.) This problem of permeability can be reduced by the use of a suitable thickness.

Fluorinated polymers can be reinforced with polyester fibres and polyester resins to give improved mechanical strength for applications at higher temperatures and pressures

2.4.3.1. PTFE

PTFE resists to AHF/HF. Special care needs to be taken at high temperatures. Where PTFE is used as a protective layer, care must be taken to guard against attack on the supporting material. For supporting material and lined vessels, it should be considered that the material is provided with vent-holes to purge out the hydrogen coming from the unavoidable corrosive attack and also allowing draining of the HF permeated before attacking the support.

2.4.3.2. FEP, PFA, ETFE

These fluorinated copolymers are also used because of their resistance to AHF/HF and for easier preparation of protecting layers and lower permeation rate than PTFE.

2.4.3.3. ECTFE

ECTFE has a good resistance to AHF/HF.

2.4.3.4. PVDF (polyvinylidene fluoride)

PVDF has a good resistance to AHF/HF up to at least 90°C depending on the grade of PVDF.

2.4.4. Other materials

Mineral fibre-filled plastics, silicone rubbers, polyurethanes, methacrylates, furanes resins, polyamides should not be applied in AHF/HF service.

Vinylester resins could be used for HF up to 20 % and up to 65°C but with reinforcement without glass fibres (synthetic, carbon, etc.) The supplier of the resin should be consulted to verify the suitability of the material choice depending on operating conditions. It is known that blistering occurs in the thickness of the anti-corrosion layer but it does not impair the function of the equipment as far as this remains in the anti-corrosion layer.

Vinylester resins could also be used as external mechanical resistance layer for thermoplastic liners (anti-corrosion layer). For such applications, it is recommended to consult the supplier for the correct choice of the fibres.

3. APPLICATIONS

The following comments concern the pure materials, without plasticizers, fillers, coatings, greases or other potentially reactive ingredients. The choice of materials of construction for any systems therefore must be controlled to avoid the introduction of materials which could react with AHF/HF.

It is also important, when using any component (which is itself made from a satisfactory material for use with AHF/HF) to separate AHF/HF from other fluids, that account is taken of the potential for leakage occurring between the two fluids. This could occur in components associated with heat transfer or hydraulic systems, where it is important to ensure that the fluid is not reactive to AHF/HF.

All ancillary equipment (instruments, sealing arrangements, etc.) should always be verified for being made from components of materials which are compatible with AHF/HF. Materials used for thermal insulation should also be selected from those which do not generate corrosive products under service conditions.

3.1. Tanks

3.1.1. Tanks, vessels and ISO containers for HF concentration ≥ 85 %

The steel chosen for the construction of AHF/HF storage tanks should be of fine grain steel, readily welded and which has the appropriate level of impact strength at the minimum design temperature after welding. In order to guarantee the optimal conditions for welding, the tensile strength of the steel should be limited. The steel plate should be subjected to acceptance tests according to national or international codes. These tests are particularly important concerning the impact strength before and after welding.

The use of conventional steel has sometimes resulted in hydrogen blistering. This blistering occurs when galaxies of inclusions and laminations are present in the steel.

Carbon steel approved for use with AHF/HF shall be used to construct the tank and internal fittings. Low hardness steel is required. Steel sheets should be checked using ultrasonic to ensure it is lamination-free.

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

A corrosion allowance of 2 mm (for carbon steel tanks) is considered as a minimum requirement. Higher corrosion allowance should be considered depending on temperature and specific risks related to the application.

The corrosion rate can highly increase in case of high velocity of the flow (e.g. internal pump or dip tube) and because of temperature. Local turbulences must be avoided for the same reason.

Another problem can arise from moisture ingress. If a tank vents to the atmosphere, the moisture in even low humidity air can dilute the surface layer of AHF/HF so this layer can become more corrosive. It is therefore suggested to avoid that the liquid remains at a constant level for long periods of time. The same could happen if the moisture ingress causes AHF/HF to reach the dew point in the vapour space with subsequent condensation. For these reasons it is recommended to inert the vapour space with a dry gas (nitrogen or dry air), or to maintain the closed vessels under slight over pressure.

In addition the thickness of the wall shall be monitored periodically by ultra sonic tests.

3.1.2. Tanks, vessels and ISO containers for aqueous HF between 70 % and 85 %

The material of construction depends on the concentration of the acid and the storage temperature. Advice from the manufacturer of this equipment is necessary.

Steel containments are suitable when avoiding the introduction of any moisture. Lined containments and high density polyethylene containments can also be used according to the conditions. See section "*3.1.3.1. Lined steel tanks and vessels*" for more details on the lining.

For transportation equipment, the minimal design pressure of the shell is 10 barg according to RID/ADR. The 10 barg design pressure allows a minimum thickness of the shell as a good protection against mechanical impact in case of accident.

The concentration of the acid and the expected temperature must be taken into account. High temperatures increase the rate of corrosion and low temperatures may lead to embrittlement of the carbon steel.

The steel must have good weld properties, good resilience (min 27 J at -20 °C) after welding and good ductility characteristics.

For welded shells, only materials of faultless weldability shall be used, whose adequate impact strength at an ambient temperature of -20 °C can be guaranteed, particularly in the weld seams and the zones adjacent thereto. If fine-grained steel is used, the guaranteed value of the yield strength shall not exceed 460 N/mm^2, and the guaranteed value of the upper limit of tensile strength Rm shall not exceed 725 N/mm^2, in accordance with the specifications of the material.

The elongation for fine-grained steels shall be not less than 16 % in any case, and not less than 20 % for other steels.

Carbon steel may suffer hydrogen stress corrosion cracking and hydrogen blistering in contact with aqueous HF.

The steel should be tested for resistance to hydrogen assisted stress corrosion

Construction of ISO tanks or railway tanks for HF should only be carried out by an approved contractor.

Carbon steel approved for use with HF shall be used to construct the tank and internal fittings. Steel sheets should be checked using ultrasonic to ensure they are lamination-free.

Higher corrosion allowance should be considered depending on the HF concentration, temperature and specific risks depending on the application.

Example for calculation:

Wall thickness according to mechanical strength and design pressure	X	mm
Lowest limit of the wall thickness (X) for atmospheric pressure operation	6	mm
Corrosion allowance for 20 years 25 °C (20 x 0.4 mm*)	8	mm
Total minimum thickness	8 + x (minimum 14)	mm

(*) 0.4 mm corrosion per year for HF 70 % at 25 °C (additional thickness to be added for higher temperatures)

In addition, the thickness of the wall shall be monitored periodically by ultra sonic tests.

3.1.3. Tanks, vessels and ISO containers for aqueous HF ≤ 70 %

For concentrations up to 70 % lined or plastic containments are required.

3.1.3.1. Lined steel tanks and vessels

The lining must consist of a suitable material e.g. a double layer of butyl rubber or chlorobutyl rubber that should have at least a thickness of 3 mm each, in order to avoid HF diffusion through the lining, thus attacking the steel associated with formation of hydrogen.

In case of organic impurities, special care must be taken to ensure the durability of the lining.

Note: it is very important to choose carefully the manufacturer who will prepare and carry out the lining on the metallic wall. The quality of the lining sticking is fundamental because it affects significantly the mechanical resistance and the porosity of the plastic liner, and consequently, the final resistance of the lined tank against corrosion.

A successful construction starts from metallic surface preparation: high care must also be taken to correctly prepare the surface to support the lining (e.g. welds must be levelled by grinding and sharp connections rounded). This requires a deep interaction between the vessel constructor and the manufacturer of the liner.

3.1.3.2. Plastic tanks and small packaging

Eurofluor does not recommend the use of polypropylene as material of construction because of the relatively quick sunlight ageing.

High density polyethylene can be used as material of construction for the storage of solutions up to 70-75 % HF at ambient temperature.

For outdoor installation, the choice of high density polyethylene stabilized against sunlight ageing is recommended.

The wall thickness depends on the hydrostatic pressure: this plastic tank should be limited to atmospheric pressure storage.

Glass fibre Reinforced Plastic (GRP) could be used as dual laminate with thermoplastic liner (e.g. fluoroplastics, see section "*2.4.3. Fluorinated polymers*") and with the recommendation of using ECR glass or carbon fibres to avoid any corrosion of fibres, and using vinylester as resin.

Note that this risk increases with temperature, pressure and concentration.

Polyethylene can be used for small drums and containers for transportation of limited quantities of solutions up to 70-75 % HF, with a lifetime of maximum 2 years, and in accordance with RID/ADR regulations limitations.

Such drums and containers exist for concentrations:

- up to 60 % HF, containers of maximum 1,000 litres and a maximum lifetime of 2 years;
- up to 75 % HF, drums of maximum 200 litres and a maximum lifetime of 2 years.

Note: the lifetime of the drum / container is calculated from the date of manufacture, whatever the tank has been or not in contact with HF. This lifetime limitation is due to the loss of flexibility of the plastic with time.

3.2. Piping and pumps

3.2.1. Piping and pumps for AHF and HF concentrations ≥ 85 %

All materials and components used in liquid AHF/HF piping systems should at least comply with national codes and standards.

This guide however is not intended to limit the use of other codes and standards, but only to provide information as to possible choice.

All components used in piping systems should be fabricated in materials which are compatible with liquid AHF.

Carbon steel is however the most commonly used material, but care should be taken to limit corrosion according to temperature.

Mechanical properties

Pipe wall thickness for liquid AHF/HF lines: various standards are available which provide guidance to the designer for calculating the mechanical strength and wall thickness of pipes.

Certain national codes can require impact tests to be carried out to determine the impact strength of materials to be used in construction as well as all other parts and fittings undergoing static or dynamic loads.

Piping systems which handle liquid AHF/HF should be capable of resisting all static or dynamic forces for the temperature. If one is seeking to handle liquid or gas at a temperature below -10 °C, one should seek a quality of material which gives the same quality of impact resistance as carbon steel at room temperature.

Generally, carbon steel seamless pipe is recommended for AHF and is normally a readily welded, fine grain steel that is suitable for the temperature options stated above. Where welded pipe is used it should be obtained from approved suppliers and the quality controlled using the documented quality assurance procedure.

Velocity in the pipes for liquid AHF/HF should be limited to 1.5 m/s at room temperature. At higher temperature, the velocity of the AHF must be reduced.

3.2.2. Piping and pumps for HF solutions < 85 % HF

It is recommended to use lining for pipes within this concentration range. For lining, all materials mentioned in section "*2.4.3. Fluorinated polymers*" are suitable.

At room temperature and limited pressure high density polyethylene piping is suitable.

The design of the steel pipe must be the same as for non-lined steel pipes and in accordance with national codes and regulations.

All parts of pumps in contact with HF solutions should be HF resistant (see chapter "*2. Materials*").

3.2.3. Articulated arms for AHF loading and unloading

Metallic components in the bearing surfaces of the articulations should preferably be manufactured from material which is resistant to gaseous and liquid AHF, either dry or slightly moist (for example Alloy 400, Alloy C-276, Alloy 600 or Alloy 825).

In addition, any metallic component which can be in contact with AHF due to seal failure should be preferably made in materials resistant to slightly moist AHF, e.g. Alloy 400, Alloy C-276, Alloy 825 or PTFE or PFA (polyfluorinated alkoxy) lining (see also section "*2.4.3. Fluorinated polymers*") on steel when possible.

3.3. Connections (i.e. branches, flanges nuts and bolts)

3.3.1. Branches and flanges

The metal used for flanges, branches, nuts and bolts should have the same quality as the material used in the construction of the stock tank. The overall arrangement of flange and jointing material should be studied in such a way to provide a system from which the joint cannot be expelled by excess pressure.

High tensile strength steel for bolts and nuts must be avoided in order to be protected from hydrogen stress corrosion (for example B7M ASTM Standard A193 can be used). The hardness of the steel should be limited.

The connections to the liquid phase of the mobile tank should be made of steel pipes, PTFE flexible hoses (see "*3.6. Hoses and flexible steel pipes*") or articulated arms (see "*3.2.3. Articulated arms for AHF loading and unloading*"), 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 lined (e.g. with PTFE), Alloy 400, Alloy C-276, Alloy 600 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 must be carried out (twice a year), and changed if necessary.

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.

The arrangements flange-gasket for permanent connections in the plant for AHF and HF solution above 85 % concentration can be in

- tongue and groove arrangement with 100 % PTFE gaskets (with care of possible corrosion of the tongue)
- flat face flanges with metal spiral wound gaskets, filled with PTFE or graphite (with careful choice of the metal spiral wound, e.g. stainless steel for AHF below 50 °C)
- flat face flanges with 100 % PTFE gaskets (with care of possible cold flow of PTFE)

Choice of connection arrangement will depend on conditions of application (e.g. temperature, pressure, etc.). PTFE glass filled type must be avoided. The resilience of metals used must be at least equal to that defined by international rules.

The materials of the flanges should be suitable for the selected temperature conditions and be compatible with the associated pipe and fittings. Metal shall be checked for lamination and inclusions defects and suitable hardness.

For flanges that are frequently opened, the tongue and groove arrangement (with 100 % PTFE gaskets) is not recommended because of possible corrosion and mechanical degradation of the tongue.

Connections for HF solutions below 85 % concentration must be arranged according to the general design of the storage and piping, and with consistency with the recommended materials of chapter "*2. Materials*".

3.3.2. Nuts and bolts

Bolting for securing flanges must have adequate resistance to hydrogen assisted stress corrosion cracking (HSCC), sufficient strength for use with the type of selected gasket and must be quality controlled.

Bolts and nuts should conform to a recognised national standard and be suitable for the selected temperature conditions.

The manufacture and testing of the various alloys recommended above are covered in the appropriate national standards. It is recommended as an added precaution that the supplementary requirement of 100 % hardness testing of the bars, of ASTM A193 B7M for example, is requested.

The recommended material for bolts and nuts is ASTM A193 grade B7M.

The strength of these various metals varies considerably. The strength must be considered as different gasket materials require different loading. The grade B7M of the ASTM A193 is suitable for use with plain PTFE gaskets.

3.4. Valves

3.4.1. Valves for AHF

The valves used in the pipe work in the liquid phase must be confirmed by experience, for example:

- steel body with Alloy 400 or austenitic steel stem and plug, PTFE seating and stuffing box
- or steel plug cock valve with PTFE lined plug, PTFE membrane and packing.

If cast steel bodies are used, precautions have to be taken to avoid imperfections in the casting.

All pieces concerned with static or dynamic stresses should be made of a material suitable to AHF service and should present sufficient mechanical and resilience characteristics to withstand the conditions of pressure and temperature.

In order to take into account the potential risks associated with AHF, it is recommended that a maximum of 80 % of the nominal pressure is allowed for which the valve has been constructed.

As a consequence the maximum operating pressure is given by the following table as a function of the nominal design pressure of the valve.

Nominal pressure	Maximum service pressure authorised at ambient temperature
PN 16	12,8 bars effective
PN 25	20 bars effective
PN 40	32 bars effective

Pay special attention to the possible occurrence of vacuum. Minimum allowed pressure has to be checked according to the model of the valve.

The resilience of metals used must meet the standards.

The body and the cap of the valve should not be made of cast iron but preferably made of forged or cast steel.

The plug cock should be made of stainless steel or Alloy 400.

The inserted casing ensuring the tightness between plug cock and body should be in PTFE (plain or carbon filled).

The body and the valve head should preferably be constructed from forged steel.

All parts of the valve should be constructed in materials which are compatible with AHF.

The seat of the valve, the disk, the bellow and the other parts of the closure exposed to corrosion by intermittent contact with the atmosphere must be made of material resistant to gaseous and liquid HF of more than 85 % concentration.

All the parts subjected to a static or dynamic stress must be made from a material with a resilience and tensile strength sufficient to withstand the conditions of temperature and pressure (which excludes the use of cast iron).

In the case of valves without a bellow, the spindle should be made of Alloy 400, or Alloy 600, or austenitic stainless steel.

When the bellow is employed it should be constructed in austenitic stainless steel, or Alloy 400 or in Alloy C-276. The bellows should be designed to ensure at least 10,000 operations of opening and closing at the nominal pressure of the valve and to be able to resist without permanent distortion the various static and dynamic forces to which it will be subjected, as well as the hydraulic test pressure of the valve.

Do not use plug and ball valves as a primary liquid isolation of an AHF storage tank, but only globe valves.

3.4.2. Valves for HF solutions < 85 %

Plug or ball valves lined with HF resistant material as per section "*2.4.3. Fluorinated polymers*" are normally used.

For plug valves the valve body must be of one piece. Globe valves can cause problems, because of abrasion of the valve seating. Precautions must be taken regarding the risk of quick corrosion of the steel structure in case of failure of the lining. Periodic testing is recommended.

It is recommended the use of pneumatically actuated valves fitted with an internal stop/check valve and an outlet valve, for example size PN25-DN40 DIN 2501, Form C.

The liquid valve shall have a dip pipe connected to the check valve body (if welded, it must be stress relieved and radio graphed). The pipe may be PTFE coated, with a thickness of at least 3 mm. The dip pipe will be sized to terminate in a sump, such that the end of the dip pipe is 10 mm below the bottom of the tank and at least 10 mm above the bottom of the sump. The bottom end of the dip pipe shall be secured by steady welding to the shell. It shall be possible to remove the dip pipe without having to enter the tank.

3.5. Gaskets

Gaskets must be made of material resistant to AHF/HF (e.g. pure PTFE), capable of good service proven by experience, especially for flanges in the liquid phase.

Note: **all gaskets must be replaced by a new gasket after each use and discarded as contaminated material.**

Note: even during construction and testing the gaskets used must meet this standard. This is to prevent the possibility of wrongly specified gaskets finding their way into AHF/HF service.

Note: packing materials, gaskets and pump seals will absorb HF molecules, and are difficult to decontaminate. After washing and drying, droplets of HF may form on such materials by drawing moisture from the air.

Choice of connection arrangement will depend on conditions of application (e.g. temperature, pressure, etc.). PTFE glass filled type must be avoided. The resilience of metals used must be at least equal to that defined by international rules.

	for AHF and HF solutions above 85%		for HF solutions below 85%	
Flanges	Permanent connections	Temporary connections	Permanent connections	Temporary connections
Tongue and groove arrangement with 100 % PTFE gaskets (with care of possible corrosion of the tongue)	+++	Not recommended	Not applicable	Not applicable
Flat face flanges with spiral wound metal gaskets filled with graphite or PTFE packing (with careful choice of the metal spiral wound)	+++	++	+ (caution: metal corrosion)	+ (caution: metal corrosion)
Flat face flanges with 100 % PTFE gaskets (with particular care with regard to possible cold flow of PTFE over time (potential deformation of the gasket)	+ (limited pressure)	++ (limited pressure)	++ (limited pressure)	++ (limited pressure)

Connections for HF solutions below 85 % concentration must be arranged according to the general design of the storage and piping, and with consistency with the recommended materials of chapter "*2. Materials*".

Either 100 % PTFE, PTFE loaded with CaF_2 or graphite can be used, but the glass filled type must be avoided.

Under no circumstances gaskets contact surfaces should be machined in a manner which leaves tool marks extending radially across the seating surface. Gaskets should not be reused.

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

Gaskets containing asbestos-free fibres, asbestos substitutes or enveloped gaskets containing silicate should not be used as silicate is attacked by AHF/HF.

3.6. Hoses and flexible steel pipes

3.6.1. Hoses

Transfer hoses are high-risk, critical components and must be handled carefully.

The use of stainless steel wire braid hoses lined with PTFE (minimum 3 mm) is recommended. The design of the stainless steel hoses should be the same as for non-lined types and comply with national codes.

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 armour 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.

3.6.2. Flexible steel pipes

All the parts subject to a static or dynamic stress must be made of a material with a resilience and sufficient resistance to withstand the conditions of temperature and pressure indicated below (the pipes must be connected 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 bars absolute
- Maximum working pressure 11 bars absolute

Pipes must be of seamless drawn steel tubes and with a quality according to "*3.2. Piping and pumps*". Pipes must have a minimum thickness of 4 mm.

3.7. Thin section applications (i.e. flexible bellows, bursting discs)

Certain duties such as flexible bellows, bursting discs, etc. necessitate the use of thin cross section components. In these circumstances, the material must be effectively non-reactive to HF and not relying on a protective fluoride surface layer. The most commonly used materials are PTFE and fluoropolymers elastomers (bellows) and Alloy 400 or Alloy 600 or Alloy 625 in certain applications. Silver and graphite are commonly used for bursting discs.

The material to be used will be HF resistant according to the recommendations described in chapter "*2. Materials*".

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European Technical Committee for Fluorine (CTEF)

Eurofluor (CTEF) represents the major producers and users of hydrogen fluoride (AHF/HF) and fluoride chemicals in Europe. Eurofluor aims to assure safe production, storage, transportation and use of hydrofluoric acid.

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