STS 84/47

Comité Technique Européen du Fluor

Working Group Storage, Transport and Safety

MATERIALS FOR USE WITH HYDROFLUORIC ACID

9th edition

November 1991

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PREFACE

Hydrogen Fluoride (HF) is essential in the chemical industry and there is a need for HF to be produced, transported, stored and used.

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

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

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

It results from the understanding and many years experience of the 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 HF manufacturer, supplier or user, or other experts 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 the CTEF 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 HF manufacturer before implementing it in detail.

This edition of the document has been drawn up by a Working Group "Storage, Transport and Safety" to whom all suggestions concerning possible revision should be addressed through the offices of CTEF. It may not be reproduced in whole or in part

SUMMARY

1. Introduction

This recommendation is written to provide general advice on the suitability of various materials for industrial application with hydrofluoric acid in terms of corrosion resistance. 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 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 recommendation. These recommendations, in any case of uncertainty, should not be taken as a firm guide but reference should be made to a HF manufacturer to confirm the suitability of any material for a given duty.

2. General comments

2.1 Metallic materials

2.1.1 Non-alloyed carbon steel

A - ANHYDROUS HYDROFLUORIC ACID

- Carbon steel is the most commonly used material for handling liquid anhydrous HF or dry gas. All steel components must be thoroughly cleaned and dried, before coming into contact with HF. Carbon steel when used in HF is then protected by a layer of ferric fluoride, and is resistant up to about 100°C in liquid (above 100°C some corrosion must be expected which increases drastically with temperature). If the protective layer of ferric fluoride is removed by erosion or due to the presence of reactive material or where the metal has a large specific surface area, this upper temperature limit is reduced. For practical purposes, the maximum recommended temperature for carbon steel in the presence of anhydrous HF liquid is 100°C, and the limit for dry gas is higher.

- In order to avoid destruction of the protective layer of ferric fluoride due to erosion, the linear velocity of liquid HF at the vessel wall should be limited. The normal practice for pipework is to limit HF velocities to 1,0 m/sec on average at ambient temperature and lower velocity for higher temperature. This limitation applies to all metals in connection with HF.

- 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.

B - HYDROFLUORIC ACID SOLUTIONS WITH WATER

- The corrosion resistance of steels in hydrofluoric acid is reduced as the HF concentration in solution in water is decreased. However, at ambient temperatures, carbon steel is used on HF solutions of more than 70 % weight. Under the concentration of 85 %, some corrosion must be expected. For example :

HF 70 % 0,5 mm/year

HF 65 % 1,5 mm/year

These corrosion rates are significantly increased by erosion.

- The use of carbon steel on HF solutions of less than 70 % is not recommended. Dilute solutions under 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 of more than 85 % and with anhydrous HF, 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.

A special grade which is vacuum degassed during the steel making process, which is desulphurized to below 0.010 % and which has alumina particles modified in composition and shape may be recommended. The steel sheets used in the construction of HF tanks 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.

- Steels having a hardness exceeding 225 HB (Brinell) after welding may be subject to hydrogen assisted stress corrosion cracking in anhydrous HF, particularly if HF contains high levels of surface poisons such as arsenic.

- Corrosion of steel in HF solutions will increase with temperature.

2.1.2 Cast iron

Its use in HF is not advisable due to risks of porosity and embitterment and in some cases corrosion rates much higher than carbon steel or cast steel. Under specific well defined circumstances specific grades malleable or nodular grades can however be used where there will be no problem due to mechanical shock or tensile forces. With cast iron components, the material needs to be checked for absence of defects which could cause porosity with HF.

2.1.3 Stainless steels

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

- Dilute solutions of less than 10 % show moderate corrosion rates at room temperatures for austenitic steels stabilized (316 type). A better result may be expected with high alloyed austenitic steels such as Carpenter 20, Durimet 20 ... but Monel and Hastelloy C will have normally the best resistance and therefore should be recommended. For alloys 20, seamless pipes should be preferred to welded pipes.

- Austenitic steels may be subject to stress cracking in hot (> 100°C) diluted solutions.

- Fluoride ions could promote stress corrosion cracking even at low temperature, specially with AISI 304 SS if insufficient stress relieved. Stainless steel should be used only with a low carbon content and titanium or niobium stabilization.

- Special attention for cast pieces must be taken on the silicon content which is sometimes used to increase the cast ability.

- Ferritic stainless steel should not be used in a hard condition (Brinnel over 225) due to hydrogen stress cracking.

2.1.4 Monel, Nickel, Inconel

Monel has a good resistance to HF at room temperature in HF solutions in water of more than 50 % where velocity or agitation is limited in order to prevent the removal of the passivation.

Increase of temperature up to 80°C will cause some corrosion which increases as the concentration decreases from anhydrous to 50 %.

Monel may be subject to stress corrosion cracking, especially if cold formed or if welds are not stress relieved. Do not apply Monel 60 wires for welding, these welds corrodes in HF.

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

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

- Nickel and Inconel are less resistant to HF solutions than Cooper and Monel.

- Monel, Nickel and Inconel are suitable for HF gas up to 600°C even in the presence of moisture.

2.1.5 Copper and Bronze

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

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

These materials are subject to embitterment.

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 oxidizing agents, such as sulphuric acid.

2.1.7 Magnesium

Magnesium is resistant to HF at all concentrations at room temperatures. Magnesium alloy (6 % Al - 1 % Zn) is fairly resistant (< 0,2 mm per year) but the corrosion increases with temperature.

2.1.8 Titanium, Tantalum

Titanium and Tantalum are strongly attacked by hydrofluoric acid at all concentrations.

2.1.9 Aluminium, Aluminium alloys (without Copper), Tin, Zinc, Yellow brass, Zirconium

None of these materials should be used with hydrofluoric acid, not should alloys based on these metals except Copper alloys (see Copper) despite the fact that pure aluminium has some resistance to anhydrous HF.

2.1.10 Silver, Platinium

Silver is resistant to HF solutions up to 50 % at temperatures up to the solutions boiling point.

Platinium is resistant in all concentrations at temperature up to the boiling point of the solution.

2.2 Ceramics glass – Bricks - Asbestos

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

Only carbon bricks are suitable for HF.

2.3 Organic materials

The following comments deal only with the use of the materials on construction duties or as a lining. Their behaviour when used on specialised duties are dealt with in paragraph 4. 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.

2.3.1 Rubber and Ebonite

All forms or synthetic or natural rubber lack mechanical strength and are attacked by 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 weak solutions lining (less than 50 %) and room temperatures. Care must be taken of the quality of the filling materials and their resistance to HF.

2.3.2 Polyethylene, Polypropylene, PVC

Polyethylene, Polypropylene and PVC are fairly resistant to weak hydrofluoric acid solutions up to 40 to 50 % at ambient temperatures up to 40°C.

High density polyethylene can be used up to 75 % at room temperature.

Polypropylene and PVC can be reinforced with polyester fibber-polyester resins (glass fibbers must be avoided for this application).

Polyethylene and Polypropylene are suitable for weak acid bottles construction but care must be taken to the resistance to shock (wall thickness, reinforcements, ...) and to the U V and heat sensitivity of the materials.

Small drums made of polyethylene are used for HF solutions up to 70% with a maximum service of two years.

Under certain conditions of stress and in the presence of some environments including HF, polyethylene may exhibit mechanical failure by cracking. Therefore it is not recommended to built large vessels with this material for HF solutions.

Unless polypropylene is less susceptible of stress corrosion cracking, the above recommendation should be extended to this material.

Polyethylene in the presence of concentrated HF solutions will allow penetration of HF in material and therefore reduction of the mechanical properties. Penetration increases with the concentration. Polyethylene and polypropylene should be avoided on anhydrous HF. If bottles are used for sampling the total contact time must be limited to 24 hours maximum.

2.3.3 Cotton, Asbestos

Asbestos filled plastics, silicone rubbers, polyurethane's, methacrylates, furanes resins, polyamides :

Do not apply in HF service.

2.3.4 Graphite - Carbon

Graphite equipment (specially with PTFE impregnation) can be used on HF up to 50 % concentration and up to the boiling point.

Graphite treated with PTFE for impermeability is resistant to higher liquid concentrations (60 to 70 %). Normal impregnation should only be used for weak solutions and low temperatures.

Pure graphite can be used for gaskets, packings, etc...

2.3.5 PTFE

PTFE resists hydrofluoric acid anhydrous and solutions pretty well. It should be noted however that PTFE is not completely impervious. This problem of permeability can be reduced by the use of a suitable thickness. Where PTFE is used as a protective layer, care must be taken to guard against attack on the supporting material.

2.3.6 FEP, PFA, ETFE

These fluorinated copolymers are also used because of their corrosion resistance to HF and their better possibility than PTFE for protective layers.

2.3.7 PTFCE (Polytrifluorochloroethylene)

PTFCE has a good resistance to HF and can be used for fittings or pump pieces (particularly for sight glass as the material is transparent).

2.3.8 PVDF (Polyvinylidene fluoride)

PVDF has a good resistance to HF solutions up to, at least, 60 % and up to their boiling points.

PVDF can be reinforced with polyester fibbers and polyester resins to give improved mechanical strength for applications at higher temperatures and pressures. (Care must be taken of the differential expansion of the materials).

3. Special applications

3.1 Gaskets

. For anhydrous HF and metallic flanges, gaskets should be preferably made of PTFE treated to avoid cold flow (filled with calcium fluoride) or PTFCE or soft graphite or spiral metal and PTFE gaskets or jacketed gaskets in extra low carbon steel, copper, monel or nickel.

Asbestos or enveloped gaskets containing asbestos should not be used as asbestos is attacked by HF.

. For HF solutions

Gaskets shall be made of fluoropolymers rubbers (PTFCE - E-TFCE polymers, VF_2-TFCE polymers, propylene tetrafluoroethylene rubber, P-TFE) without any filling able to react with HF (for example calcium hydroxide or silica or asbestos, etc...). Polyethylene can also be used on weak acid and low temperatures, but polyethylene gaskets are subject to embitterment and must be removed and changed before they become defective.

3.2 Thin section applications

Certain duties such as flexible bellows, bursting discs etc... necessitate 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 Monel or Inconel 600 or 625 in certain applications. Nickel, Silver and Graphite are commonly used for bursting discs.

4. Precautionary comments

The above comments 2.3, 3.1 and 3.2 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 hydrofluoric acid.

It is also important when using any component (which is itself made from a satisfactory material for use with HF) to separate 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 HF.

All ancillary equipment (instruments, sealing arrangements etc...) should always all be verified as made from components of materials which are compatible with HF. Materials used for thermal insulation should also be selected from those which generate corrosive products under service conditions.

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