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Materials of Construction Task Group

Materials of Construction Guideline for Anhydrous Hydrogen Fluoride

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MATERIALS OF CONSTRUCTION GUIDELINE FOR ANHYDROUS HYDROGEN FLUORIDE

This document has been prepared by the "Materials of Construction Task Group" of the Hydrogen Fluoride Industry Practices Institute (HFIPI). The members of this Task Group participating in preparation of this guideline were:

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SECTION 1 PREFACE

This guideline was developed from the present understanding and experience of the Hydrogen Fluoride producers and shippers of the Hydrogen Fluoride Industry Practices Institute (HFIPI), a subsidiary of the American Chemistry Council (ACC). It does not attempt to describe all possible safe options for materials of construction for use in anhydrous hydrogen fluoride (AHF) service. This guideline does not attempt to optimize materials costs or to balance them against available resources. It is not intended to be used as a standard or a comprehensive specification, but rather, as a guide to be utilized in consultation with your acid manufacturer, supplier or user, or other experts in the field.

This guideline is intended to address materials considerations for new or replacement facilities handling anhydrous HF, which for the purposes of this guideline is defined as containing less than 400 ppm of water. Many other contaminants in the acid can promote materials failures in AHF service. It is beyond the scope of this document to address all the possible combinations of contaminants that could be found in acid in its myriad industrial uses. Much of the information present in this document is also useful in HF alkylation units where the water content is higher. However, it is recommended that persons interested in the suitability of various materials of construction in HF alkylation units refer to American Petroleum Institute document RP-751.

It is hoped that the information presented in this document will help improve an already impressive industry safety record. However, the HFIPI, the CMA, and the authors cannot accept any legal liability or responsibility for the use, or misuse, of information contained in this document.

It is the intent of the HFIPI that this guideline be periodically reviewed and updated, approximately every five years, 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. The status of the guideline can be ascertained from HFIPI, c/o Collier Shannon Scott PLLC, 3050 K Street, NW, Suite 400, Washington, DC 20007-5108, telephone 202-342-8538, telefax 202-342-8451.

This guideline, or extracts from it, are not to be copied without the prior written approval from the HFIPI. Suggested revisions are invited and should be submitted to the HFIPI.

SECTION 2 MATERIALS SAFETY

Hydrogen fluoride is an extremely hazardous material, in the liquid or vapor form. Prolonged exposure to even a few ppm can cause painful irritation. Proper selection of materials of construction is a critical part of assuring AHF containment integrity.

Most metals react with AHF to form metal fluorides and hydrogen. These fluorides can retard further corrosion, as in the case of iron fluoride formed on the surface of carbon steel. However, these fluoride scales can also cause burns, if handled improperly, even when they appear dry. Packing materials, gaskets and pump seals will absorb AHF, and are difficult to decontaminate. After washing and drying, droplets of HF may form on such materials by drawing moisture from the air. Clearly, great care must be taken in handling any material that has been exposed to AHF.

SECTION 3 CORROSION RESISTANCE OF MATERIALS IN AHF

3.1 General

This document does not include all acceptable materials of construction. It also does not discuss those materials of construction which are unsuitable under all circumstances. Process vessels and piping constructed for AHF service should follow recognized design codes, such as ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, and ASME B31.3, Process Piping Code.

3.2 Metallic Materials

3.2.1 Carbon Steel

Carbon steel has been found to have satisfactory corrosion resistance to liquid AHF at temperatures up to 150°F (66°C). Carbon steel may withstand temperatures of up to 180F (82C)____, but thicker accumulation of iron fluoride film and higher corrosion rates are likely to result at these higher temperatures. The corrosion rate in AHF storage vessels at ambient temperature is usually very low, on the order of one mil per year (MPY)(.025 mm/yr.). Short term laboratory data often show up to ten times this rate, but this reflects the high initial corrosion as a protective fluoride film is formed. Limiting velocity of liquid AHF in carbon steel is important to avoid damaging the protective fluoride film. The European CEFIC-CTEF STS 89/66 bulletin recommends a maximum velocity for liquid AHF of 5 feet per second (FPS)(1.5 meters per second (MPS)) at ambient, while other references quote 6 FPS (1.8 MPS). Velocities at elevated temperatures, 150°F (66°C) or above, should be limited to less than 2 FPS (0.6 MPS), as the protective film becomes more easily damaged at higher temperatures. Steels usually show higher corrosion when the sum of the residual elements Cu, Ni, and Cr exceeds 0.2 percent by weight. The residual elements are usually not a problem when the temperature is near ambient since the corrosion rate is low. The presence of these residual elements in carbon steel seems to degrade the protective scale which is more easily removed by velocity, turbulence, or and increase in temperature.

Carbon steel has been found satisfactory in AHF vapor service to at least 392°F (200°C) when the pressure and the velocity are low. At one atmosphere of pressure 33 FPS (10 meters per second) is a reasonable limit. Entrainment of liquid AHF droplets in vapor greatly accelerates the corrosion of carbon steel and other metals. A chart is attached for reference in Appendix A. Information is based on 100 hour exposure data developed in the laboratory by NACE International.

3.2.2 Stainless Steels and Super Austenitic Stainless Steels

Austenitic stainless steels are resistant to liquid AHF up to at least 212°F (100°C). These alloys include type: 304 (S30400), 316 (S31600), 304L (S30403), 316L (S31603), A744 CF8 (J92600), CF8M (J92900), CF3 (J92700), CF3M (J92800), CN7M (J95150), Alloy 20 (N08020), Alloy 825 (N08825) and Alloy G 30 (N06030). The above alloys have been used successfully for valve and pump parts in AHF service. Casting integrity issues, such as segregation and microfissuring in castings of Alloy 20 compositions, can be reduced by specifing ASTM A-990. Numbers in parentheses represent the Unified Numbering System.

Hardenable duplex alloys, ferritic grades, and severely cold worked austenitic grades of stainless steel should be avoided because of potential problems with hydrogen assisted stress corrosion cracking.

3.2.3 Nickel Base Alloys

Nickel base alloys such as Alloy 400 (N04400), Alloy 600 (N06600), Alloy C-276 (N10276), Alloy G-30 (N06030) and ASTM A 494 cast alloys M-35-1, M-30C, CY40 and CW2M are satisfactory for use in liquid AHF service to at least 257°F (125°C). Seamless Alloy 600 (NO6600) heat exchanger tubing and Cast Alloy CY40 Class 2 valves have been successfully used in AHF vaporizer service at 275°F (135°C). The nickel base alloys listed above are satisfactory in vapor AHF up to a temperature of at least 572°F (300°C); with Alloy 600 the temperature can be at least 625°F (330°C).

Note that Alloy 400 (N04400) and Alloy K-500 (N05500) are susceptible to stress corrosion cracking in the vapor space if moisture and oxygen are present. It is desirable to specify a stress relief at 1300°F (704°C) for process equipment to improve resistance to stress corrosion cracking in both liquid and vapor. Alloy 400 (NO4400) fasteners are susceptible to cracking.

Alloy 500 (N05500) fasteners have cracked in liquid AHF. Alloy 600 (NO6600) has been successfully used for pressure vessels at 932°F (500°C) in AHF vapor. Welding wire AWS A5.14 ERNiCr-3 commonly used with Alloy 600 is attacked by HF at elevated temperature because the wire contains 2-3% Nb.

The other nickel base alloys listed above are resistant to stress corrosion cracking in AHF but may become susceptible if used in the same system with copper base alloys if cupric fluoride is present.

3.2.4 Copper-Nickel Alloys

Copper-nickel alloys such as 90/10 (C70600) and 70/30 (C71500) cupronickel are satisfactory in liquid AHF at ambient temperature.

3.2.5 Copper and Copper Alloys

Copper and copper alloys other than cupronickel can be used in AHF service under certain conditions, but are sensitive to oxygen and other oxidizing impurities, and to velocity. These alloys should be used with great caution in AHF service.

3.3 Non-metallic Materials

The use of solid plastics, elastomers and ceramics under pressure without external containment should be avoided in AHF service.

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 service.

PTFE	polytetrafluoroethylene
FEP	copolymer of PTFE and HFP (hexafluoropropylene)
PFA	copolymer of PTFE and a fluorinated ether
MFA	copolymer of PTFE and a fluorinated ether
ETFE	copolymer of PTFE and polyethylene
PVDF	polyvinylidene fluoride, also can refer to a copolymer of PVDF with HFP
CTFE	polychlorotrifluoroethylene
ECTFE	copolymer of CTFE and polyethylene

TFM PTFE with PFA

In some applications provisions must be made to safely vent AHF that permeates the plastic. The effect of fillers added to these plastics is discussed below in section 6.5, Gasketing Materials. Coatings and bonded linings using these fluorocarbons may not exhibit the same properties as the unbonded material and should be tested under appropriate conditions before use.

Specific compounds of the following elastomers have been found to be suitable for AHF service at ambient temperatures, but testing has suggested that these materials are not suitable at higher temperatures:

- FKM (designated by ASTM D1418) - Fluoroelastomers that meet the following requirements: peroxide cured, carbon black filler, with either no metal oxide or only lead oxide addition. This material is no longer avialable with the lead oxide treatment, therefore, many compounds of FKM are not suitable for use in AHF even at ambient temperatures. Specific formulations may be acceptable but must have been specifically tested under the conditions of use.
- FFKM (designated by ASTM D1418) - Perfluoroelastomers with carbon filler. This class is generally resistant to AHF. However, differences in performance do exist among the various commercial grades.

Consult with elastomer suppliers for more information about their specific materials and products. Note that many suppliers may provide this information via their websites.

Other non-metallics with usefullness in AHF service include:

- Flexible graphite.
- Alumina above 99.7% purity.
- Carbon with very low ash content, used in seals and bearings.
- Silicon carbide with no free silicon present such as alpha- sintered silicon carbide.
- In some applications, FEP fluoroplastic encapsulated fluoroelastomer can be an effective substitute for elastomeric o-rings.

SECTION 4 APPLICATIONS BELOW AMBIENT TEMPERATURE

When metals and non-metals are used at temperatures below ambient, the additional effect of low temperature on the properties of the materials must be considered. For example, design codes restrict the use of certain steels at low temperature because of reduced toughness. Shrinkage and possible embrittlement must be considered when using plastics and elastomers below ambient temperatures.

SECTION 5 CARBON STEEL VESSELS

5.1 General

Carbon steel vessels used to store and transport AHF have experienced three types of damage caused by hydrogen evolved during corrosion:

- Hydrogen assisted stress corrosion cracking has occurred along a hardened heat affected zone (HAZ) adjacent to welds.
- Hydrogen blistering, caused when atomic hydrogen from corrosion migrates through the steel to oxide/sulfide inclusions or laminations and combines there to form molecular hydrogen that cannot escape.
- Cracking has been found connecting microblisters which occur at individual inclusions. This is known as stress oriented hydrogen induced cracking (SOHIC). This type of cracking also occurs around large blisters that are tightly constrained at the periphery of the blister.

Hardening occurs when a steel weld is rapidly cooled. Higher carbon equivalent[1], and, therefore, generally higher tensile strength in steel plate increases the tendency for hardening to occur due to welding. Also, a weld on a thick plate cools more rapidly than a weld on a thin plate. Rapid cooling of welds can be minimized by using preheat and by using high heat input welding methods. The hardening can be reduced by lowering the carbon equivalent and tensile strength of the plate. Post weld heat treatment is strongly encouraged. A post weld heat treatment at a minimum temperature of 1150°F (621°C) is recommended to achieve sufficient stress relief. Stress relief lowers the hardness somewhat and significantly reduces residual stress, thereby reducing, but not eliminating, the potential for cracking. For stress relief to be effective the sum of the vanadium and columbium (niobium) content of the steel should not exceed 0.1 per cent.

Microhardness testing is another important technique in the strategy of limiting the risk of cracking in hard welds and weld HAZ. Portable microhardness test equipment is available that is effective in measuring hardnesses within narrow bands. Details of two recommended procedures are given in Appendix B. The carbon equivalent limit of 0.42 for plates up to 1' and 0.40 for the thicker plates is

[1] Carbon Equivalent (CE) is a commonly used method of correlating the hardenability of steel with its composition. One example is as follows:

$$CE = \%C + \frac{\%Mn}{6} + \frac{\%Cr + \%Mo + \%V}{5} + \frac{\%Ni + \%Cu}{15}$$

generally specified. It is generally recognized that Rockwell C22 is a limit for hardness.

The risk of hydrogen blistering and SOHIC associated with oxide/sulfide inclusions can be nearly eliminated by specifying calcium treated steels with very low sulfur. To be acceptable for either stationary vessels or rail cars and trailers, SA 516 steel should have 0.003% or lower sulfur content. It is also often processed in a special way to remove most of the oxygen, and with inclusion shape control provided to produce a steel with very few elongated inclusions. In the past plates have been ultrasonically tested for absence of planes of inclusions to meet ASTM A 578-96, level II, supplement S1, using a one inch diameter acceptance criterion in paragraph 8.1. Recent experience with plates one inch and thinner and with 0.003% or lower sulfur shows that ultrasonic testing may no longer be needed.

Shielded metal arc welding and submerged arc welding have both been successfully used for AHF service. The tensile strength and composition of the weld metal should be similar to that of the plate. Spot and microhardness testing on the fabricated item can be useful in assuring that proper welding conditions have been met. Refer to Appendix B for guidance on performing this hardness testing.

5.2 Stationary AHF Vessels

A desirable steel for stationary AHF vessels is normalized SA 516 Gr 55 (K01800) which specifies a 75,000 psi (517 MPa) maximum tensile strength. SA 516 Grades 60 (K02100), 65 (K02403), or 70 (K02700) may also be specified with a maximum tensile strength of 75,000 psi (517 MPa). Whenever practical, these vessels should have post weld heat treatment. The process is outlined in Section 5.3.

Carbon steel SA 516 grades 55 (K01800), 60 (K02100), 65 (K02403), and 70 (K02700) made in accordance with the recommendations of this section should have adequate toughness down to a temperature of -50°F (-46°C) for the thicknesses commonly used for AHF containers. SA 20 lists the impact properties that should be attained for various grades, thicknesses and temperatures.

When vessel design temperature is -20°F (-29°C) or above, openings should be SA 106 Gr B for nozzle necks and SA 105 for nozzle flanges. For AHF vessels designed to -50°F (-46°C) consider nozzle necks of SA 333 Gr 1, and flanges of SA 350 Gr LF-2.

5.3 Rail Cars and Tank Trailers

Rail cars and tank trailers commonly are built of normalized and inclusion shape controlled SA 516 Gr. 70 (K02700) steel with 70,000 psi (483 MPa) minimum tensile strength to reduce the weight of the vessel. Although these vessels are always given a post weld heat treatment, it is still necessary to minimize hardenability. Since the closest predictor of hardenability is carbon equivalent, the agreement with the steel mill should include the lowest carbon equivalent that will allow the minimum 70,000 psi tensile strength. Slight differences in steel making practice will vary the relationship between carbon equivalent and tensile strength. This makes it undesirable to specify a maximum carbon equivalent that all steel mills must meet. The mill also should be told that the steel will be given post weld heat treatment at 1150°F (621°C) minimum for the time that has been chosen. Using this approach should result in most steels having tensile strengths between 70,000 and 80,000 psi (483-552 MPa), although a few lots may have tensile strengths as high as 85,000 psi (586 MPa). The carbon equivalent should not generally be over 0.42.

Some steel vendors are now offering a SA 516 grade steel with tensile strength between 70,000 and 75,000 psi (483-517 MPa) that will meet all the SA 516 grades. This appears to be a particularly desirable way of obtaining a satisfactory tensile strength steel for AHF service.

To reduce the possibility of hydrogen blistering to a minimum, there are alternate methods to assure significant reduction of inclusions.

- Specifying a sulfur content of 0.003% maximum requires steel producers to follow practices including calcium treatment, argon degassing, and processing controls which result in minimal inclusions.

- The use of through thickness ultrasonic inspection techniques such as ASTM A 578-96 (modified to a 1' diameter acceptance criteria) over 100% of the area.

- HIC testing per NACE TM-0284 utilizing the acidic solution media and an acceptance criteria of a crack length ratio of 15 or less.

Another option for AHF cargo tank trailers is stainless steel. If this option is chosen, the steel shall be SA 240 Type 316L stainless steel (UNS S31603). Forgings will be per SA 182 Type 316L, pipe will be per SA 312 Type 316L, and pipefittings will be per SA 403 Type 316L.

SECTION 6 FASTENERS, STUDS AND GASKETS

6.1 General

The proper selection of flange fasteners is very important for AHF service. While the fastener is rarely exposed to AHF, small acid leaks can expose fasteners to risk of failure if the incorrect fastener material has been used. Care should be taken to insure all fasteners in AHF facilities are suitable for AHF service. This is particularly important for valve bonnets and small fasteners associated with instruments. The size of these fasteners and their proximity to the gasket increases the risk of failure in event of an acid leak. There have been cases documented in which the bonnet has separated from the valve body due to hydrogen assisted stress corrosion cracking of excessively hard carbon steel bonnet fasteners.

6.2 Fastener Failure Mechanisms

When a small AHF leak mixes with moisture in the air it forms a highly corrosive aqueous HF acid. This will corrode both carbon steel and austenitic stainless steel fasteners. The corrosion rate on carbon steel is much higher than that on the stainless steel. If allowed to continue unchecked, corrosion will result in failure of both types of fasteners. If there is sufficient room between flanges for observation, the corrosion products may be plainly visible and this type of fastener damage might be detected before failure by routine operator surveillance.

Another significant risk of fastener failure is that from cracking. Cracking failures can occur in a very short period of time and without visible reduction in fastener diameter. Carbon steel fasteners are susceptible to hydrogen assisted stress corrosion cracking if the hardness and tensile strength exceed acceptable levels.

Austenitic stainless steel fasteners are generally resistant to cracking from exposure to AHF, but is susceptible to chloride stress corrosion cracking. Chlorides in the form of HCl are generated at some plants that use or store AHF. Chlorides are also present in the air in marine environments.

6.3 Acceptable Fastener Materials

Below are listed four classes of fastener materials that have been found to be suitable for AHF service. It is important that the user of such fasteners, or studs, carefully verify that the specifications for these fasteners have been met before using in AHF service. The hardness of low and intermediate strength fasteners is particularly important. The user should consider replacing fasteners after each use due to the possibility of over-torquing or exposure to AHF wisps in service. Consider tightening fasteners smaller than five-eighths inch diameter with a torque wrench to prevent possible work hardening which would increase their susceptibility to cracking.

- Low strength carbon steel fasteners, of which an example is SA 307 Grade B. The hardness is HRB 95 maximum. The lower hardness limit associated with hydrogen assisted stress corrosion cracking is generally considered to be HRB 99. Since these fasteners have a minimum tensile strength of 60,000 psi (415 MPa), they should be used only with sheet fluoropolymer (usually PTFE) gaskets which require a nominal load for seating. Fasteners should have heavy hexagonal heads.

- Intermediate strength carbon steel SA 193 B7M, S3, 100% hardness tested by indentation method is a suitable external flange fastener for anhydrous HF service. This designation specifies a minimum and a maximum hardness and a tensile strength suitable for use with spiral wound gaskets as well as sheet fluoropolymer (usually PTFE-based (either filled or unfilled) gaskets. Fasteners should have heavy hexagonal heads, and SA 194 2HM nuts.

- Intermediate strength stainless steel such as SA 193 B8 Class 2, or SA 193 B8M Class 2 and SA 194 GR 8 or 8M nuts. Stainless steel fasteners should not be used if a chloride environment is present.

- High strength fasteners, if required, can be provided by precipitation hardened nickel alloys such as Alloy 718 (N07718). The chemistry and heat treatment of this alloy are given in ASTM B637. Although experience with fasteners with this heat treatment has been good, there have been isolated examples of environmental cracking. NACE MR 0175 provides an alternate heat treatment which provides a somewhat lower hardness and strength and even greater resistance to cracking. In a nitrogen atmosphere solution anneal the Alloy 718 at 1875°F (1024°C) holds for one hour at temperature and water quench. Precipitation harden at 1450°F (788°C) for six to eight hours air cool to room temperature. The desired hardness is 37 HRC but acceptable hardness is 35.5 to 39.

6.4 Gasketing Materials

The following gasket materials have been used successfully in flanged closures in AHF service. This is not meant to be an exhaustive list, other gasket materials and forms may be suitable for specialized applications.

- Spiral wound gaskets with PTFE and flexible graphite fillers. The tape material can be 304 S/S (S30400), 316 S/S (S31600), Alloy 400 (N04400), Alloy 200 (N02200), Alloy C-276 (N10276) or Alloy 600 (N06600). Steel centering (external) rings provide mechanical strength and keep the gasket centered, while inner rings matching the tape material help to prevent crevice corrosion on the flange face.

- PTFE sheet without filler

- 100% virgin expanded PTFE

- 100% virgin oriented PTFE

- PTFE sheet with calcium fluoride filler

- PTFE sheet with carbon filler

- PTFE sheet with totally encapsulated metal grid reinforcement
- Flexible graphite-filled double-jacketed copper ring gasket
- Flexible graphite* (with or without) reinforcement
- Flexible graphite* applied to both sides of a continuous corrugated metal core (laminate gasket) -- Tanged styled gaskets are not recommended for this service.

*Where flexible graphite is specified, it should be nuclear-grade, low ash content (e.g., 0.1% ash).

The standard grade of flexible graphite typically contains about 3% ash (mainly SiO_2 and Al_2O_3) which would be attacked by AHF. Normally, this does not create leaks when using the standard grade for gasketing. However, occasionally there has been evidence of attack on the metal touching the graphite and the metal when water is present as a conductor. The use of the nuclear grade with controlled ash of flexible graphite which is 99.8% graphite would prevent this from occurring.

Sheet gaskets used with tongue and groove flanges can provide additional protection against blow-out.

New gaskets should be used each time flanges are separated.

Note that fluorocarbon PTFE sheet with barium sulfate addition has not proven suitable for AHF service. Gasketting materials containing PTFE are subject to permeation. PTFE gasket materials are subject to plastic flow under load, and their slow recovery when the load is removed has contributed to gasket leaks in systems that are subject to temperature changes. This should be considered when making a gasket selection.

SECTION 7 VALVES FOR AHF SERVICE

7.1 General

As outlined above in Section 6, proper selection of fasteners is one of the most important considerations in insuring the safety of valves in AHF service.

Leakage through the packing along the stem and leakage at the bonnet gasket are occasional problems with AHF valves. To minimize packing leakage, valve manufacturers have used stacked PTFE packing, pre-formed graphite packing, and nickel-based spring loaded washers to apply load to the packing. HF alkylation valves usually use extra deep stuffing boxes to allow extra seals with flexible graphite to make them fire safe. Lantern rings with grease seals are also used for better sealing in the stuffing boxes. These valves have been used in nonflammable AHF service as well to improve sealing. In general, there will be less leakage along the stem when the stem is made of a material resistant to AHF and the aqueous acid formed when AHF contacts moist air.

7.2 Manual Valves

Ball and plug valves are commonly used in AHF service. Gate and bellows sealed globe valves are also used successfully.

Valves also are needed for AHF vapor at a temperature that is often too hot for PTFE. These valves are commonly nickel base alloy globe and gate valves. In some services cobalt based alloys may be useful. Flexible graphite is used for the packing. (See the note in Section 6.5 concerning the grades of flexible graphite.)

Carbon steel valve bodies are considered adequate for AHF service. However, the iron fluoride corrosion products can occasionally cause difficulty by accumulating in the moving parts of the valves. This can make the valve stem hard to turn, interfere with seating and provide paths for leak-through. Valves with alloy bodies have had fewer of these scale related problems. Alloy materials that have been used with success include stainless steels CF8M (J92900) and CF3M (J92800), CN7M (J95150) and Alloy 400 (M35-1).

The valves used on AHF rail cars, truck trailers and ISO tanks include the following:

- Angle ball valves with carbon steel body and Alloy 20 (N08020) or Alloy C-276 (N10276) trim.
- Angle globe valves with carbon steel body and Alloy 400 (N04400) trim.
- Special angle valves with a bellows seal and a permanently installed actuator. This valve has two closing mechanisms. A portion inside the vessel functions as a check valve, closing with its own spring when the air pressure to the actuator is interrupted. A second portion of the valve is outside the vessel and includes another sealing surface and a plug which is held tight to the seat when air to the actuator is interrupted. This valve is commonly used in Europe and is beginning to be used in North America. Alloy C-276 is suitable for the bellows and internal fasteners in these valves. Note: Highly stressed Alloy 400 presents a stress cracking risk in the presence of moist aerated HF.

7.3 Primary Isolation Valves

The primary isolation valve should incorporate various upgrades to optimize its reliability. These upgrades have included added stem packing, the use of a bellow seal in the stem and Alloy C-276 (N10276) bonnet and flange fasteners. A design of a bellow isolation valve is described below. Globe valves have an advantage over ball or plug valves in that closing the valve will isolate a bonnet or packing leak provided that the inlet flow to the valve is under the plug. Some desirable features which have been incorporated into one such globe valve include:

- A remote automated actuator with a manual override
- A soft seat of PTFE
- An alloy bellows seal, Alloy C-276 (N10276) preferred
- Tongue and groove flange faces
- Cast carbon steel or CN7M(J95150)
- Alloy 20 (N08020) trim
- ANSI Piping Class 300 design minimum
- Alloy C-276 (N10276) fasteners

Note: That it is desirable to have multiple locations from which the valve may be actuated as protection against inaccessibility due to a single location being engulfed in an AHF cloud.

SECTION 8 RUPTURE DISK MATERIAL

Rupture disks for AHF service are usually made of Alloy 200 (N02200), or Alloy C-276 (N10276) although other nickel based alloys also have been used without problems. An exception is Alloy 400. When exposed to moist air rapid cracking can occur. Gold and platinum are also used occasionally for rupture disks. The disks have been used both with and without a loose PTFE liner or fluoropolymer plastic coating on the process side. Rupture disks in AHF service should always be replaced after they have been exposed to moist air, for example, during safety relief valve maintenance or other inspections.

SECTION 9 PIPING MATERIALS

Carbon steel piping is normally used for AHF, respecting the temperature and velocity considerations outlined in Section 3.2.1. Steels usually show higher corrosion when the sum of the residual elements Cu, Ni, and Cr exceeds 0.2 percent by weight, and where temperatures exceed 140°F/60°C.

At this time, there is no practical way of purchasing pipe and fittings meeting this residual elements requirement. Therefore, it is recommended that a rigorous piping inspection program such as outlined in API 570 should be followed. Every pipe section and fitting used in AHF above ambient temperature should periodically be checked for thickness to locate steel which may have a higher corrosion rate. Mill test results should also be checked for residual elements.

Seamless grades of carbon steel pipe, such as SA 106 Gr B (K03006), are preferred. However, welded grades of carbon steel pipe have been used successfully. A minimum of Schedule 80 should be specified for two inch and smaller sizes of pipe to assure adequate wall thickness for mechanical strength.

Pipe should be butt welded rather than threaded whenever possible. Threaded connections should not be used for greater than one inch pipe. Threaded connections to some pieces of equipment, however, may be unavoidable. These are suitable, provided the pipe is extra heavy wall (Schedule 160). PTFE tape should be used with threaded joints. Back welding also may be acceptable. Note: When back welding do not use PTFE tape.

Weld neck flanges are preferred to stub ends. Rolled flanges and slip-on flanges should be avoided for AHF service. Hydrogen can accumulate at >1000 psig (>6.9 MPa), between the welds of a slip-on flange.

Gas tungsten arc welding (GTAW), gas metal arc welding (GMAW), and shielded metal arc welding (SMAW) have all been used successfully on piping in AHF service. It is desirable to radiograph 100% of welds in AHF piping. Any slag inclusions are readily corroded by AHF. Branch connections should be made with welding tees so that the welds can be radiographed. Weld examination should follow ASME B31.3, as outlined for "severe cyclic condition."

Side branches should be one inch NPS or larger to provide adequate mechanical strength and avoid damage.

Pipe specification SA 106 Gr B specifies a minimum, but no maximum tensile strength. It is theoretically possible to have a pipe with a high carbon equivalent and high tensile strength which would result in a hard HAZ after welding. Experience shows that the pipe wall thickness is thin enough that hardening in the HAZ leading to cracking is generally not a problem. It is desirable, however, to use preheat and high heat input welding methods to minimize hardening however, note that if in an excessively cold environment, preheating may be necessary. Post weld heat treatment can further reduce any risk of cracking in AHF service. The control of carbon equivalent can also reduce risk of cracking in AHF service.

Flange specification SA 105 is looser in some of the important properties listed above than the piping specification. Particular attention should be paid to pipe to flange weld quality.

SECTION 10 TRANSFER HOSE

Transfer hoses are high-risk, critical components and must be handled carefully. These hoses normally have a reinforced rubber body with a PTFE inner liner, but other fluoropolymer liners also are used occasionally. Most commercially available hoses do not use reinforcement around the inner liner, which is resistant to AHF/aqueous HF. Therefore, it is imperative that the hoses be adequately supported so that the inner liner is not mechanically damaged. Since these hoses are used intermittently at ambient temperature, permeation of HF through the fluoropolymer liners has not been enough to degrade significantly the outside reinforcement, provided the fluoropolymer liner is not cracked.

SECTION 11 REFERENCES

- ASME Boiler and Pressure Vessel Code, The American Society ofMechanical Engineers, 345 East 47th Street, New York, NY 10017.
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APPENDIX A – NACE CHART

This chart will be added once NACE provides reprint authorization.

APPENDIX B

PORTABLE HARDNESS TESTING

Hard weld heat affected zones (HAZ) may crack when exposed to hydrogen fluoride. These HAZ may be 0.03" to 0.1" (0.76 to 2.54 mm) wide. Therefore, standard field hardness tests with ball indentations may miss a thin hard zone. Below are two portable microhardness test procedures that have been used to screen the hardness of welds, base metal, and heat affected zones in vessel construction and repairs. Procedure I is more suitable for screening purposes over a large area. Procedure II provides a more through analysis of hardness at a specific location of interest.

It is recommended that an ultrasonic microhardness measurement device with a Vickers diamond tip be used (e.g., a Krautkramer MIC 10). Hardness readings should be made on the Rockwell C scale. When hardness readings below the range of the Rockwell C scale are encountered, change to the Rockwell B scale. The Vickers hardness scale may also be used for hardness readings but the hardness criteria must be converted.

PROCEDURE I

1. Use a power tool to remove any rust, scale, fine corrosion pits, or other roughness from the surface to be tested. Finish the surface to be tested with a high-speed medium sandpaper disc or a wire wheel to create a suitably smooth surface. The surface finish is satisfactory when the majority readings are consistently within 1 or 2 units of Rockwell or 5 units of Brinell hardness. There will always be out-lying readings because individual crystals or grain boundaries will be unusually hard or soft. These readings should be ignored and will require experience and judgment to identify.

2. At each test station, the hardness of the base metal on each side of the weld, the two heat affected zones immediately adjacent to the toe of the weld, and three spots across the face of the weld deposit itself should be tested and recorded separately.

3. Tests should be performed on both the inside and outside of the vessel. Test stations should be selected to provide a representative selection of welding positions and work done by individual welders.

4. Take five readings at each location and average them together. If an extremely large or small reading occurs take more readings immediately adjacent to the questionable reading. If no other readings are extreme, delete the reading. Continue taking more readings while observing how the average changes. Continue taking readings until the average "settles down" by changing less than one Rockwell B or C unit with each new reading.

5. The reported results will be the average at each of the seven locations for each test station.

As an alternate procedure, some users utilize a higher level of surface preparation to insure locating the heat-affected zone. This procedure consists of the following steps.

PROCEDURE II

1. Using a sander with a 100 grit flexible disk, remove the weld reinforcement flush with the shell surface. Prepare an area at least 4" in diameter and include both heat-affected zones.

2. Use a ¾ to 1-inch diameter high-speed flexible abrasive sander with a 120-grit disk. Remove all marks from the previous 100 grit sanding.

3. Using 180 grit emery cloth, hand polish the test area to remove all marks from the 120 grit sanding. The finished area should be flat (with the contour of the vessel) and smooth.

4. Etch the polished area with nital etch solution (10% concentrated nitric acid in 90% methanol) by swabbing with cotton swabs. Etch until the weld heat affected zones are clearly defined.

5. Rinse with methanol and allow drying.

6. Perform microhardness scans:

   - Make two parallel scans through each heat affected zone of the weld.

   - Each scan should start in the base metal, traverse the heat affected zone and end in the weld

   - Utilize a magnetic holder with a micrometer adjustment to take readings spaced 0.010 inch (0.25 mm) apart, with a minimum of 25 readings per scan.

   - Two readings should be made on a test block at the beginning and end of each scan. The test block should have hardness approximating 22 HRC.

7. Analyze each series of hardness readings. A hard HAZ is indicated by two or more adjacent readings which have hardness over HRc 22.5 (HV 250).