

# Safe Operation of Hydrofluoric Acid Alkylation Units

## 1 Scope and Purpose

API 751 provides requirements (shall) and recommendations (should) for practices and procedures related to safety, operations, design, inspection, and maintenance to support the safe and reliable operation of hydrofluoric acid (HF) alkylation units. Topics include hazard management; operating procedures and worker protection; materials, construction, inspection, and work practices; transportation and inventory control; pressure-relief, product treatment, and utility systems; and risk mitigation. This document contains requirements and recommendations that have been found effective based on broad industry acceptance, proven effective industry practices, testing, and regulatory requirements.

## 2 Normative References

The following documents are referred to in the text in such a way that some or all of their content constitutes the requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API 510, *Pressure Vessel Inspection Code: In-Service Rating, Repair, and Alteration*

API 570, *Piping Inspection Code: In-service Inspection, Rating, Repair, and Alteration of Piping Systems*

API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction*

NOTE Whenever API standards are referenced, where equivalent national standards exist, they may be used in accordance with other applicable regulations for non-U.S. jurisdictions.

## 3 Terms, Definitions, Acronyms, Abbreviations, and Symbols

### 3.1 Terms and Definitions

For the purposes of this document, the following definitions apply.

#### 3.1.1

##### **acid detecting paint**

Acid detecting paint is a durable, industrial coating with a unique acid-sensitive component, which changes color (e.g. golden yellow to brilliant red) when exposed to an acid or acid vapor of pH 3 or lower. (Also known as “acid indicating paint.”)

#### 3.1.2

##### **acid relief neutralizer**

##### **ARN**

This system is where the flow from acid-containing relief valves is routed to allow the acid to be neutralized before being routed to the non-acid flare system. Vapor flow is typically routed to the general refinery flare header once neutralized. This can refer to a flare gas scrubber (FGS), a relief gas scrubber (RGS), or an acid relief neutralizer (ARN).

#### 3.1.3

##### **acid soluble oil**

##### **ASO**

Typically seen as the waste stream created by secondary or side reactions in the presence of feed contaminants or unfavorable reaction conditions. Ranges from light to heavy material and will vary depending upon reaction conditions. This byproduct may be referred to as polymer.

### 3.1.4

#### **bad actor**

An asset that experiences a history of issues causing concerns with continued mechanical integrity (e.g. an unusually short life cycle, unexpected short mean time between failures).

### 3.1.5

#### **blistering (damage)**

A void, either at the subsurface or deeper, created in the metal due to molecular hydrogen (from re-combined hydrogen atoms) accumulating in laminations or other conducive sites in the steel. See 6.4.3.6 and G.2.1.2.

### 3.1.6

#### **bolt**

An assembly of a nut(s) and a stud for fastening objects together.

### 3.1.7

#### **caustic**

Refers to aqueous solutions of either sodium hydroxide (NaOH) or potassium hydroxide (KOH) that are both inorganic compounds and strong base materials.

### 3.1.8

#### **cladding**

A metal plate bonded onto a substrate metal under high pressure and temperature whose properties are better suited to resist damage from the process than the substrate metal. (e.g. explosion bonded plate, roll bonded plate).

### 3.1.9

#### **clamp**

An engineered mechanical enclosure applied to an asset, which meets design conditions, to prevent or contain a loss of containment of the pressure boundary.

### 3.1.10

#### **coating**

A nonmetallic (inorganic or organic) material installed on the exterior or interior of an asset whose properties are better suited to resist damage from the atmosphere or process than the substrate material. (e.g. coal tar epoxy, external paint).

### 3.1.11

#### **cold flow**

A load applied to an elastic material that will compress and deform it, allowing it to take up the irregularities between the two surfaces being sealed. The material may take on a permanent deformation or, in some cases, continue to deform. In a bolted joint, the compressed gasket creates the torque in the securing bolts, but as the gasket material creeps and the gasket thins, the bolts can relax, reducing the torque and loosening the joint (also known as gasket relaxation, gasket creep, viscoelastic creep).

### 3.1.12

#### **condition monitoring location**

##### **CML**

Designated areas on pressure vessels and piping where periodic external examinations are conducted to directly assess their condition.

### 3.1.13

#### **controlled deposition welding**

##### **CDW**

Any welding technique used to obtain controlled grain refinement and tempering of the underlying heat-affected zone (HAZ) in the base metal. Various controlled-deposition techniques, such as temper bead

(tempering of the layer below the current bead being deposited) and half bead (requiring removal of one-half of the first layer), are included.

#### **3.1.14**

##### **corrosion control document**

##### **CCD**

A document or other repository or system that contains the necessary information to understand materials damage susceptibility issues in a specific type of operating process unit at a plant site.

#### **3.1.15**

##### **corrosion specialist**

A person acceptable to the owner-operator who is knowledgeable and experienced in specific process chemistries, degradation mechanisms, materials selection, corrosion mitigation methods, corrosion monitoring techniques, and their impact on process equipment, including pressure vessels and piping systems and associated components.

#### **3.1.16**

##### **corrosion under insulation**

##### **CUI**

External corrosion of piping, pressure vessels, and structural components resulting from water trapped under insulation.

#### **3.1.17**

##### **corrosion zone**

Describes specific HF services that have similar corrosion characteristics and consequences in HF alkylation units (see G.3).

#### **3.1.18**

##### **credible design point**

This establishes a scenario basis for evaluating/constructing a toxic refuge shelter including the benefits derived from safety systems functioning as designed.

#### **3.1.19**

##### **critical check valve**

Critical check valves are those that need to operate reliably to avoid the potential for hazardous events or substantial consequences in situations where reverse flow may occur.

#### **3.1.20**

##### **crossover line**

A section of pipe on an HF trailer used to leak test the unloading hose or purge HF vapors from the hose before disconnecting.

#### **3.1.21**

##### **dead-leg**

Components of a piping system that normally have little or no significant flow. Some examples include blanked (blinded) branches, lines with normally closed block valves, lines with one end blanked, pressurized dummy support legs, stagnant control valve bypass piping, spare pump piping, level bridles, pressure-relieving valve inlet and outlet header piping, pump trim bypass lines, heat exchanger bypass lines, high-point vents, sample points, drains, bleeders, and instrument connections. Dead-legs also include piping that is no longer in use but still connected to the process.

#### **3.1.22**

##### **decontamination**

The removal of hazardous products from people, protective gear, or equipment.

### **3.1.23**

#### **delayed hydrogen cracking**

Cracking occurring in carbon or low-alloy (ferritic) steels, when molecular hydrogen has been entrapped as part of the welding process, embrittling the metal. This happens generally in the HAZ but could possibly extend into the weld metal. The cracks can form immediately after welding, a short time after welding (hours), or days afterwards. (Also known as “cold cracking” or “delayed cracking.”)

### **3.1.24**

#### **dilute HF acid**

A term used to designate a corrosion area of high-water concentration with some HF.

NOTE This term was used in earlier API 751 versions (Fourth Edition and earlier). It has been superseded by the defining of corrosion zones (as of the Fifth Edition) and is no longer used. It is maintained for reference only.

### **3.1.25**

#### **dilute HF in water corrosion zone**

The corrosion zone where the aqueous phase condenses, and contains a low concentration of HF in water (see G.3.5).

### **3.1.26**

#### **dispersion release plume**

This is the region affected by a potential release and is determined by dispersion modeling. Dispersion release plumes typically have varying shapes with a centerline concentration that progresses downwind.

### **3.1.27**

#### **dissimilar metal weld**

##### **DMW**

Signifying the weld that joins two metals of different compositions.

### **3.1.28**

#### **egress**

The act of exiting an area.

### **3.1.29**

#### **emergency stop system**

A system designed to stop the flow of HF acid during the unloading process.

### **3.1.30**

#### **equivalent industry standards**

Codes and standards accepted by the jurisdiction or locality (e.g. country, region) as having equally rigorous requirements and recommendations as those codes and standards referenced herein.

### **3.1.31**

#### **fractionator HF corrosion zone**

The corrosion zone between the bottom of the fractionator where HF is produced by thermal defluorination and the location where the HF and water in the fractionator feed is completely vaporized (see G.3.6).

### **3.1.32**

#### **fresh HF corrosion zone**

The corrosion zone where fresh HF acid is received, transferred, and stored (see G.3.2).

### **3.1.33**

#### **grounding/bonding cable**

A cable used to join two pieces of equipment together to eliminate the buildup of static electricity during the unloading process.



### **3.1.34**

#### **HF regeneration system**

The equipment in this system removes acid soluble oil (ASO), water, and other contaminants from the circulating acid. This system is referred to as the acid rerun or the acid regenerator.

### **3.1.35**

#### **HF service**

A process stream containing inorganic HF above de minimis concentrations during normal operations.

### **3.1.36**

#### **high residual element**

#### **high RE**

Carbon steel that does NOT meet the following criteria.

- For Base Metal:  $\%C \geq 0.18 \text{ wt } \%$ ,  $\%Cu + \%Ni \leq 0.15 \text{ wt } \%$ .
- For Base Metal:  $\%C < 0.18$  or unknown,  $\%Cu + \%Ni + \%Cr \leq 0.15 \text{ wt } \%$ .
- For Weld Metal:  $\%Cu + \%Ni + \%Cr \leq 0.15 \text{ wt } \%$ .

### **3.1.37**

#### **hot bolting**

Replacing bolts on flanges that are in service and under pressure.

### **3.1.38**

#### **hydrogen bake-out**

A heating procedure (time- and temperature-based) used prior to welding to drive hydrogen out of an asset manufactured from carbon steel and that is susceptible to atomic hydrogen dissolution and entrapment (derived from the process environment) in order to make it hydrogen-free, easily weldable, and less susceptible to hydrogen cracking due to the welding process.

### **3.1.39**

#### **injection point**

Injection points are locations where water, steam, chemicals, or process additives are introduced into a process stream at relatively low flow/volume rates as compared to the flow/volume rate of the parent stream.

### **3.1.40**

#### **inspection plan**

A documented set of actions and/or strategies detailing the scope, extent, methods, and timing of specific inspection activities to determine the condition of a specific piece of equipment.

### **3.1.41**

#### **inspection program**

A program that develops, maintains, monitors, and manages a set of inspection, testing, and preventative maintenance activities to maintain the mechanical integrity of equipment.

### **3.1.42**

#### **inspector**

A shortened title for an authorized pressure vessel, piping/piping component, or tank inspector qualified and certified in accordance with API 510, API 570, and API 653, respectively; not specifically assigned to the HF alkylation unit but may conduct inspection work within the boundary limits at the discretion of the owner-operator.

### 3.1.43

#### **integrity operating window**

##### **IOW**

Established limits for process variables (parameters) that can affect the integrity of the equipment if the process operation deviates from the established limits for a predetermined length of time [includes critical, standard, and informational integrity operating windows (IOWs)] developed in accordance with API RP 584.

### 3.1.44

#### **licensor**

A business, organization, or individual who grants official (legal) permission to another entity (e.g. owner-operator) to make, do, operate, or own something the originator holds patent or ownership to.

### 3.1.45

#### **lining**

A nonmetallic or metallic material installed on the interior of an asset whose properties are better suited to resist damage from the process than the substrate material (e.g. strip lining).

### 3.1.46

#### **loss of primary containment**

##### **LOPC**

An unplanned or uncontrolled release of any material from primary containment, including nontoxic and nonflammable materials.

### 3.1.47

#### **low-alloy steel**

A family of steels containing up to 9 % chromium and other alloying additions for high-temperature strength and creep resistance. The materials include C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25 Cr-0.5Mo, 2.25Cr-1.0Mo, 5Cr-0.5Mo, and 9Cr-1Mo. These are considered ferritic steels.

### 3.1.48

#### **low residual element**

##### **low RE**

Carbon steel meeting the following criteria.

- For Base Metal:  $\%C \geq 0.18 \text{ wt } \%$ ,  $\%Cu + \%Ni \leq 0.15 \text{ wt } \%$ .
- For Base Metal:  $\%C < 0.18 \text{ wt } \%$  or unknown,  $\%Cu + \%Ni + \%Cr \leq 0.15 \text{ wt } \%$ .
- For Weld Metal:  $\%Cu + \%Ni + \%Cr \leq 0.15 \text{ wt } \%$ .

### 3.1.49

#### **main acid**

A term used to indicate any service where a free HF phase is present or could be present due to condensation or entrainment during normal operation.

NOTE This term was used in earlier API 751 versions (Fourth Edition and earlier). It has been superseded by the defining of corrosion zones (as of the Fifth Edition) and is no longer used. It is maintained for reference only.

### 3.1.50

#### **material verification program**

##### **MVP**

A documented quality assurance (QA) program used to assess metallic alloy materials (including weldments and attachments where specified) to verify conformance with the selected or specified alloy material designated by the owner/user.

NOTE This program may include a description of methods for alloy material testing, physical component marking, and program recordkeeping.

### **3.1.51**

#### **maximum credible event**

##### **MCE**

A hypothetical event that releases HF from among the HF-containing equipment on the alkylation unit and reaches the greatest downwind distance at a specified hazard endpoint. See K.2.2.

### **3.1.52**

#### **mechanical integrity**

The management of the activities necessary to ensure that equipment/assets are designed, fabricated, installed, operated, and maintained in a way that provides the desired performance in a safe, environmentally protected, and reliable fashion. Mechanical integrity is a subset of an effective reliability program and overall asset management, specific to equipment types, and more tactical in nature including the evaluation of condition requirements through regular monitoring and inspection of the condition of these assets.

### **3.1.53**

#### **mix point (mixing point)**

Mixing points are locations in a process piping system where two or more streams meet. The difference in streams may be composition, temperature, or any other parameter that may cause deterioration and may require additional design considerations, operating limits, inspection, and/or process monitoring.

### **3.1.54**

#### **modified HF**

##### **MHF**

A passive mitigation system whereby an additive to the HF acid is used to lower the acid volatility.

### **3.1.55**

#### **Ni alloy**

A family of metal alloy materials that the primary element is nickel (Ni). These are used because of their corrosion resistance. For HF units, the major alloy types that are used are nickel-copper (Ni-Cu) alloys (e.g. Alloy 400) and nickel-chromium-molybdenum alloys (e.g. Alloy C-276).

### **3.1.56**

#### **nondestructive examination**

##### **NDE**

The act of determining the suitability of some material or component for its intended purpose using techniques that do not affect its serviceability.

### **3.1.57**

#### **nontoxic refuge structure**

Buildings that are not a safe haven or a shelter-in-place. This can include administration buildings, maintenance buildings, and/or other buildings not needed for critical control activities.

### **3.1.58**

#### **on-stream inspection**

An inspection performed from the outside of a pressurized asset while it is operating using nondestructive examination (NDE) procedures to establish the suitability of the pressure boundary for continued operation.

### **3.1.59**

#### **phase change HF corrosion zone**

The corrosion zone where HF is either being condensed or vaporized, either by design or inadvertently. Phase change HF also occurs where a rich HF phase is either being absorbed into a liquid hydrocarbon stream or is forming by separating from a liquid hydrocarbon stream (see G.3.4).

### **3.1.60**

#### **piping specification break**

The location where the pipe specification changes to accommodate the piping design requirements, such as changing the material of construction, changing pressure rating, or changing temperature rating.

### **3.1.61**

#### **postweld heat treatment**

##### **PWHT**

A controlled process in which a material that has been welded is reheated to a temperature below its lower critical transformation temperature, and it then is held at that temperature for a specified period. A postweld heat treatment (PWHT) is performed to alleviate residual stresses, reduce hardness, and lower the risk of cracking.

### **3.1.62**

#### **potential hazard zone**

This is the reach of the centerline dispersion at a given concentration considered hazardous to human health regardless of wind direction. Potential hazard zones are typically circles; however, they can be strongly influenced by topography such as valleys, hills, or other dispersion modifiers.

### **3.1.63**

#### **pressure-relief valve**

##### **PRV**

A device used to protect equipment by reducing hazardous internal pressure before the equipment fails.

### **3.1.64**

#### **pressure testing**

A test performed on pressure vessels and/or piping that have been in service and that have undergone an alteration or repair to the pressure boundary(s). The test result will indicate whether or not the integrity of the pressure components is still compliant with the original construction code. The pressure test can be hydrostatic, pneumatic, or a combination thereof. Pressure tests at less than those specified by the construction code to determine if there may be leaks in the system are generally referred to as tightness tests.

### **3.1.65**

#### **pressure vessel**

A container designed to withstand internal or external pressure. This pressure may be imposed by an external source, by the application of heat from a direct or indirect source, or by any combination thereof. This definition includes heat exchangers, air coolers, columns, towers, unfired steam generators (boilers), and other vapor generating vessels that use heat from the operation of a processing system or other indirect heat source.

### **3.1.66**

#### **proactive initiator/instrument**

Also known as feed-forward control. A term describing an element or pathway within a control system that passes a controlling signal from a source in its external environment to a load elsewhere in its external environment. This is often a command signal from an external operator.

### **3.1.67**

#### **process hazard analysis**

##### **PHA**

An analysis designed to identify, safeguard, and mitigate potential process safety events.

### **3.1.68**

#### **purged**

To fill a piece of equipment with an inert gas to remove unwanted materials.

**3.1.69**  
**qualified**

Meeting the requirements and expectations of the owner-operator.

**3.1.70**  
**quality assurance**  
**QA**

All planned, systematic, and preventative actions required to determine if materials, equipment, or services will meet specified requirements so that the asset will perform satisfactorily in service. Quality assurance plans will specify the necessary quality control (QC) activities and examinations.

**3.1.71**  
**quality control**  
**QC**

Those physical activities conducted to check conformance with specifications in accordance with the QA plan (e.g. NDE techniques, hold point inspections, material verifications, checking certification documents, etc.).

**3.1.72**  
**rapid acid transfer system (RATS)**  
**rapid acid deinventory system (RADS)**  
**rapid acid dump system (RADS)**  
**acid evacuation system (AES)**

A system designed to move the bulk HF acid inventory from the rich HF section into a safe location. See 9.6.3.

**3.1.73**  
**reactive initiator/instrument**

Also known as feedback control.

Feedback loops consider the system output and enable it to adjust its performance to meet the desired output response.

**3.1.74**  
**remotely activated valve**

An actuated valve designed, installed, and maintained for the primary purpose of achieving rapid operation.

**3.1.75**  
**residual element**  
**RE**

The composition level of copper (Cu), chromium (Cr), and nickel (Ni) in carbon steel materials that can contribute to higher corrosion rates.

NOTE Formulas for calculation are provided in 6.2.2.1 and G.2.2.

**3.1.76**  
**rich HF**

Rich HF comes primarily in two forms—reactor acid and boot acid—and includes areas where a hydrocarbon stream contains residual amounts of entrained acid.

**3.1.77**  
**rich HF corrosion zone**

Areas of the unit where the HF phase is circulating through the unit at acid strengths generally over 80 wt % and is not being condensed, vaporized, or dropping out as a second liquid phase. See G.3.3 for further details.

### **3.1.78**

#### **Risk-Based Inspection**

##### **RBI**

A risk assessment and management process that is focused on the loss of containment of pressurized equipment in processing facilities, due to material deterioration. These risks are managed primarily through equipment inspection.

### **3.1.79**

#### **rundown**

Primarily product rundown systems that contain less than 1 ppm inorganic HF acid.

### **3.1.80**

#### **safe haven**

A building that has a specifically engineered design level of protection.

### **3.1.81**

#### **safety system**

Equipment and instrumentation that either protects against loss of containment of hazardous materials, protects unit personnel or mitigates the impact of a release that has occurred.

### **3.1.82**

#### **sample container**

A device used to obtain a sample of a process stream to assess the composition of the process stream.

### **3.1.83**

#### **shelter-in-place**

A building that gets additional isolation by the occupants closing doors, closing windows, and shutting off heating, ventilation, and air conditioning (HVAC) systems.

### **3.1.84**

#### **shelter-of-opportunity**

These are intended as a very short time shelter during an evacuation process. Examples include vehicle cabs, small storage sheds, and equipment enclosures. This is a shelter of last resort that may be used by occupants who unexpectedly find themselves inside a dispersion plume to provide a level of isolation between themselves and the ongoing dispersion.

### **3.1.85**

#### **small-bore piping**

Pipe or pipe components that are less than or equal to nominal pipe size (NPS) 2.

### **3.1.86**

#### **stainless steel**

Alloy steel containing 12 wt % or more Cr, so as to be resistant to rust and attack from various chemicals; may contain other elements to enhance corrosion resistance or physical properties; broken down primarily into ferritic, martensitic, austenitic, and duplex families.

### **3.1.87**

#### **stress corrosion cracking**

##### **SCC**

Progressive fracturing (e.g. crack formation) that occurs in metals as a result of the combined influence of tensile stress and a corrosive environment and that can lead to the unexpected sudden failure of normally ductile metal alloys.

### **3.1.88**

#### **strongback**

A mechanical device used to constrain the separation of damaged piping resulting from axial thrust loads on clamped piping components.

### **3.1.89**

#### **temporary repair**

A repair made to pressurized assets to maintain integrity and to continue safe operation until permanent repairs can be scheduled and accomplished within a time period acceptable to the inspector and/or engineer and applicable in-service mechanical integrity code.

### **3.1.90**

#### **tightness testing**

A test that is performed to ensure the overall leak tightness of the system or its connections before the process medium is introduced.

### **3.1.91**

#### **toxic refuge**

A structure designed to protect occupants from external hazards based on the credible design point scenario.

### **3.1.92**

#### **trace acid**

A term used to indicate only those process streams that contain primarily liquid hydrocarbons and any HF that is present is fully dissolved in the hydrocarbon.

NOTE This term was used in earlier API 751 versions (Fourth Edition and earlier). It has been superseded by the defining of corrosion zones (as of the Fifth Edition) and is no longer used. It is maintained for reference only.

### **3.1.93**

#### **turnaround**

A planned, scheduled shutdown of a unit or partial unit at the end of its normal operating cycle.

NOTE This time is used to perform routine cleaning, repairs, any special modifications, and inspections that cannot be done while the unit is in operation.

### **3.1.94**

#### **unit inspector**

In the context of API 751, this is the title for an authorized pressurized asset inspector qualified in inspection methods/techniques and certified in accordance with API 510 and API 570, who is responsible for the HF alkylation unit inspection program.

### **3.1.95**

#### **vent gas absorber**

#### **VGA**

This is a small heat exchanger located within the depropanizer overhead accumulator intended to condense HF vapors within the drum that decreases HF losses and neutralization demand in the downstream acid neutralization scrubber.

### **3.1.96**

#### **weathering area**

An area set aside with restricted access to let assets previously in HF service become neutralized through exposure to atmospheric conditions.

### **3.1.97**

#### **weld overlay**

A welding process where one or more layers of metal with specific characteristics are deposited to the surface of a base metal as a layer to impart desirable properties that are not inherent to the base metal or to restore the

original dimension of the component. In the former, this is completed to improve the corrosion, erosion, and/or wear resistance over the original base metal (also known as an overlay, weld overlay cladding, or hard facing).

### 3.1.98

#### **wrap**

A nonmetallic composite wrap is a temporary repair comprising two constituents: a fabric woven from a fiber (such as graphite) and a thermoset polymer (such as a two-component mix epoxy resin). A wrap may also be referred to as fiber-reinforced polymer (FRP) or a “polymeric wrap.” See 6.3.2.12 for further information regarding the use of wraps as a temporary repair.

## 3.2 Acronyms, Abbreviations, and Symbols

For the purposes of this document, the following acronyms and abbreviations apply.

ACGIH®	American Conference of Governmental Industrial Hygienists
ACFM	alternating current field measurement
AEGL	acute exposure guideline level
AHF	anhydrous hydrogen fluoride or anhydrous hydrofluoric acid
AIChE	American Institute of Chemical Engineers
AIHA™	American Industrial Hygiene Association
ARN	acid relief neutralizer
ASO	acid soluble oil
AWS	American Welding Society
BEI®	Biological Exposure Index
CCD	corrosion control document
CDW	controlled deposition welding
CE	carbon equivalent
CEMS	continuous emission monitoring system
CML	condition monitoring location
Cr	chromium
CTFE	polychlorotrifluoroethylene
CUF	corrosion under fireproofing
CUI	corrosion under insulation
Cu-Ni	copper-nickel (alloys)
Cu-Zn	copper-zinc (alloys, also known as brass alloys)



DMW	dissimilar metal weld
DOT	U.S. Department of Transportation
DP	differential pressure
DT	differential temperature
EIV	emergency isolation valve
EPA	U.S. Environmental Protection Agency
ERPG™	Emergency Response Planning Guidelines
FCAW	flux-cored arc welding
FCC	fluidized catalytic cracker
FEP	fluorinated ethylene propylene
FFS	Fitness-For-Service
FGS	flare gas scrubber
FTNIR	Fourier transform near-infrared technology
GMAW	gas metal arc welding
GTAW	gas tungsten arc welding
HAZ	heat-affected zone
HF	hydrofluoric acid or hydrogen fluoride
HIC	hydrogen-induced cracking
HSC-HF	hydrogen stress cracking in hydrofluoric acid
HVAC	heating, ventilation, and air conditioning
H <sub>2</sub> S	hydrogen sulfide
IDLH	immediately dangerous to life and health
ICHMAP	Industry Cooperative Hydrogen Fluoride Mitigation/Assessment Program
iC <sub>4</sub>	isobutane
IOW	integrity operating window
KF	potassium fluoride
KOH	potassium hydroxide
LEPC	local emergency planning committee

LIBS	laser-induced breakdown spectroscopy
LOPA	layers of protection analysis
LOPC	loss of primary containment
LPG	liquid petroleum gas
MCE	maximum credible event
MDMT	minimum design metal temperature
MHF	modified HF
MSDS	material safety data sheet
MT	magnetic particle testing
MTR	material test report (mill test report)
MVP	material verification program
NaF	sodium fluoride
NaOH	sodium hydroxide
NDE	nondestructive examination
Ni	nickel
Ni-Cu	nickel-copper (alloys)
NPS	nominal pipe size
OES	optical emission spectrometer
PAUT	phased array ultrasonic testing
PEL	permissible exposure limit
PFA	perfluoroalkoxy
PHA	process hazard analysis
PMIV	positive material identification and verification
PPE	personal protective equipment
PQR	procedure qualification record
PRV	pressure-relief valve
PSM	process safety management
PT	penetrant testing

PTFE	polytetrafluoroethylene
PWHT	postweld heat treatment
QA	quality assurance
QC	quality control
RATS	rapid acid transfer system
RBI	Risk-Based Inspection
RE	residual element
RBV	remote block valve
REL	recommended exposure level
RGS	relief gas scrubber
RHF	rich hydrofluoric acid
RT	radiographic testing
RTJ	ring type joint
SAW	submerged arc welding
SCBA	self-contained breathing apparatus
SCC	stress corrosion cracking
SDS	safety data sheet
Si	silicon
SMAW	shielded metal arc welding
SME	subject matter expert
SOHIC	stress-oriented hydrogen-induced cracking
SOL	standard operating level
STEL	short-term exposure limit
SWUT	shear wave ultrasonic testing
TDL	tunable diode lasers
TEMA	Tubular Exchanger Manufacturers Association
TLV®	Threshold Limit Value
TWA	time-weighted average

UNS	Unified Numbering System
UT	ultrasonic testing
VGA	vent gas absorber
VT	visual testing (visual inspection)
WEEL™	Workplace Environmental Exposure Level
WFMT	wet fluorescent magnetic particle testing
WMT	wet magnetic particle testing
WPS	weld procedure specification
XRF	X-ray fluorescence

## 4 Hazards Management

### 4.1 Process Hazards Management Plan

#### 4.1.1 General

Process hazards management applies to HF alkylation units. These units handle liquefied petroleum gas (LPG) and hydrofluoric (HF) acid, which if released in quantity, may cause significant fire and toxic hazards. Each operating HF alkylation unit shall have a process hazards management plan, which covers the critical safety risks and equipment associated with the operation of this unique process unit. While the specific and detailed individual elements of the process hazards management plan may be located within overall refinery safety plans or emergency response documents, the HF alkylation unit should maintain a document that references these individual components to ensure quick and easy access to all unit personnel.

This Section (Process Hazards Management Plan) provides a summary of the systems and practices in place for managing the unique hazards associated with HF Alkylation process safety including the key systems in place to minimize the potential for releases of HF to the atmosphere, minimizing the corrosive effects of HF, ensuring that runaway reactions do not occur, and responding quickly and properly when incidents do occur.

Examples of key systems and practices that could be included in the plan are:

- HF Risk Management – PHA, QRA, Ensuring Safe Operations with Integrity Operating Windows, Auditing Practices

- Safe Handling of HF practices

- HF Release Emergency Preparedness

- HF Release Detection, Isolation and Mitigation Systems including testing and inspections

- Corrosion Control and Inspection Practices

- Maintenance and Mechanical Guidelines – Critical Check Valves

- Acid Runaway Prevention

- Shutdown and Turnaround practices

- Auxiliary Systems include Relief Gas Scrubbers

## 4.1.2 Process Hazard Analysis (PHA)

### 4.1.2.1 Overview

A PHA shall be conducted in all HF alkylation facilities. The permissible interval between PHAs shall meet applicable regulations. However, the maximum interval between analyses shall be 5 years. Once an initial PHA has been completed for the alkylation unit, each subsequent analysis may either be a revalidation of the previous analysis or a completely new analysis. More information can be found in Annex A.

### 4.1.2.2 Methods and Considerations

Many analytic techniques are available to the refinery owner-operator for evaluating process hazards. The PHA methodology selected shall satisfy applicable regulations.

Prior to initiating the PHA, the facilitator or other responsible party shall gather up-to-date process safety information for review by the PHA team, including the previous PHA reports, the implementation status of any previous PHA recommendations, and available industry incident experience. The PHA team identifies scenarios that could occur and evaluates the consequences of those scenarios. The PHA and associated risk management programs shall address routine and transient operations including:

- a) HF unloading and transfer;
- b) sampling;
- c) start-up;
- d) shutdown;
- e) upset and failure mechanisms, conditions, including mechanical integrity, that can result in an unintentional loss of HF or LPG, including losses to sewer effluent, product (such as propane, butane, and alkylate) streams, condensate, cooling water, and flare systems;
- f) human factors; and
- g) facility siting.

Upon completion of the PHA, the findings, recommendations, and any associated resolution shall be documented. The documentation shall include:

- h) a plan to resolve any recommendations in a timely manner, including interim measures if applicable;
- i) an implementation schedule;
- j) the identity of the individual(s) accountable and/or responsible for the resolution of any recommendations;
- k) the actions taken to resolve any recommendations; and
- l) the completion dates.

### 4.1.2.3 PHA Team

A team of qualified individuals to conduct the initial and any subsequent PHAs, at a minimum, shall include a facilitator, operator, and engineer [in addition, subject matter experts (SMEs) may be needed on an ad hoc basis] with experience and knowledge in the HF alkylation unit design and operations, including applicable standards, codes, specifications, health effects, and regulations. If the PHA team is lacking adequate support

for any specific area of expertise, then the need for third-party resources should be considered. Management of Change

In addition to the procedures required by applicable process hazards management regulations, any proposed change in controls, critical alarms, instrumentation, equipment, piping, operating limits, operating procedures, relief systems, safety systems, technology, safety mitigation systems, or facilities in an HF alkylation unit shall be subject to some form of management of change analysis. This shall include management of temporary equipment or piping installed on the HF alkylation unit, including for troubleshooting purposes. The management of change system shall also cover unit equipment installed and owned by third parties. Changes that have the potential to impact the mechanical integrity of a system should include a review by mechanical integrity personnel. Also, the refinery owner-operator shall review proposed changes to the organizational structure of the unit personnel prior to implementation to minimize the potential adverse impacts on the safety, health, and environmental performance of the HF alkylation unit.

#### 4.1.4 Emergency Response and Control

##### 4.1.4.1 General

Effective Toxic Chemical Management requires extensive preparation in the following three areas:

1. Emergency Response Planning
2. Scenario Development
3. Toxic Refuge Design

More information is found in Annex C of API RP 752 *Management of Hazards Associated with Location of Process Plant Permanent Buildings* Fourth Edition January 2024.

Emergency Response Planning will be discussed in this section and the following sections provide details of Scenario Development and Toxic Refuge.

Emergency response is one of three parts that work together for effective toxic chemical management.

Each facility shall have written procedures for initiating an emergency response at the alkylation unit. These procedures should include the required actions of HF alkylation unit personnel, other refinery personnel, and external emergency services for initiating an emergency response or for responding to an emergency.

Each facility shall establish a written emergency response and control plan for each HF alkylation unit. The emergency response and control plan may be either a standalone document or incorporated into the overall refinery emergency response and control plan.

##### 4.1.4.2 If the facility emergency response plans include the evacuation of occupied buildings or use evacuation alone (without the concept of toxic refuges), then an analysis of the scenarios from 4.1.5 should be completed to determine that a safe egress path exists for occupants of buildings near alkylation units. Emergency Response and Control Plan Content

The emergency response and control plan shall include the following.

- a) For streams of HF and HF-containing LPG, evaluation of the consequences of a potential HF release as well as evaluation of the consequences of the LPG release.
- b) Notification, interfaces, and expected response of external emergency services, including, but not limited to, police, fire, mutual aid, hospitals, and local emergency planning committees (LEPCs).
- c) The need for, and location of, emergency medical treatment for HF exposure, including the location of clinics and hospitals that are familiar with HF burn care.

- d) A system for communicating internally within the refinery and externally to the surrounding community on a response appropriate to the situation, e.g. evacuation or shelter-in-place.
- e) The frequency and methodology of testing of all communication systems.
- f) The scope and frequency of emergency response drills for LPG, HF-containing LPG, or HF releases.

In addition, the emergency response and control plan should address the following items.

- 1) The decision criteria to issue an evacuation or shelter-in-place instruction for the community.
- 2) Actions required to protect individuals within the toxic refuge (safe haven or onsite shelter-in-place buildings) for scenarios that potentially exceed the credible design point scenario.
- 3) How and when to evacuate buildings so that occupants who may be safer inside a toxic release shelter are not placed at greater risk by evacuating into a potential dispersion release plume pathway.
- 4) The need for or access to off-site emergency response equipment and emergency response personnel trained in handling HF and personal protective equipment (PPE) suitable for HF exposure.
- 5) Identify where the next available medical supplies are located and how to get them to the site if a credible design point scenario is exceeded (potentially more people impacted).
- 6) Identification of the number of HF medical kits that are needed for site occupants (inside the toxic refuge and outside on the units) based on the credible release scenario.
- 7) The potential for HF contamination in runoff water, including a strategy to manage the potential acidic runoff being sent to the refinery's wastewater system or off site.
- 8) The mechanism for assessing the condition of and decontaminating equipment, soil, buildings, and standing water inside and outside the alkylation unit after an HF release is over.

#### **4.1.4.3 Emergency Response Team**

The purpose of an emergency response team is to help establish on-site control of an HF alkylation emergency. Typically, this team is part of the refinery's general emergency response organization. Emergency response team criteria shall define minimum shift staffing levels.

Emergency response training specific to HF shall include, but not be limited to, physical and health hazards associated with HF, PPE (types, use, and limitations), medical response, decontamination, and heat stress.

#### **4.1.5 Scenario Development**

Scenario development is the second of three parts that work together for effective toxic chemical management.

When managing toxics, there are often multiple independent layers of protection that are in place such that the frequency of larger releases has been minimized. Because of the cumulative effect of the independent protection layers, the design basis of toxic refuge may be based on a credible design point scenario vs a worst-case scenario. While there are many ways that a company/site can determine the credible design point scenario, the basis of the credible design point scenario used by the company/site should be written, documented, and incorporated into the emergency response plan. The credible design point scenario may be different for different buildings.

#### **4.1.6 Toxic Refuge**

Toxic refuge design is the third of three parts that work together for effective toxic chemical management.

#### 4.1.6.1 Development and Selection of Credible Design Point Scenario for Toxic Refuge

A toxic refuge is designed to protect occupants from external hazards based on the credible design point scenario. As there are many different dispersion models that can calculate the concentration vs time profile at the toxic refuge, the dispersion model selected, as well as the dispersion model assumption basis, shall be documented.

Toxic refuges can be exposed to a range of potential scenarios.

Toxic refuges can be of varying designs and include various tightness levels. The tightness level is determined by measuring the air change rate of the building. The process of determining the actual air change rate can be completed using a technique such as ASTM E741-80, *Standard Test Method for Determining Air Leakage Rate by Tracer Dilution*.

#### 4.1.6.2 Safe Havens

As safe havens can be of varying designs, including fresh air supplies for essential occupants at a minimum and scrubbing systems for air ingress points, engineering is involved in determining the suitability of the safe havens response for a given external release condition. If a site has a safe haven, then the design basis of the safe haven shall be documented. The safe haven design basis uses an external contaminant concentration and duration profile to determine the exposure level for occupants inside the building (or inside a particular designated area of the building) based on infiltration.

Safe havens can allow typical control functions to continue as occupants required to stay can bring a facility to a safer state. Safe havens can typically include elements of pressurization, supplied breathing air, door airlocks, scrubbing systems, or duct isolation controls. A safe haven should have periodic testing to assure that the design features are in place and functioning to achieve the design basis.

Some buildings (or internal room) may be designated as a safe haven. For the defined credible release scenarios, these spaces provide adequate protection for personnel to perform critical control and operation functions. Safe havens have a specifically engineered design level of protection to prevent the migration of outside airborne contaminants from infiltrating these buildings while the occupants carry out operational activities. Written procedures shall be available to guide personnel in activating the safe haven mode. Equipment required to implement the procedures shall be maintained. Either a toxic concentration alarm in the safe haven (based on the credible design point scenario) shall be installed or a means for testing the atmosphere inside the safe haven shall be provided.

Written procedures for safe havens should include the following.

- a) Safe haven locations.
- b) Criteria and signals for enabling and ending safe haven status.
- c) Steps to secure safe havens against HF intrusion, such as HVAC shutdown and securing of external penetrations such as HVAC inlets and exhaust ductworks, vents, doors, and windows.
- d) A list of equipment to be maintained at each safe haven location, including communications equipment (radio, telephone), gas testing equipment, and materials for securing the safe haven.
- e) A process for periodically checking each safe haven location to ensure the equipment is being properly maintained and inspected.
- f) Training and criteria for drills on the use of safe havens. If the safe haven design intent is to protect the personnel who are located in the building when the incident starts (i.e. the building is on lockdown and



personnel are not allowed to enter or leave) or if the intent is that external workers may enter these buildings in an emergency, then procedures to enter in an emergency should be included in the drills as well as verification that the design preference to enter and leave through airlock lobbies rather than emergency exits is achieved during the drill.

#### **4.1.6.3 Shelter-in-Place Building**

A building designated as a shelter-in-place building can also include supplies to allow the doors and windows to be taped to limit leakage around openings.

Where on-site buildings are used for shelter-in-place, written procedures shall be developed to guide personnel in entering and securing the shelters. Equipment required to implement the procedures shall be maintained. The procedures should include the following.

- a) Shelter-in-place building locations.
- b) Criteria and signals for entering and leaving shelter-in-place buildings.
- c) Steps to secure shelter-in-place spaces against HF intrusion, such as HVAC shutdown and sealing of doors and windows.
- d) A list of equipment to be maintained at each location, including communications equipment (radio or telephone) and materials for securing the shelter-in-place.
- e) A process for periodically checking each shelter-in-place location to ensure the equipment is being properly maintained.
- f) Criteria for drills on the use of shelters-in-place and training as required.

### **4.2 API 751 Audits**

#### **4.2.1 Comprehensive Audits of the HF Alkylation Unit Systems and Procedures**

A comprehensive audit is a periodic review of a representative sample of the systems and procedures in place at an HF alkylation unit. To ensure that agreed-upon actions are resolved, management shall establish a system to address the audit's findings and recommendations, document action item resolution, and communicate the findings and recommendations to appropriate personnel. Interim visits by select audit team personnel have been found to be effective in monitoring progress on audit findings.

An example comprehensive audit approach is provided in Annex C. The example approach provides elements that may be considered when an audit process is developed. Note that the list in Annex C is not to be considered exclusive or exhaustive in nature.

Each operating unit shall have a comprehensive written audit plan as part of the Process Hazards Management Plan.

#### **4.2.2 Frequency of Audits**

Auditing allows an organization to systematically review its HF alkylation operations relative to the guidance of API 751 and to assess conformance with the organization's internal hazards management policies and procedures. Each operating unit shall be audited at least every 3 years.

#### **4.2.3 Audit Plan Content**

The audit plan should cover the safety, inspection, maintenance, hazard, and operability aspects of the HF alkylation unit.

The plan should identify, by title, the individuals responsible for carrying out the audit and should specify the appropriate HF alkylation unit experience for these individuals. The audit team should include representation from outside the facility such as one or more qualified individuals from other facilities within the same organization (such as corporate or sister refinery) or from an outside source.

The audit plan should provide a checklist specific to the HF alkylation unit including items such as those listed below (see Annex C for further details).

Auditors should review a representative sample of each of the following items, concentrating on the time period since the last audit.

- a) HF-related incident reports, including lessons learned and follow-up actions.
- b) Unit records, including operating procedures, logs, checklists, and operator training records.
- c) Equipment inspection and maintenance records.
- d) Training records for personnel who operate and perform work in the unit, including emergency response personnel.
- e) Mechanical and procedural changes in the unit.
- f) Testing and maintenance records and procedures for HF mitigation systems, including detection, monitoring, automatic control, water suppression, and rapid acid transfer system (RATS).
- g) Evidence of compliance with and understanding of established procedures from observation of and interviews with unit and plant personnel.
- h) Field inspection of the condition of alkylation unit equipment, including safety and mitigation equipment.
- i) Corrosion control document (CCD)/IOWs.

#### **4.2.4 Audit Follow-up**

All audit findings and recommendations shall be tracked and stewarded to resolution by the refinery owner-operator.

### **4.3 Environmental Impact**

Operation of an HF alkylation unit generates waste material and byproducts that, because of their physical or toxicological properties, may require on-site processing prior to final disposition. To achieve this, procedures and facilities should be in place for the safe handling of these materials, both on site and off site, and comply with applicable environmental regulations. See Section 8 for additional information.

### **4.4 Lifting Over In-service Equipment**

Use of a crane to lift materials or equipment over piping and/or vessels that contain HF should be avoided. For all lifts over HF-containing equipment and piping based on crane radius, a lift plan shall be prepared, documented, and reviewed. As such, lifts on adjacent units may need to be considered due to crane radius concerns. The lift plan shall include appropriate management approval as well as a consequence analysis that includes, at a minimum, assessing the radius of the lift from the start through the destination plus any additional area that could be affected as a result of failure or error. The lift plan shall include a written rigging plan and cover details such as alternative lifting schemes; placement, mechanical condition, and capacity of the crane; and location of underground piping, including sewer lines. If the lift is over equipment and piping

containing greater than 5 % HF based on crane radius, the lift shall require a plan review and approval by owner-operator leadership.

Synthetic slings shall not be used unless concerns with chemical compatibility (with both HF and any neutralizing chemicals that may be used on the sling), service life, inspection, cleaning, and handling have been adequately addressed. ANSI/ASSP A10.42 addresses critical rigging activities over hazardous materials and gives examples. Appendix B of that document is especially helpful for lifting activities on HF alkylation units.

#### 4.5 Incident Review

All visible HF vapor leaks including smoking or dripping, HF exposures, and potentially serious incidents shall be investigated.

The investigation should:

- a) evaluate the extent of the release and how detection and mitigation, including RATS, performed during the incident;
- b) identify the root causes;
- c) identify any detection and mitigation system deficiencies;
- d) identify any associated corrective actions;
- e) have a system in place to track corrective actions identified by the investigation team to resolution.

Procedures should specify the level of investigation to be conducted based on the severity of the event, the format and distribution of the investigation report, and the parties responsible for taking corrective action to prevent recurrences. For additional information, see API 585 Pressure Equipment Integrity Incident Investigation.

#### 4.6 Security

Facility security plans shall be established based on site-specific considerations and comply with local and national regulatory requirements.

#### 4.7 Safety Systems

Each site shall maintain a list of safety systems and equipment (Note this does not have to be a separate list from the site safety systems). Safety systems identified as safeguards (for example from a PHA, QRA or LOPA) shall be included in an inspection, testing and preventative maintenance (ITPM) program that designates device or controls service and maintenance requirements for each.

A backup power supply shall be provided for the critical electrically powered instruments and unit control systems. Fireproofing of cabling and components should be considered. Refer to Section 9.

Work processes shall be in effect for testing these systems based on availability requirements needed for that service. The associated procedures should potentially include valve stroking, isolation and testing of primary elements and controls, and testing of critical pump auto start/stop systems in addition to system-specific recommendations listed below. The service history for these critical systems should also be maintained to assist the site in identifying and correcting problem areas. Any deficiencies noted in performance prior to or during testing should be noted in the test records and should be addressed by means such as increased testing/maintenance frequency or considering alternate designs.

Written procedures shall be in place describing how to maintain safe operations and respond to emergencies when a safety system is out of service for any reason, including equipment malfunction and bypassing for system testing.

Systems and equipment that are common to HF alkylation units and shall be on the safety systems and equipment list include, but are not limited to, the following.

- a) Safety shower and eyewash station alarms.
- b) Key components of safety systems related to protecting against loss of containment due to HF intrusion in propane and butane rundown treatment systems.
- c) Breathing air system alarms.
- d) ARN caustic circulation system: flow.
- e) ARN caustic circulation: low temperature.
- f) HF levels: high acid boot level on the receiver upstream of the HF/propane stripper.
- g) Mitigation systems described:
  - 1) continuous HF release detection systems, including HF sensors and video surveillance equipment;
  - 2) key components of remotely activated and remotely controlled water mitigation systems;
  - 3) key components of the mitigation system that limit the duration of the event to the user-defined evaluation criteria, which may include:
    - i) rapid HF acid transfer or evacuation systems,
    - ii) remotely activated block valves for HF isolation;
  - 4) other key systems identified as contributing to the overall mitigation system per the required quantitative assessment.
- h) Applicable emergency isolation valves (EIVs).

Testing of systems and equipment that are specific to HF alkylation units should include, but are not limited to, the following.

- i) All components of remotely activated and remotely controlled water mitigation systems should be tested as a whole system to confirm they will work as designed.
- j) The rapid HF acid transfer systems tested as a whole system to confirm it will work as designed (such as when de-inventorying acid in preparation for turnaround).
- k)

## 5 Operating Procedures and Worker Protection

### 5.1 General

Operating personnel at the HF alkylation unit play a key role in safe and reliable operation. They should be well informed, trained, and equipped. All personnel entering the HF alkylation unit can work safely if they follow the special requirements developed for this operation.

HF alkylation units shall have specific written operating procedures that address the toxic and corrosive nature of the HF catalyst. Because HF is not usually found in other operating parts of the refinery, some of the procedures are unique to the HF alkylation unit; therefore, special equipment and training are warranted.

### 5.2 Health Hazard Information

Pure anhydrous hydrofluoric acid (AHF) is a clear, colorless, corrosive liquid that boils at 67 °F. AHF can form a vapor cloud if released to the atmosphere and may behave like a dense gas traveling at ground level for a time before dispersing. It has a sharp, penetrating odor that humans can detect at very low concentrations in the air. It is completely soluble in water, forming HF solutions. In concentrated solutions, the HF fumes when exposed to air. While the HF in HF alkylation units is not pure or anhydrous, its physical properties and health effects are essentially the same as pure AHF.

Even brief contact with HF liquid or vapor can produce serious, painful chemical burns, sometimes with delayed onset. Large skin burns may be life-threatening. The vapor can be corrosive to the eyes, skin, and respiratory tract. Short-term exposure at higher concentrations can lead to serious health effects or death as a result of extensive respiratory damage. There may be chronic health effects, such as fluorosis, from repeated exposure.

ASO is a light-to-dark colored liquid that can contain varying concentrations of HF. Depending on its HF content, it may have a sharp, pungent, irritating odor. It is relatively insoluble in water. Contact with unneutralized ASO can produce serious, painful HF burns, sometimes with delayed onset.

Additional health hazard information may be available from the manufacturer or supplier of the material or within the safety data sheet (SDS) (previously known as material safety data sheet or MSDS).

Facilities shall comply with the requirements of worker protection health standards and regulations applicable to the facility's location. For example, OSHA 29 *CFR* Part 1910.1000 currently sets routine workplace exposure limits for HF exposure. Full-shift and/or task-based employee exposure monitoring/sampling shall be performed with the assistance of a qualified individual. If there is a substantial change in operations and/or equipment the employee exposure monitoring should be repeated. Annex D provides examples of limitations and guidelines from multiple sources in effect at the time of publication. Definitions of terms and applications of limits or guidelines in Annex D should use regulatory or sponsoring professional organization sources. Users of this recommended practice should consult the most recent edition of the source for each limitation or guideline for the most current information. Some local agencies may have more stringent requirements that should be consulted as applicable.

Facilities shall also comply with applicable hazard communication regulations. For example, OSHA 29 *CFR* Part 1910.1200 addresses labeling, SDSs, worker training, and recordkeeping requirements.

### 5.3 Plant Operations

#### 5.3.1 Document Control

Unit documentation shall fall within a document control program. Unit documents should include procedures, operating manuals, training manuals, operating envelopes, sample schedules, and analysis performed on samples. The document control program should consist of the following elements.

- a) Approval process—procedures to review and approve documents, approval authorities by title/position.
- b) Review process—procedure for periodic review/re-validation, review approval authorities by title/position.
- c) Identification—title, date of issue, approver(s), revision number, designation as controlled/uncontrolled copy.
- d) External documents—identify external documents and control their distribution and utilization (e.g. OSHA regulations *CFR* 1910, API 751, ASTM metallurgy standards, etc.).
- e) Obsolete document management process—a procedure to identify, prevent improper use, and removal from the system if no longer needed.

### 5.3.2 Operating Manuals and Unit Documentation

#### 5.3.2.1 General

Site and unit information and procedures shall be developed and made available to all assigned operating personnel of an HF alkylation unit. These documents shall be unit- and site-specific and shall, at a minimum, include the following.

- a) Descriptive information called for in applicable local process safety management (PSM) regulations and recommended practices.
- b) Site-specific emergency procedures including those for an HF release.
- c) Detailed HF exposure first aid procedures.
- d) HF sampling.
- e) Unit shutdown.
- f) Unit neutralization to prepare for maintenance.
- g) Unit chemical cleaning.
- h) Unit dry-out and start-up.
- i) Unloading of fresh HF shipments.
- j) Operator unit surveillance.

The unit piping and instrument diagrams and appropriate electrical diagrams shall be accessible to operators, maintenance, and inspection personnel as required per their task.

Information on piping and equipment limitations should be readily available to operators. Other procedures are mentioned in the applicable sections of this recommended practice. An example of a procedure for unloading fresh HF is provided for reference in Annex I.

#### 5.3.2.2 Specific Procedural Guidance

##### 5.3.2.2.1 Removing Oxygen

Unit start-up procedures shall emphasize removing oxygen from the unit, with particular attention paid to high points such as vents, thermowell connections in the vertical position that are not close coupled to the process

piping, pressure gauges, and dead-legs. Oxygen ingress into the unit during normal operations as well as after maintenance activities should be minimized.

#### **5.3.2.2.2 Impulse Lines During Commissioning**

The entire length of instrument impulse lines from the process equipment to the instrument shall be flushed through several times during the dry-out phase of the unit start-up to remove traces of water, thus minimizing the potential for corrosion and plugging. For instruments and associated impulse line components that are susceptible to environmental cracking (e.g. Alloy 400), the entire length of the line from the process equipment to the instrument shall be purged through a minimum of two times with an inert gas to remove any oxygen that might be present. These flushing operations during start-up are important, given the typical small line diameter and lack of flow under operating conditions.

#### **5.3.2.2.3 Unit Dry-out**

Due to the effects of high local water concentrations on carbon steel corrosion rates, start-up procedures shall include strategies to remove free water from the unit prior to the introduction of HF. Annex G.4.6.4 lists several means commonly used to do this.

#### **5.3.2.2.4 Internal Regeneration**

In some units, a slipstream of HF can be injected into the hot fractionation part of the plant to regenerate the HF (a practice known as "internal regeneration"). Internal regeneration should not be used if the circulating HF acid water content is  $> 1\%$ . If internal regeneration is used, the amount of this HF injection shall not exceed the HF solubility in the hydrocarbon at the operating temperature to avoid the accelerated corrosion of carbon steel. See G.2.3 for more information.

#### **5.3.2.2.5 Turnarounds**

Written procedures shall be developed for preparing equipment for maintenance. These procedures should include steps for neutralization, purging, and isolation before the equipment is turned over to maintenance personnel. A corrosion specialist should be involved with planning the cleaning and neutralization process per the materials and inspection plan.

Temporary connections, fittings, and piping utilized for the draining and purging of the unit should be managed and coordinated between operations, maintenance, and inspection. Temporary connections and equipment should be dismantled and removed promptly after use. Procedures should be developed for the use of rod-out tools as described in 6.6.6.

Specific written procedures shall exist for preparing the HF alkylation unit for the turnaround that includes the shutdown, deinventory, purging/sweeping, neutralizing, and safely handing over the equipment for maintenance work. If HF acid is stored on the unit during a turnaround, a plan shall be developed to secure this inventory and prevent tampering with the vessel and associated equipment. All flanges and connections that remain in HF service during turnarounds shall be made inaccessible to prevent inadvertent opening. Special markings shall alert the presence of acid and access to the area should be restricted. The area should be monitored, and mitigation equipment should be available in case of a leak.

Training of all turnaround personnel (including contractors) should include an emphasis on the location of any HF that is stored in the unit during the turnaround and the activities that are allowed and the activities that are prohibited in that area. Any maintenance work near or above the HF storage vessel that might disturb or damage the vessel or piping that contains HF should be minimized.

#### **5.3.2.2.6 Operations and Solids/Sludge**

Units that have been neutralized and cleaned with a water-based cleaning agent can result in the presence of sludge and solids in piping and components that promotes under-deposit corrosion and fouling. Units or



sections of a unit that are neutralized with anhydrous ammonia will generate large volumes of ammonium fluoride salts. Iron fluoride scale is generated from carbon steel piping components and accumulates during a normal run, in low-points, valves, areas of low flow, trays, tower internal parts, etc. The site should develop protocols to address the potential problems that iron fluoride solids and sludge create (examples include plugged relief-valve inlet lines, tower feed lines, low-point piping, check valves, instrumentation, etc.). Valves that are susceptible to scale buildup should be exercised on some frequency to prevent sticking. Regeneration systems with multiple feed legs should be alternated regularly to prevent plugging. Instruments can be supplied with flush [e.g. isobutene (iC4)] to sweep away scale and solids (see 6.6.8 regarding solids and sludge remaining after cleaning).

#### 5.3.2.2.6.2 Solids and Sludge Remaining After Cleaning

Equipment and piping that has been washed with a water-based agent to remove residual HF and iron fluoride scale shall be internally visually examined for cleanliness before being returned to service, regardless of whether the equipment and piping are scheduled for internal inspection. The presence of sludge and solids (including blasting media) can promote localized under-deposit corrosion upon unit restart. This is due to the formation of iron fluoride and water from iron oxide and HF once the acid is reintroduced to the unit. The presence of sludge and solids can also cause fouling/plugging of unit equipment and piping upon unit restart.

The visual examination should include checking for solids/sludge, scale that is not tightly adhered to vessel surfaces, and free water. Low-point piping should be included in the examination. If solids, sludge, loose scale, or free liquid are found, they shall be removed.

See G.4.6.4 for more information on turnaround water, G.4.6.6 for more information on low point dead-legs, and API 570 and API 574 for information on inspection of dead-legs.

### 5.3.3 Operating Envelopes

Operating envelopes, which define and limit process, mechanical, safety, and environmental constraints for unit operation, shall be established and monitored and should address normal limits, acceptable limits, and critical limits.

Roles and responsibilities should be established to indicate responsible parties for:

- a) monitoring,
- b) reporting and notification,
- c) performing follow-up investigations, and;
- d) approving and implementing corrective actions,

Normal limits typically set the minimum and maximum, as required, for an ongoing stable and economical unit operation that is within the boundaries of acceptable and critical limits.

Acceptable limits, also known as integrity operating windows (IOWs), are used to minimize process parameter exceedances that may negatively impact the mechanical integrity of HF alkylation units (see 6.1.5 for requirements and recommendations on IOWs). IOWs for physical and chemical process parameters that could affect equipment integrity if not properly controlled shall be established for HF alkylation units. These limits should be set to ensure that unit operations do not present a concern to unit equipment or the environment. IOW limits should be established in accordance with recommendations within API 584. Additionally, a table of suggested IOWs is provided in G.5 of this document.

Critical operational limits shall be set to prevent any operation that could result in rapid damage to equipment integrity resulting in negative consequences to safety and/or the environment. Operation beyond these limits



shall require immediate action to return the unit to acceptable conditions. Exceedances of critical limits should require a formal review to determine the cause and to provide corrective actions to minimize the likelihood of a repeat occurrence. Inspection and monitoring programs should be reviewed for adjustments to address equipment integrity concerns after exceedances in critical limits.

An IOW program should be developed and implemented in accordance with API 584, including defining limits and appropriate responses to exceedances, to reduce the risk of loss of primary containments (LOPCs). IOWs are a subset of operating limits/windows covered in 5.3.3 and should be integrated with control systems that monitor those limits. Inspection plans and intervals are typically based on measured damage rates, which resulted from previous operating conditions and/or forecasted by corrosion specialists. Without an effective IOW program, process conditions that have changed or deviated from normal that could affect unit mechanical integrity or alter the effectiveness of the inspection plan may not be effectively communicated across all affected disciplines. Process upsets that result in temporary deviations (exceedances) outside of established IOW limits should be reported for review and possible follow-up by an appropriate SME. Sustained or continued operation outside of IOW limits should only be authorized after a review of the hazards and risk of the proposed operation have been performed and approved and any changes to inspection and monitoring programs to address equipment and piping integrity/reliability have been implemented.

### **5.3.4 HF Sampling and Handling of HF-containing Samples**

#### **5.3.4.1 General**

HF sampling and testing shall be completed on a frequency to ensure adequate control of HF quality (especially HF strength and water content) and proper calibration of the online HF analyzer (where applicable). Minimum sampling and testing frequency should be once per week with an online analyzer and three times per week without an online analyzer. Sampling of streams that contain potentially harmful quantities of HF require special precautions. Written procedures for HF-containing sampling shall be in place. These procedures should include sampling techniques, a diagram of the sampling manifold, PPE requirements, and communication of hazards.

#### **5.3.4.2 Training for HF Sampling**

Training shall be provided for all operating personnel who may collect or handle samples that contain or may contain HF. This training should include sampling techniques, PPE requirements, and communication of hazards.

#### **5.3.4.3 Design of Sampling Stations**

##### **5.3.4.3.1 Location**

HF sampling connections should be located at grade or on an unobstructed structure that permits easy egress for persons taking samples. A safety shower and eyewash station should be in close proximity to the sampling station.

##### **5.3.4.3.2 Minimizing Exposure**

Sampling systems for streams that contain HF shall be designed to minimize HF exposure to personnel. Sites should have a closed-loop flow through HF sampling system with flush and/or nitrogen purge capability and that, if vented, is vented to the acid flare.

Continuous online analyzers should be used to minimize the sampling frequency of samples pulled from the rich acid, fresh acid, or phase change corrosion zone.

### **5.3.4.3.3 Valves and Piping for HF-containing Sampling Stations**

Sample points should be permanent installations that minimize the use of tubing and compression fittings. There has been a history of leaks on concentrated acid sample systems tubing and compression fittings due to oxygen-induced stress corrosion cracking (SCC) (see 6.5.6.6). Circulating acid sample cylinder connections should avoid quick connection fittings as they are more likely to become plugged or leak.

Any sample connections to the atmosphere and sewer vents shall have two block valves per connection including double isolation. When the connection is in use, both valves to the atmosphere/sewer should be closed. When the connection is not in use, all these double block valves should be closed, and the open end of the sample connection should be sealed or plugged. When sampling piping is not in use, it should be purged with unit flush or nitrogen, depressurized, and isolated.

### **5.3.4.3.4 Identifying Sample Points That May Contain HF**

Sample points for streams that contain HF, shall be clearly identified in the field as potentially containing HF. Streams that may contain HF in the event of a unit upset should be identified in the field as potentially containing HF. Supply, return, and vent piping, if applicable, should be labeled.

### **5.3.4.4 HF-containing Sample Containers**

Written procedures shall be established for the management of sample containers for streams that normally contain HF. The containers shall be clearly and uniquely identified as being in HF service. These containers shall only be used for samples that contain HF. See 6.5.11 for the design and inspection of sample containers.

The written procedures for HF-containing sample containers shall include methods for neutralizing, cleaning, and storing the containers. External surfaces of sample containers should be neutralized and have residue removed prior to transporting from either the HF alkylation unit to the laboratory for analysis or returning from the laboratory to the HF alkylation unit post-analysis. External neutralization may be accomplished by submerging in a neutralization bath (e.g. soda ash, or equivalent) and/or spraying the exterior with a neutralizing solution and thoroughly wiping down, depending on the potential for sample contamination.

Sample cylinders that contain or may contain HF shall not be stored with sample cylinders that are in other services. The storage location for full sample cylinders in HF service awaiting laboratory analysis should be specifically designated and selected to minimize the potential for personnel exposure in the event of a leak in the cylinder (e.g. inside laboratory fume hood). After analysis, sample containers shall be purged of residual sample material prior to storing for later use.

### **5.3.4.5 Safe Transportation and Storage of Reactor Circulating HF Acid Samples**

Procedures shall outline the site requirements for storage and transportation of the HF sample container used for sampling reactor circulating HF acid. If this sample is transported outside the battery limits of the unit, the sample container shall be placed in an outer container for transportation and that container shall be labeled to indicate that it is in HF service. The transportation container shall have a means to visually determine if the cylinder is leaking prior to opening the transportation container. A good practice is painting the transportation container with HF detecting paint. A good practice is to include neutralizing material, such as an inch layer of soda ash and vermiculite, in the sample's transport container to neutralize and absorb any acid in the unlikely event of a leak.

Safety and personnel exposure considerations shall be taken into account when establishing the transport route the sample takes to the testing location within the site laboratory. The sample shall be placed in a well-ventilated restricted area until the actual testing of the HF can be performed.

### **5.3.5 Operations Response to HF Leaks**

#### **5.3.5.1 Operations Response to an Incipient HF Leak**

A regular equipment monitoring program shall be in place to identify small HF leaks so that timely repairs can be made before they increase significantly. This program shall outline routine operator surveillance requirements and reporting for identified leaks. Procedures shall be in place for assessing and addressing leaks, including monitoring until the leak is permanently repaired. These procedures shall include written expectations for the timeliness of addressing leaks based upon their severity, inspection by an inspector within a defined timeframe based upon their severity, and a method of tracking each leak using a unique identifier. A visual cue (e.g. numbered tag at leak location) may be used for monitoring and awareness purposes. An example of a successful HF equipment leak monitoring program, including pictures of different levels of leak severity, is provided in Annex E.

Regular operator surveillance shall include visual inspection (VT) of vessels, valves, piping connections, pressure gauges, instrumentation and associated tubing, pump cases, flanges, and seals. A checklist that includes remote or limited-access valves and instrument connections shall be included in the program. Operators shall be alert for such signs as acid detecting paint that has changed color, buildup of corrosion products between flanges, and the distinctive odor of HF. If transparent flange covers are used, the regular equipment monitoring program shall include routine observation through the covers for leakage and corrosion and allow rapid response to mitigate the leak and address bolting that has been exposed to HF. When transparent flange covers deteriorate and inhibit visual observation of the flange joint, they shall be replaced. The operating procedures shall cover information pertaining to these surveillance techniques, including notification to the defined site responsible discipline for any acid detecting paint maintenance needs (see 6.5.13). All who enter the unit shall receive sufficient instruction so that they are able to recognize and know how to report HF leaks.

#### **5.3.5.2 Operations Response to a Beyond Incipient HF Leak**

Operations shall have written procedures, specific to the HF Alkylation unit, describing appropriate responses upon detection of all visible vapor HF leaks beyond smoking or dripping. The operating range of detection systems along with their alarm setpoints should be identified and included in these procedures. HF release response procedures should guide alkylation unit operations staff in the steps to be taken if an HF release occurs, including the following:

- a) accounting for all personnel in the unit;
- b) determining the source, composition, and magnitude of the leak, if possible;
- c) isolate leak, if possible;
- d) determining wind conditions and establishing potential impact areas;
- e) determining the extent of mitigation required;
- f) activating site-specific emergency mitigation systems and adjusting for maximum effectiveness (see Section 9);
- g) initiating site emergency response plans, as appropriate (see 4.1.4);
- h) implementing procedures for site personnel protection, as appropriate (see 4.1.4).

## **5.4 Laboratory Safety**

### **5.4.1 Designated Area**

Laboratories shall provide a designated area for storing, handling, and analyzing both HF samples and HF-containing samples such as iC4 recycle and ASO. The area should be designed to restrict entry by unauthorized personnel.

### **5.4.2 Fume Hood**

Laboratories shall be appropriately equipped with a fume hood to prevent HF ingress into the lab. The fume hood shall be equipped with a face velocity indicating device and a low face velocity alarm. A good practice is to maintain a face velocity of at least 100 ft/min with the velocity indicating device alarming at 80 ft/min. The fume hood's face velocity indicating device shall be routinely tested and the results documented. Fume hood and exhaust components and contents should be inspected annually for exposure to and degradation from HF and replaced as appropriate (see ANSI/AIHA Z9.5 and OSHA 29 CFR Part 1910.1450 for additional information).

### **5.4.3 HF Sample Testing Personal Protection Equipment**

#### **5.4.3.1 General**

Written procedures shall be in place to cover the PPE requirements for the laboratory technician performing the testing of HF and HF-containing samples. PPE shall include a minimum of upper body protection including arms, gauntlet type gloves (gauntlets are to cover the wrists when the arms are extended), face shield, and safety glasses with side shields. Laboratory PPE neutralization, cleaning, and testing procedures shall be consistent with the HF alkylation unit requirements.

#### **5.4.3.2 Training for HF Laboratory on HF Sample Handling**

Training shall be provided for all personnel who may handle or analyze samples that contain or may contain HF acid. This training shall include handling techniques, PPE requirements, and communication of hazards. See 5.5.3.

## **5.5 Training**

### **5.5.1 General**

Refinery safety orientation materials shall alert all people who enter the refinery to the presence of the HF alkylation unit, the demarcation of the unit, and the special training and PPE necessary to enter the HF alkylation unit.

A safety orientation to the HF alkylation unit shall be developed and communicated to all persons who work on or enter the HF alkylation unit. This orientation shall address the hazardous nature of HF, including appropriate first aid procedures for HF exposure, location of HF-containing process equipment, PPE requirements, small HF leak recognition and reporting, and steps to be taken in the unlikely event of an HF release.

Because of the numerous issues associated with the compatibility of HF and various metals and chemical substances, a materials segment shall be included in the general HF orientation for those who will enter the unit. The intent of this training is to provide all who enter the unit with an understanding of the issues associated with the materials used in the unit and the ability to apply this information in their daily work practices. Annex G provides an overview of some of the metal and chemical compound issues associated with HF.

Additional HF alkylation specific training material should be developed and communicated to certain personnel as discussed in 5.5.2 to 5.5.4. Emergency response training specific to the HF alkylation unit is discussed in 4.1.4.3. A process should be in place to verify the training of any person entering the unit.

### **5.5.2 Training of Operators**

Operating personnel shall be trained in the process, mechanical, and materials limitations of the HF alkylation unit, routine operating procedures, start-up, shutdown, emergency procedures, and mitigation systems. As systems for detection and mitigation of HF releases are unit-specific and may be complex, training on these systems should emphasize their operation and optimization as well as their proper care and maintenance (see 9.2).

### **5.5.3 Training of Maintenance, Engineering, Inspection, and Other Support Personnel**

Employees and contractors working in the alkylation unit, as well as off-unit personnel that work on equipment that originated inside the unit, shall be trained on the procedures and safe work practices applicable to their jobs, including the hazards of HF. This includes but is not limited to maintenance, engineering, inspection, safety, and any other support personnel working in the unit. Those involved in maintaining the mechanical integrity of equipment in the HF alkylation unit shall be trained in the mechanical and materials limitations of the unit (e.g. carbon steel specifications, excluding stainless steels and silica, temperature limits, and special gaskets).

### **5.5.4 PPE Training**

Training shall be provided for all personnel who enter or work in the HF alkylation unit or who are designated to respond to emergencies in the unit, in the use of applicable PPE and clothing. This training shall cover the explanation of each class of clothing, integrity checking of this equipment prior to donning, donning and removal steps, and cleaning procedures. Donning and removal steps should include hands-on training and physically putting on and removing a suit in front of trained personnel.

For those individuals that are expected to perform work that requires traditional Class D (OSHA "Level A") and traditional Class C (OSHA "Level B") suits, training shall include performing a simulated work task while wearing the suit. Those trained to use traditional Class D (OSHA "Level A") suits shall meet the fitness for duty medical recommendations of OSHA 29 CFR 1910.134(e) or alternate applicable local requirements.

## **5.6 PPE and Clothing**

### **5.6.1 Availability and Written Policy**

PPE shall be available for all personnel who work in or enter an HF alkylation unit for any reason. The site should define the minimum amount of PPE to be available. Each HF alkylation unit shall have a written policy that should outline requirements for use and training on protective equipment and clothing, including the potential health impact of using protective equipment under extreme ambient conditions. Heating and cooling systems for personnel who wear PPE in extreme working conditions are commercially available and should be considered.

### **5.6.2 Classes of PPE and Clothing**

In selecting PPE for planned work activity, a combination of clothing and equipment shall be chosen to conform to applicable regulations and to provide an appropriate level of protection without significantly impairing work performance. As conditions change, the level of protection should change in a way that is appropriate to the situation.

Levels of protection are typically divided into four classes. Traditionally, sites have designated "Class A" as the lowest level of protection and "Class D" as the highest. This classification system is widely used in the refining industry. However, many sites have adopted a lettering system that is similar to both the EPA and

OSHA organizations. In this system, “Level A” is the highest level of protection and “Level D” is the lowest. This change in classification was adopted by these sites to reduce potential confusion if external responders are called into an event. The substantive criteria within each letter level may not be completely comparable between the industry and government schemes. Therefore, the table below should be used in the context of OSHA regulations on PPE and respiratory protection (see OSHA 29 *CFR* Part 1910.120, 132–136). Regardless of the classification used, the clothing classification nomenclature shall be clearly communicated to all site personnel and any external hazardous materials teams responding to an event.

Table 1 outlines the minimum requirements of the four classes of PPE for planned work activity, not for emergency response activity, from the highest level of protection to the lowest. Site-specific requirements or specific work tasks may call for additional PPE within a specified classification (e.g. the use of a neck cape for traditional Class A and Class B clothing).

Annex F outlines typical tasks that help define the need for clothing in each of the classes listed in Table 1.

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**Table 1—Minimum Requirements of the Four Classes of PPE for Planned Work Activity**

Traditional Industry Classification	Closest Corresponding OSHA Level	Description	Use
Class D	Level A	<ul style="list-style-type: none"> <li>— Totally enclosed chemical-resistant suit with self-contained breathing apparatus (SCBA) or with air-line-fed respirator with escape pack.</li> <li>— These suits should include provisions for positive remote communications, such as a radio inside the suit.</li> <li>— Option to consider new suits that provide flash fire protection.</li> </ul>	Where exposure to HF vapor is expected and where there is potential for exposure to liquid HF. Direct contact with liquid HF should be avoided whenever possible.
Class C	Level B	<ul style="list-style-type: none"> <li>— Air-supplied chemical-resistant hood or hood/ jacket combination. If a higher level of respiratory protection is needed, based on site-specific considerations and the type of work being performed, a positive-pressure SCBA or an air-line-fed respirator with an escape pack should be used under the chemical-resistant hood.</li> <li>— Chemical-resistant jacket and chemical-resistant overalls.</li> <li>— Chemical-resistant gauntlet type gloves sealed to the jacket sleeves.</li> <li>— Chemical-resistant rubbers/alky boots.</li> </ul>	When low-level HF exposure is anticipated.
Class B	Level C	<ul style="list-style-type: none"> <li>— Face shield.</li> <li>— Safety glasses with side shields or chemical splash goggles.</li> <li>— Chemical-resistant jacket and chemical-resistant overalls.</li> <li>— Chemical-resistant gauntlet type gloves (gauntlets are to cover the wrists when the arms are extended). Option to seal or attach the gloves to the jacket sleeves.</li> <li>— Chemical-resistant rubbers/alky boots.</li> </ul>	For routine work on HF-containing equipment when no HF exposure is expected.
Class A	Level D	<ul style="list-style-type: none"> <li>— Chemical splash goggles or face shield with safety glasses with side shields.</li> <li>— Chemical-resistant gloves, such as Nitrile or Viton. Optional chemical-resistant gauntlet type gloves should be carried on the person if not worn (gauntlets are to cover the wrists when the arms are extended).</li> <li>— Chemical-resistant rubbers/alky boots or leather boots with chemical-resistant soles.</li> <li>— Optional chemical-resistant jacket.</li> </ul>	When no physical contact with HF-containing equipment is to be made.



### 5.6.3 PPE Exceptions

Alkylation unit PPE policy should acknowledge the different types of special tasks involved in performing craftwork on the HF alkylation unit. In some cases, the hazards associated with the work require a different type of hand protection. For example, Insulators handle sheet metal with sharp edges that could cut through normal unit PPE and may require cut-resistant gloves.

Welders should be allowed to use welding gloves and hoods when working in the area. At times, crafts such as, instrument technicians, machinists, inspectors, and electricians are required to do very detailed work that can be cumbersome in traditional alky gloves. Nitrile or Viton<sup>®1</sup> type gloves offer protection against HF while improving the worker's dexterity. This glove option should be allowed for use by crafts requiring this type of detailed work.

Nitrile or Viton<sup>®</sup> gloves offer added HF protection and shall be worn under leather gloves for craftsmen such as insulators and welders. Nitrile or Viton<sup>®</sup> gloves are not durable and shall be replaced if the gloves are damaged or are suspected of being damaged.

Procedures should be in place for proper handling and disposal of gloves and other PPE issued for special tasks on the alkylation unit.

### 5.6.4 Breathing Air

Breathing air shall meet the requirements for Grade D breathing air as defined in CGA G-7.1 or other applicable standards. Breathing air may be supplied from cylinders or a specially dedicated compressor. If a compressor is used, then a site assessment shall be conducted to determine the appropriate monitoring of the air supply and for an emergency backup supply in case of compressor failure. The capacity of the breathing air system and how many workers it can support at one time shall be established and documented in unit procedures.. See 4.7 for critical alarms associated with breathing air systems.

### 5.6.5 Backup Personnel for Non-emergency Situations

When work is performed that requires traditional Class C or D PPE (OSHA Level B or A) as described in 5.6.2, standby personnel shall be present, equipped with equivalent PPE, to assist the work party with egress from the work area for non-emergency situations. Note that per OSHA 29 *CFR* 1910.120(a)(3), "incidental release of hazardous substances where the substance can be absorbed, neutralized or otherwise controlled at the time of release by employees in the immediate release area, or by maintenance personnel are not considered to be emergency responses."

### 5.6.6 Multiple Storage Areas

Provision for an inventory of PPE in at least two different wind directions from the alkylation unit should be evaluated in the event that one location becomes inaccessible during an incident. In cold climates, heated storage areas should be considered for PPE.

### 5.6.7 Care, Cleaning, and Handling

Designated areas and facilities shall be provided for neutralizing, cleaning, and storing of all protective clothing. The facilities should be segregated into an HF-free or "clean" area where clean PPE is stored and donned and a contaminated or "dirty" area where used PPE is removed, neutralized, and cleaned.

Written procedures shall be established to remove, neutralize, and clean clothing and to prevent contamination of HF-free areas. Protective clothing should be neutralized and cleaned after each use per the

<sup>1</sup> This term is used as an example only and does not constitute an endorsement of this product by API.



manufacturer's suggested guidelines. Since protective clothing is chemical resistant, not HF proof, it shall be washed and neutralized immediately after any contact with HF.

### **5.6.8 Inspection and Testing of PPE**

All protective equipment, including new clothing, shall be inspected per the manufacturer's suggested guidelines before use. Procedures shall be developed for inspection and testing of protective clothing and equipment. Also, procedures shall provide criteria for removing the PPE from service if the results of the inspection and testing demonstrate the failure of that equipment. These procedures should be readily available for reference to the individuals using the clothing. Testing of gloves and inspection of boots shall be done before each use. The method for testing gloves shall be pressuring with air and immersing in water. Facilities should be available for the end user to do this test.

## **5.7 Safety Showers and Eyewash Stations**

Easily identifiable safety showers and eyewash stations shall be provided in the HF alkylation unit and other areas of the refinery where HF may be present (e.g. laboratory, shops). These showers and eyewash stations shall be located to provide timely and unrestricted access by personnel in the event of HF exposure. Control room and/or local alarms shall be provided to alert personnel when a safety shower or eyewash is activated and be designed to ensure immediate help is sent to the person using the shower or eyewash. Each shower shall be tested at a defined frequency, and the results of the tests shall be documented (see ANSI/ISEA Z358.1).

## **5.8 Controlled Access to the HF Alkylation Unit**

### **5.8.1 Unit Demarcation**

The HF alkylation unit shall be distinctively marked to avoid inadvertent entry onto the unit. Such markings shall warn people that HF is present, that access is strictly limited and that special protective clothing is required. These markings should not prevent egress from the unit.

#### **Unit Access**

All sites shall have in place a procedure to account for personnel entering the unit and to ensure that only people that have received the HF alkylation unit safety orientation (see 5.5.1) may enter. The procedure (e.g. sign-in/sign-out) should allow for the accounting of these individuals to be documented at a single location for quick reference.

## **5.9 Medical Response to HF Exposure**

### **5.9.1 General**

Written procedures shall be established for medical response to HF exposure. The procedures shall outline an appropriate response when personnel are exposed to HF vapor or liquid including inhalation, eye exposure, ingestion, or skin exposure. Symptoms of exposure and the critical role speed of response plays in minimizing the impact of HF exposure shall be included. HF first aid trained personnel shall include Alkylation unit operators and laboratory personnel to ensure appropriate speed of response. Training in HF first aid shall include an appropriate response for each type of exposure and be conducted on an annual basis, at a minimum.

On an annual basis, individual sites shall communicate and discuss preparedness with the local medical facility equipped to treat HF exposure. Procedures should include instructions on transportation to a medical facility and appropriate communication with that facility. Preparedness discussions and communication should include all medical facilities if there are multiple in an area. A knowledgeable employee should accompany the affected person to the medical facility to ensure that prompt treatment is provided. This employee can ensure

that attending medical personnel are aware of the HF involvement and can furnish them with copies of any prearranged treatment plans.

Since HF can readily mix with and be retained by certain hydrocarbons (e.g. HF is contained in ASO and may be associated with fluoride scale found in alkylation unit equipment), personnel shall be trained to take precautions to avoid unprotected exposure to these materials.

## **5.9.2 First Aid**

### **5.9.2.1 First Aid Kits**

Suitably equipped HF first aid kits shall be readily available for use in HF alkylation units and other areas of the refinery where HF may be present or where HF exposure treatment may be given. First aid kit contents should be stored in a manner consistent with the manufacturer's guidelines. Established HF release emergency scenarios and availability of local backup medical resources should be considered when determining the quantity of HF first aid supplies immediately available to the refinery. Procedures shall indicate the number, location, content, and replenishment schedules and include a process for routinely checking the kits to ensure the contents are present and within their expiration date. Personnel should be designated to inspect the kits. All first aid kits should be equipped with tamper-evident seals and the seals verified to be in place on a routine basis.

### **5.9.2.2 Portable First Aid Kits**

A portable first aid kit shall be available to accompany affected individual(s) being transported to off-site medical facilities.

Placement of additional portable first aid kits at the site of work should be considered during turnarounds or where work is taking place in enclosed, difficult to access areas.

### **5.9.2.3 Availability of Trained Personnel**

HF first aid trained personnel shall be available on site during all shifts to quickly respond to the unit or laboratory in the event of an exposure. Established HF release emergency scenarios and availability of local backup medical resources should be considered when determining the number of trained on-site personnel per shift.

## **5.9.3 Follow-up Medical Treatment**

The owner-operator should develop a prearranged plan for follow-up medical examination and treatment, as needed after initial first aid, at one or more nearby medical facilities. The plan should include written protocols for treatment of HF exposures, provision of protective equipment for facility personnel as needed, stocking of supplies for HF treatment, appropriate training, communication with refinery medical personnel, and procedures for hospital admissions that may be required after emergency treatment.

## **5.10 Maintenance and Related Work Practices**

### **5.10.1 General**

Maintenance programs apply to all processes and systems within an HF alkylation unit. However, there are other related work processes that do not fit the previous sections and/or topics yet affect equipment and piping mechanical integrity. The intent of this section is to bring these items into one area that provides the operator-user information and requirements to successfully maintain the mechanical integrity in an HF alkylation unit.

### **5.10.2 Maintenance Program**

A maintenance program shall be in place for HF alkylation units. This program should have the following elements:

- addressing specific equipment issues (e.g. tubing connections, flanged joints) in HF service;
- removal of equipment, materials, and tools from the HF alkylation unit;
- equipment and materials stored in the HF alkylation unit;
- Tightness testing;
- rod-out tool inspection and maintenance;
- cleanliness of equipment required for inspection;
- cleanliness of equipment and piping required for unit start-up;
- cleanliness of equipment and piping following chemical cleaning;
- an acid detecting paint maintenance program.

### 5.10.3 Equipment and Materials Removed from the Unit

The owner-operator shall have a documented system in place to manage the risk associated with handling equipment and materials that are being removed from the unit and are potentially contaminated with HF (even in trace amounts), iron fluoride scale, or ASO. This shall include process equipment and piping, non-process equipment and piping, tools, and various types of waste that originate inside the HF alkylation unit battery limits. The documented system shall include PPE requirements for handling such equipment.

Process equipment and piping, non-process equipment and piping, tools, and waste to be removed from the unit should be decontaminated in designated areas. The decontamination should occur inside the battery limits if practicable. All HF service equipment, piping, and materials to be removed from the unit shall be identified to indicate decontamination status and that the component originated from the HF alkylation unit. Owner-operator procedures shall include, at a minimum, when identification is to be attached, changed, and removed, and the job function responsible for these activities. For this identification, “decontaminated” shall be defined as neutralized. This is completed by submersion in a neutralization solution when equipment is; disassembled to the smallest component and all iron fluoride scale and ASO have been removed from all interior and exterior surfaces. Any HF service equipment and piping not meeting this definition shall be identified as “neutralized-potentially contaminated.”

The equipment that has been or may have been contacted by HF, including the exterior surfaces of non-process equipment that cannot be neutralized by submersion, shall be decontaminated with a neutralizing agent (e.g. an ammonia-based cleaner) after being handled inside the unit. For example, this equipment may include but not be limited to forklifts, cranes, metal scaffolding, electronics, switchgear, motors, inspection equipment, tools used for maintenance work, etc. The equipment shall be submersed, sprayed down, external surfaces wiped down, or neutralized by other effective means as defined in the site procedures. The use of disposable covers to protect sensitive equipment (e.g. inspection UT meters) has been used by some owner-operators as an alternative. Affected equipment shall not be removed from the unit until this is completed.

Safety equipment such as ropes, slings, and harnesses may be reused inside the unit and should be wiped down with a neutralizing agent between uses. That equipment shall be neutralized and rendered unusable (e.g. cut into small sections) before removal from the unit for disposal.

Site disassembly procedures shall define what constitutes complete disassembly and the techniques needed (e.g. chemical cleaning, hydro-blasting, etc.) to remove residual HF, residual iron fluoride scale, and ASO for each type of equipment and piping. When decontamination inside the battery limits is impracticable (e.g. before pre-pop testing of unit PRVs), appropriate handling procedures shall be developed.

Disassembly procedures should specify inaccessible areas associated with each equipment and piping type and appropriate handling considerations. Specific examples of inaccessible areas that have been known to release HF when disassembled are the space behind wear rings in HF service pumps and the space behind sleeves in HF service plug valves. Tube bundles that have either plugged tubes or fouling deposits shall be considered contaminated. Any piece of equipment, piping, or material that has inaccessible areas that cannot be completely decontaminated shall be treated as contaminated for handling and maintenance purposes.

PPE requirements shall be specified for personnel who decontaminate and/or disassemble HF service equipment, piping, and materials inside unit battery limits or elsewhere on site. Unit and off-unit personnel that are involved in disassembly, repair, or handling of HF alkylation unit equipment, piping, and materials shall receive training per 5.5.3 and on special considerations per this section.

The use of wood (such as wooden scaffolding) and other porous materials should be minimized in the HF alkylation unit. Wooden materials have the potential to absorb HF, making them difficult to fully neutralize. Iron fluoride scale can become embedded in the wood, and thus it is very difficult to fully decontaminate. When wood or porous materials are used in the HF alkylation unit, a written plan shall be developed to properly handle it after use to prevent accidental personnel exposure to residual HF and iron fluoride scale. The plan shall include identification of the potentially contaminated materials, as well as disposal and on- and/or off-unit storage procedures.

When repair or disposal of unit equipment or piping requires further off-unit decontamination (e.g. at a wash pad) or disassembly (e.g. at a machine shop), site procedures should give specific guidance for area isolation, availability of safety equipment (e.g. safety showers and eyewash stations), and required PPE for handling. When these areas are temporary, the site procedure should include when the area controls are established and removed. If equipment and piping repair or disposal requires shipment to an off-site facility, site procedures shall include steps to notify the receiving facility in writing of the hazards associated with HF and iron fluoride scale and provide them with typical precautions and safeguards used to minimize the potential for personnel exposure.

When the owner-operator has established a segregated and secure area outside of the unit battery limits for storing equipment, piping, and materials removed from the unit (aka, a weathering area), a written program that manages the addition and removal of items to and from this area shall be in place. This should include the type of items to be placed in the area, the minimum time to be retained within the area, and the PPE required to handle items in the area.

#### **5.10.4 Equipment and Materials Stored on the Unit**

If potentially contaminated equipment, piping, and materials are stored on the unit, they shall be stored in a segregated storage area and be clearly identified to indicate decontamination status. A system should be used to track these materials as they enter and leave this area.

Mechanical tools that remain stored in the unit should be specially marked as such..

#### **5.10.5 Rod-out Tools**

Rod-out tools are used to remove pluggage from drains and vents. For HF alkylation units, pluggage usually consists of iron fluoride and/or ASO. After use, rod-out tools shall be immediately neutralized. Rod-out tools shall be inspected for damage before each use. If found damaged (e.g. indications of corrosion or cracking are found) or if they are unable to be used as intended, they shall be decontaminated per 6.6.3 and removed from the unit. Owner-operators have successfully used Alloy 400 and stainless steel rod-out tools subject to the guidance of this section.

## **6 Materials, Fabrication, Inspection, and Maintenance Practices**

### **6.1 Common Discussion about Section 6**

#### **6.1.1 Applicability and Organization of Section 6 and Annexes G/H**

The materials, design, fabrication, repair, inspection, and maintenance guidance provided in Section 6 and Annex G and Annex H of this recommended practice are based on reported owner-operator experiences, testing, and evidence presented in industry forums. Usually, unexpected corrosion or deterioration can be avoided by following the materials requirements and recommendations in this recommended practice and by maintaining unit conditions within properly specified process limits.

The Fifth Edition of API 751 was reorganized to conform to API style requirements for a publication. As such, in prior editions this section was known as “Section 3” and was associated with “Annex D.” With the current revision, this is now Section 6 and is associated with Annex G (corrosion and materials) and Annex H (inspection).

Further, Section 6 contains all the requirements and recommended practices for this subject matter. Annex G provides information on what equipment and piping belong in each corrosion zone, information on how materials perform in each zone, and descriptions of the types of damage that can be expected in each zone. Annex H provides information on the inspection practices specific to each zone or specific areas of concern (e.g. critical check valves). As such, Annex G and Annex H are intended to be used in conjunction with Section 6 to help establish inspection plans and help select appropriate materials of construction for components. Please note that while Annex G covers many of the corrosion mechanisms and materials in HF service, it may not cover everything that can or has occurred in any particular HF alkylation unit.

The owner-operator of each HF alkylation unit shall develop, implement, and maintain comprehensive inspection and maintenance programs that include written procedures aimed at monitoring and preserving the unit’s mechanical integrity. Some sites have developed a single electronic repository referring to all the mechanical integrity guidance documents (e.g. local/company requirements, Section 6, Annex G, and Annex H) for easy access by all stakeholders. The repository may also include how the owner-operator adheres to the requirements and recommendations stated herein.

### 6.1.2 Corrosion Zone Terminology

The terms “trace acid,” “main acid,” and “dilute HF acid” have historically been used in previous editions of API 751 (Fourth Edition and prior, see Section 3 and Annex D). These terms have been discontinued in the Fifth Edition. These discontinued terms are defined in Section 3, Terms and Definitions. The previous editions could have been interpreted that all trace acid services have a similar risk (the combination of probability and consequence of failure) and that all main acid services also have similar risk, although different than trace acid service risk.

Since the likelihood of corrosion or other damage is higher in some areas, the combined probability and consequence of failure (i.e. risk) in all main of trace acid services are not the same, the HF alkylation unit has been redefined into services that are similar with respect to corrosion rates. The new categories are termed corrosion zones and are:

- a) fresh HF,
- b) rich HF,
- c) phase change HF,
- d) dilute HF in water,
- e) fractionator HF.

Annex G provides information on each corrosion zone.

### 6.1.3 API and ASME Codes and Standards Applicable to HF Alkylation Units

Equipment, including piping, used within HF alkylation units shall be designed and constructed to the appropriate ASME Codes or other applicable governing standards. For example, in the United States this would include ASME BPVC Section VIII for pressure vessels, ASME B31.3 for process piping, and API 520 for pressure-relief devices.

Additionally, API 510, API 570, and API 653 are the bases for inspecting, maintaining, altering, and repairing pressure vessels, piping, and storage tanks. Other applicable recommended practices (RPs) for equipment and piping, referenced by these codes, include but are not limited to:

- API 571 (for guidance on damage mechanisms),
- API 572 (for guidance on inspection),
- API 573 (for guidance on the inspection of heaters),
- API 574 (for guidance on the inspection of piping systems),
- API 575 (for guidance on the inspection of storage tanks),
- API 576 (for guidance on inspection and maintenance of pressure-relief devices),
- API 577 (for guidance on welding issues applicable to fixed equipment),
- API 578 (for guidance on material verification),
- API 579-1/ASME FFS-1 [for guidance on Fitness-For-Service (FFS) evaluations],
- API 580 [for guidance on Risk-Based Inspection (RBI)],
- API 582 (for guidance on welding),
- API 583 [for guidance on corrosion under insulation (CUI)],
- API 584 (for guidance on IOWs),
- API 585 (for guidance on investigating equipment failures),
- API 970 (for guidance on CCDs).

The content of the above documents will not be repeated herein except to note and emphasize issues that are specific to HF alkylation units. Also, where reference to an industry document is made within this section, it is implied in all cases the most recent edition of that document is to be utilized.

#### **6.1.4 CCDs for HF Alkylation Units**

Each HF alkylation unit should have a comprehensive CCD in accordance with API 970 or equivalent industry practice. The CCD should cover the credible damage mechanisms for each corrosion zone defined in this document.

#### **6.1.5 IOWs for HF Alkylation Units**

IOWs for physical and chemical process parameters that could affect equipment and piping integrity shall be established for HF alkylation units. A multi-disciplinary team consisting of operations, process engineering, mechanical integrity and inspection should be utilized to review and develop integrity limits and define response and notification parameters for all affected discipline groups (ie operations and inspection). The owner-operator shall evaluate the IOWs listed in Table G.1 for inclusion in the site's IOW program, as appropriate. Annex G.5 provides a listing and rationale on the process variables that may need IOWs created and implemented. The owner-operator should also include any IOWs that are important to the mechanical integrity even if they are not identified in Table G.1. See API 584 for more information on the work process for establishing and implementing IOWs.



## 6.2 Materials of Construction

### General

Piping and equipment operating in all process wetted HF corrosion zones shall be constructed of HF resistant materials.

The principal HF Resistant materials of construction for HF alkylation units are carbon steel and nickel-copper Unified Numbering System (UNS) N04400 (Alloy 400) (e.g. Monel® 400 hereafter referred to as Alloy 400). Other materials, such as copper-nickel (Cu-Ni) alloys (e.g. UNS C71500, 70/30 copper-nickel) and nickel-base alloys [e.g. UNS N10276 (Alloy C-276) (e.g. Hastelloy® C-276 hereafter referred to as Alloy C-276) and UNS N10665 (Alloy B-2) (e.g. Hastelloy® B-2 hereafter referred to as Alloy B-2)], have been used in a limited number of selected applications. Annex G contains more detail regarding additional HF resistant materials.

Typical materials that are not suitable for HF service include but are not limited to (note: exceptions to this list are outlined in the separate materials sections and Annex G

- Aluminum
- Stainless Steel
- Low Alloy Steels
- Titanium
- Brass
- Copper
- Silicon including glass, ceramics and silicon containing filler materials

Composite gaskets Other materials not specifically listed as HF resistant may be evaluated for HF service as long as the manufacturer has considered use in HF Alky process service.

Additional information and guidance on how materials perform in the various corrosion zones can be found in Annex G. Not all aspects of corrosion of these materials can be adequately addressed in this recommended practice. NACE 5A171 and MTI MS-4 provide overviews of materials performance in HF service.

Other limitations on specific materials and their use within an HF alkylation unit are also provided within this section.

### 6.2.1 Carbon Steel

#### 6.2.1.1 Residual Elements (REs) in Carbon Steel

Corrosion rates on carbon steel are a function of carbon steel composition with respect to RE content as well as operating conditions. The presence of high-RE carbon steel components can affect corrosion rates in all corrosion zones and on all types of carbon steel, including welds. In dilute HF in water corrosion zones, the low-RE carbon steel components tend to corrode preferentially where connected to high-RE carbon steel components but not where low-RE carbon steel components are connected to each other. In the other corrosion zones, preferential corrosion of the entire component and/or localized corrosion may also occur on the high-RE carbon steel components. Regardless of RE content, localized corrosion may exist in all corrosion zones but may be more pronounced in the dilute and phase change corrosion zones.

Low-RE carbon steel should be used for new and replacement equipment and piping in all five HF corrosion zones where carbon steel is normally specified. When replacing individual components, the impacts of mixed RE components should be considered, especially in the dilute HF corrosion zone. Many ASTM specifications



for carbon steel [such as ASTM A106, A333, A516, A960, or A961 (A105, A350)] include optional supplementary specifications for HF service (such as S9, S2, S54, S78, S62) that meet the recommended limits for RE content. If carbon steel meeting the RE requirements for HF service is not used or is unavailable, upgrading the metallurgy (typically to Alloy 400) or performing ongoing individual component thickness monitoring per 6.4.2.3.2 should be utilized. These RE requirements should also be applied to welds.

When low-RE materials are specified, they shall meet the following criteria.

- a) For Base Metal:  $\%C \geq 0.18 \text{ wt } \%$ ,  $\%Cu + \%Ni \leq 0.15 \text{ wt } \%$ .
- b) For Base Metal:  $\%C < 0.18$  or unknown,  $\%Cu + \%Ni + \%Cr \leq 0.15 \text{ wt } \%$ .
- c) For Weld Metal:  $\%Cu + \%Ni + \%Cr \leq 0.15 \text{ wt } \%$ .

A significant number of owner-operators have reported positive material identification (PMI)-measured RE does not always match the MTR. Because of this issue, using PMI to verify the RE content of carbon steel components and welds should be part of the material verification program (MVP). See 6.2.5 for recommendations and requirements regarding PMI and Annex G and Annex H for further information.

#### 6.2.1.2 Hydrogen Damage of Carbon Steel

HSC-HF in HF service is typically managed by limiting hardness in carbon steel and welds. Blistering, HIC, and SOHIC base metal hydrogen damage is typically managed by specifying requirements for steel making cleanliness controls and PWHT. See 6.3.2.1 and Annex G for further details.

#### 6.2.2 6.2.1.3 Other Metallic Materials

##### 6.2.2.1 Stainless Steels

Because of their high corrosion rates relative to carbon steel as well as their potential for fluoride stress cracking, stainless steels are not to be used in HF services, including temporary process hoses. An exception is the transportation and unloading hoses used in AHF and modified HF (MHF) services. This applies to all versions of stainless steel (ferritic, martensitic, austenitic, and duplex) and in all areas of the unit where HF is normally present, including samples that contain HF. This should be extended into areas that are not normally in HF service but could be in HF service during transitional operation (i.e. start-up, shutdown, upsets, or component failure). Some owner-operators prohibit the use of stainless steels inside the HF alkylation unit except for some specific locations.

Information on specific locations can be found in G.2.4. In addition, stainless steel in HF service shall not be used for:

- a) bolting on pressure boundaries, including instrumentation,
- b) pressure gauge bourdon tubes, even if a diaphragm seal and barrier fluid are used, or
- c) new or replacement components in seal flush systems for pumps regardless of design.

Existing seal flush systems on HF service pumps where stainless steel components are installed shall be evaluated for replacement with a more suitable metallurgy.

Materials selection and materials verification processes (including PMI) shall be in place for avoiding the installation of stainless steel components in HF services. See G.2.4 for further information on stainless steels.

Use of stainless steel in anhydrous HF service (i.e. loading hoses, transportation containers, etc) is acceptable.

### 6.2.2.2 Copper and Nickel Alloys

The combined presence of HF and oxygen can cause SCC of copper and nickel alloys and may also cause pitting and denickelification (see G.2.5). A program shall be in place to minimize the potential for SCC of equipment constructed of these alloys when there is a potential of simultaneous exposure to oxygen and HF.

The program should include the following elements.

- a) Procedures to neutralize the internal surfaces of equipment and piping that has been previously exposed to HF (e.g. placed in HF service) prior to performing any maintenance activities that may expose those surfaces to oxygen.
- b) Procedures to purge equipment to remove oxygen before placing equipment and piping in service and after any maintenance activities prior to exposing to HF (e.g. placing in HF service).
- c) Procedures to maintain a nitrogen purge on equipment that may not be neutralized and planned to be opened—to address oxygen ingress while idling a unit or portion of a unit.

Ni alloys (e.g. Hastelloy® C-276) can be used instead of Ni-Cu alloys (e.g. Alloy 400, Alloy K-500) to reduce the potential for SCC where simultaneous exposure to HF and oxygen is difficult to eliminate. If environmental cracking for Ni and Ni-Cu alloys is a potential, then heat treatment should be considered to reduce the risk of cracking when welded or cold-worked. See Annex G for a discussion of heat treatment temperature for welded components. Cu-Ni and Ni-Cu alloys shall not be used for pressure boundary bolting in HF services, including instrumentation, pumps, and valve bonnets in HF service.

Liquid metal embrittlement of Alloy 400 and Ni Alloys is known to occur when exposed to mercury. Units that may process mercury-containing feeds should evaluate the use of mercury-adsorbing materials as part of unit feed treating. Units that either run or potentially run mercury-containing feeds should set an upper IOW limit for refinery crude mercury content and/or the unit feed mercury content (G.5).

Although Ni alloys may be less susceptible to SCC than Alloy 400, they are not immune to it. Where Ni alloy components exist or are being planned for installation, the potential for environmental cracking at welds should be evaluated. If environmental cracking for Ni and Ni-Cu alloys is a potential, then heat treatment has been found to reduce the risk of cracking. See G.2.5.2 and G.2.7 for discussion of heat treatment temperature for welded components.

As Alloy 400 corrosion rates typically increase above about 300 °F (149 °C) in the presence of HF, process temperatures should be kept below this temperature. IOW limits should be considered for Alloy 400 equipment and piping operating at process temperatures close to or above 300 °F (149 °C). Thickness inspections should be carried out at increased frequency if temperatures are close to or exceed 300 °F. In addition, IOWs should be set for limiting process temperatures in the HF regeneration section of the unit.

Alloy K-500 may be used for high-strength applications such as relief valve springs, pump shafts, valve stems, and bellows, etc. When used in these applications, the material hardness of Alloy K-500 should not exceed HRC 30 to reduce the potential for SCC.

Because of embrittlement and sensitivity to velocity-assisted corrosion, copper-zinc (Cu-Zn) alloys (brass) should not be used in HF services. Due to its susceptibility to high corrosion rates, HSC-HF, and mechanical damage due to its softness, copper should not be used for permanent installations in HF services.

Some owner-operators use copper (ie copper tubing) for short term/temporary use such as a turnaround material but copper is not a suitable material for permanent installation.

### 6.2.2.3 Castings

Due to the varied manufacturing techniques used for making castings, stringent inspection and QC parameters should be specified. Castings covered by this include components of valves (including control valves), instrumentation, pumps, etc. The inspection guidelines in API 610, Class 3 for pumps and ASME B16.34 or API 20A for valves should be followed. The amount of inspection to determine pressure boundary integrity for cast components, especially casting defects, should be specified by the purchaser. There have been cases of undetected sand hole or shrinkage defects causing through-wall leaks on cast components after being put into HF service, even after stringent inspection and testing. For this reason, cast equipment is included in the acid detecting paint program—see 6.5.13. Purchasers of cast valves should satisfy themselves that the testing requirements in API 598 and MSS-SP-160 are met, as this is often not required and does not always happen for standard valve bodies built to standard requirements. See G.2.8 for further information.

As niobium carbides are preferentially corroded by HF, Alloy 400 castings should be made of ASTM A494 Grade M35-1. Grades M25S, M30C, M30H, and M35-2 should be avoided. Note that silicon additions up to 1.25% in M35-1 castings have not been reported to impact the corrosion resistance of this alloy in HF service; however, the higher silicon content in M35-2 castings have produced higher corrosion rates.

The heat-treatment requirements and recommendations of this section should be applied to major repairs on new castings and all repairs on existing castings (reference 6.3.2.4). Some owner-operators require heat treatment of all casting repairs.

MSS-SP-160-2024, Valves for Hydrogen Fluoride (HF) Alkylation Service sets the minimum design and quality expectations for new gate, globe, check, butterfly, and plug valves manufactured for the HF Alkylation industry. Comprehensive material, inspection and QC requirements found in MSS SP-160 should be used. Note that Table 2 (below) has not always been effective in finding casting flaws such as shrinkage and tears in valves. If MSS SP-160 is not used, then the owner/operator shall specify tests necessary to ensure valve quality and integrity.

The inspection and QC parameters beyond what are normally required for all other types of cast components should include but are not limited to the types of testing from Table 2. Similar requirements should be considered for casting repairs.

**Table 2—Types of Testing Typically Recommended for Cast Components**

Type of Testing Typically Recommended	How Owner-Operators Have Specified These Tests to Be Performed (as required by the applicable code)
Magnetic particle or liquid penetrant	ASME/ANSI B16.34, Appendix II or III ASME BPVC Section V
Helium leak test	ASME/BPVC Section V, Article 10, Appendix I, Bubble Test—Direct Pressure Appendix II, Bubble Test—Vacuum Box Technique Appendix IV, Helium Mass Spectrometer Tests—Detector Probe Technique Appendix V, Helium Mass Spectrometer Tests—Tracer Probe Technique Appendix IX, Helium Mass Spectrometer Test—Hood Technique
Radiographic ASME/ANSI	ASME/ANSI B16.34, Appendix I ASME BPVC Section V
NOTE For pumps, inspection beyond what is normally required is typically performed to API 610, Class 3.	

### 6.2.3 Nonmetallic Materials

#### 6.2.3.1 Silicon

#### 6.2.3.2 HF readily attacks materials that contain silica, and the reaction products can be significantly more corrosive to unit metallurgies than HF. See Annex G.2.10. for further information. **Plastics and Elastomers**

While fully fluorinated plastics [e.g. PTFE, fluorinated ethylene propylene (FEP), and perfluoroalkoxy (PFA)] are HF resistant, they are also HF permeable. When specified for HF service, use manufacturers evaluations that any filler material has been evaluated for HF resistance .

Historically, O-rings and other elastomeric sealing elements in hydrofluoric acid (HF) alkylation HF service were manufactured from litharge-cured fluoroelastomer (FKM), utilizing lead oxide as the curing agent to enhance resistance to HF. Litharge-cured FKM is no longer commercially available, and current FKM formulations do not provide improved performance over other elastomers in HF service. FKM compounds are susceptible to swelling, degradation, and loss of mechanical integrity when exposed to HF acid and shall not be used in HF alkylation service.

Perfluoroelastomer (FFKM) compounds specifically rated for HF service have demonstrated good performance for O-rings and elastomeric sealing elements in HF alkylation units. FFKM compounds exhibit superior chemical resistance, thermal stability, and mechanical performance under HF exposure. However, resistance to HF varies among FFKM grades; therefore, selection of elastomeric sealing materials shall be based on vendor recommendations and/or internal testing, validated performance data, and verification of compatibility with HF under the expected operating conditions, including process temperature, pressure, and exposure duration.

See G.2.11 for further information.

#### 6.2.3.3 Graphite

Graphite has been used extensively in HF-services, especially in gaskets. Graphite used in HF services shall not contain any material that is known to be readily attacked by HF. See G.2.10 for further information.

#### 6.2.3.4 Anti-seize Agents

Owner/users shall have a specification for anti-seize agents that are used in HF service. See G.2.12 for further information.

### 6.2.4 Material Verification Program (MVP)

A written MVP in accordance with API 578 shall be in effect, including PMI, to verify that the nominal composition of an asset or asset component is consistent with the selected or specified construction materials. This includes all components, including instrumentation and valves, that may be exposed to HF. The HF alkylation unit PMI program requirements shall define the extent and type of PMI to be conducted during construction of new assets, retroactively on existing assets, and during maintenance, repair, or alteration. The HF alkylation unit MVP shall include PMI on all new and replacement carbon steel and alloys to be installed in HF services.

The focus on carbon steel PMI is based on the importance of identifying issues like the substitution of high-RE material for low-RE material or substitution of low-alloy steel material for carbon steel material to avoid localized acceleration of corrosion. PMI of carbon steel shall include elemental analysis (e.g. Cu, Ni, Cr). All

weld metals shall be assumed to have a carbon content  $< 0.18$  wt % for the RE calculation (Cu, Ni, Cr summation) if the carbon content is not measured. For other components, the carbon content should be assumed  $< 0.18$  wt % for the RE calculation (Cu, Ni, Cr summation), if not verified

All nonmetallic HF-resistant materials should be included in the MVP.

Field PMI of carbon steel can be used to avoid the use of inappropriate materials that may be similar in appearance to carbon steel, such as UNS K11789 (1.25Cr-0.5Mo steel) or UNS S41000 (410 SS). But most instruments are not capable of differentiating high-RE and low-RE carbon steel. The owner-operator shall review the instrument capabilities (e.g. the limits of detection) to ensure the instrument can detect the low-RE criteria. XRF, laser-induced breakdown spectroscopy (LIBS), and optical emission spectrometers (OESs) are technologies that have been used successfully by owner-operators. Additionally, the instruments shall be used per the manufacturer's requirements with careful attention to surface preparation as detailed in API 578 because small variations in technique and contamination can invalidate the results. Refer to G.2.2 and H.2 for further information.

Mill test reports (MTRs) shall not be substituted for PMIV requirements, rather they can be used in conjunction with PMI. When composition information from the MTR and PMI testing reports is different for carbon steel RE content, some owner-operators have an independent metallurgical analysis performed. Defining an acceptance criteria for variability in instrumentation versus MTR is acceptable. Elements of the MVP should be in accordance with API 578 and should include, but not be limited to, the following.

- a) A process to identify, segregate, store, and deliver materials specifically for the HF alkylation unit.
- b) Applying all elements of the MVP to all areas where alkylation unit materials are received, stored, and delivered such as "satellite" or local equipment, components, and instrument storage areas.
- c) Including the acceptable examination methods, including the use of PMI testing methods such as portable XRF, LIBS, or OES, so that the precision of the test equipment is consistent with the established test objectives.
- d) Defining field requirements for materials verification.
- e) Defining the extent of PMI:
  - 1) typically, 100 % of pressure boundary components,
  - 2) typically, 100 % of individual components such as thermowells, valves, and instrumentation,
- f) valves, pumps, instruments, and other components that consist of multiple parts are not normally disassembled for material verification purposes; however, the owner-operator should require suppliers to certify that all factory/shop-assembled components (each individual assembly) have been constructed with the materials as specified, including components that cannot be subject to PMI after assembly.
- g) Defining examination results acceptance criteria.
- h) Including timing of material verification during the work process, as applicable (i.e. warehouse receiving/issuing, point of installation, etc.).
- i) A process for managing material nonconformances.
- j) Qualification and training, including refresher-training requirements, for personnel performing PMI and/or segregating HF alkylation unit-specific materials.

- k) The method of documenting and positively identifying materials that are verified, including transferring markings on unused portions of materials and parts (e.g. plates, pipes, bolts) before returning to storage.
- l) Calibration and verification practices for PMI testing equipment using certified standards prior to use and as specified by the equipment manufacturer.
- m) Material control methods for gaskets and bolting, including a means to indicate that they were verified.
- n) Verification of materials for gaskets and bolting at the point of installation, including a means to distinguish B7 and B7M studs and 2H and 2HM nuts.
- o) A process to remove questionable and unlabeled materials from designated storage areas.
- p) A process to clearly mark and segregate materials that have been tested and accepted for HF service from other materials.
- q) A process for verifying that only materials dedicated for HF service are issued for HF service, especially after normal working hours.
- r) A process to prevent Cu-Ni and Ni-Cu alloy bolts from being issued for pressure boundary closures.
- s) A process to verify unused materials returned to the storehouse or other designated alkylation unit-specific storage area before the material is returned to stock.
- t) A process to prevent materials that have not been verified from being installed in HF service.
- u) If PMI is performed by the supplier, a process to periodically audit the supplier's MVP program(s) and periodically conduct PMI on a random basis to validate supplier materials.

### **6.3 Specifications, Fabrication, and Repair**

#### **6.3.1 Pressure Vessel and Piping Specifications**

Each new or replacement pressure vessel in HF service shall have complete written specifications that cover issues specific to HF service. These specifications shall be consistent with this document. Each operating HF alkylation unit shall have complete written specifications for piping in HF service. These specifications shall, as a minimum, cover construction materials, minimum pipe sizes, minimum wall thicknesses, corrosion allowances, welding hardness limits, PWHT requirements, flange ratings, bolting, gasketing, valves, and packing. Specifications for piping shall be maintained consistent with the requirements in this recommended practice.

The owner-operator shall have a documented process to manage the risk associated with deviations from specifications and standards for equipment and piping in HF service.

#### **6.3.2 Fabrication and Repair**

##### **6.3.2.1 Carbon Steel Base Metal Specification**

The following outlines carbon steel base metal specifications for piping and equipment in HF service.

- v) Carbon steel should be fully killed, except for air cooler and heat exchanger tubing.
- w) Carbon steel plate should be supplied in normalized, normalized and tempered, or quench-and-tempered heat-treated condition.



- x) Heat treatment of forgings shall be governed by the applicable ASME Code or ASTM Standard. Some owner-operators choose to normalize forgings.
- y) Carbon steel plate used in large diameter seamed piping and equipment should include specifying requirements for base metal cleanliness and PWHT per NACE 5A171 and NACE 8X194.
- z) Carbon steel base metal hardness shall not exceed 200 HBW per ANSI/NACE MR0103/ISO 17945.
- aa) Requirements for hardness controls for carbon steel HAZs shall be specified per NACE SP0472. NACE SP0472 contains options to limit HAZ hardness including base metal chemistry controls and PWHT. See 6.3.2.4 for further details. RE controls for carbon steel base metals shall follow the requirements of 6.2.2.1.

### 6.3.2.2 Welding General

Each owner-operator shall document welding requirements for the fabrication of carbon steel, Alloy 400, and other alloys to be used in HF service. These requirements shall be consistent with this document. The owner-operator and/or their welding contractors shall have weld procedure specifications (WPSs) and procedure qualification records (PQRs) that meet these requirements. PQRs do not require low RE carbon steel. If PWHT is not applied, the carbon equivalent (CE) and microalloying content of the PQR coupon and weld filler shall be greater than or equal to the production piece (see 6.3.2.4). For all locations in HF service where low-RE carbon steel components are used, RE for carbon steel electrodes should be controlled (e.g. MVP programs) (see 6.2.5 and G.2.2). Controlling the composition of specified elements (e.g. iron, niobium, titanium) in Alloy 400 welding electrodes can improve corrosion resistance (see G.2.5.2).

If weld RE is not controlled, then inspection requirements for mixed RE components apply per 6.4.2.3.2.

### 6.3.2.3 Weld Slag

Weld slag contains silica and as such is rapidly attacked by HF (see 6.2.4.1). Also of concern are subsurface slag inclusions that can become exposed to HF as a result of corrosion of the weld or the opening of cavities in the weld, as they can also be attacked by HF. Weld slag in HF service piping and pressure vessels should be minimized by selection of welding process and/or through increased inter-pass cleaning. See 6.3.2.8.

For single-sided welds in HF service, the root and hot pass shall be completed using gas tungsten arc welding (GTAW). GTAW is used to eliminate slag in the weld. Some owner-operators find it more efficient to complete the weld out with GTAW on pipe NPS 6 and less. AWS SFA-5.1 E6010/11 root passes shall not be used in HF services.

For double-sided welds in HF service, welding techniques such as GTAW and gas metal arc welding (GMAW) are typically used. However, other methods such as shielded metal arc welding (SMAW), submerged arc welding (SAW), or flux-cored arc welding (FCAW) may also be used with thorough inter-pass cleaning.

### 6.3.2.4 Carbon Steel Weldment Hardness Control

Pressure-containing weldments on carbon steel piping and pressure vessels in HF service have the potential for HSC-HF due to high weld metal or HAZ hardness and residual welding stresses. Control of weldment hardness has been found to correlate with the prevention of HSC-HF in HF service carbon steel weldments. For new and repaired carbon steel weldments in HF service, NACE SP0472 shall be followed to help prevent HSC-HF of the weld metal and HAZ. For weld metal, this is accomplished by filler metal selection and production weld hardness testing. For the HAZ, this is a combination of base metal composition control [i.e. carbon equivalent (CE) control and microalloying element control] and either PWHT or alternative thermal methods.

PWHT is considered the most effective method for controlling HAZ hardness in HF services by many owner-operators. As such, many opt to control the hardness of all piping HAZ by PWHT rather than by



alternative thermal methods. Where piping PWHT is specified, it shall be performed in accordance with ASME B31.3, ASME Code for pressure piping, or another equivalent national standard. New carbon steel pressure vessels in all five HF corrosion zones shall receive PWHT.

All repair weldments to the pressure boundary in carbon steel pressure vessels in fresh HF, rich HF, dilute HF in water, and phase change HF services should receive PWHT for service unless a corrosion specialist deems it unnecessary. Copper and nickel alloys cladding or weld overlay of carbon steel is not subject to this requirement unless the underlying steel is exposed to HF. The procedure for PWHT of new pressure vessels in HF service shall be in accordance with ASME BPVC Section VIII, Division 1, Paragraphs UW-40, UW-49, and UCS-56 or equivalent new construction code. For weld repairs to pressure vessels, the appropriate articles in ASME PCC-2 and WRC 452 should be followed. Alternative methods to PWHT provided in NACE SP0472 are intended for hardness control and are not effective in reducing residual weld stresses.

Where PWHT of carbon steel equipment and piping is specified, PWHT shall be performed at  $1175^{\circ}\text{F} \pm 25^{\circ}\text{F}$  ( $635^{\circ}\text{C} \pm 15^{\circ}\text{C}$ ) and held for 1 hour per inch of thickness but at least 1-hour minimum. The temperature range meets the minimum necessary for effective stress relief while preventing overheating damage. As industry experience indicates that PWHT at lower temperatures is not as effective in reducing HAZ hardness, PWHT at a lower temperature with a longer holding time (as permitted in other services by the ASME Code) shall not be conducted.

NACE SP0472 contains information on alternative thermal methods for weld and HAZ hardness control [e.g. controlled deposition welding (CDW)]. For HF service, these methods only apply to seamless piping welds and other locations where temper bead welding is approved for service by a corrosion specialist.

#### **6.3.2.5 Thermal Stress Relief of Ni-Cu and Cu-Ni Alloys**

SCC in the simultaneous presence of HF and oxygen, as well as other degradation mechanisms for copper and nickel alloys, are more likely after being cold-worked or welded. For new Alloy 400 piping and pressure vessels including heat exchanger U-bends in HF service that have been either welded or cold-worked, a thermal stress relief treatment shall be performed to reduce the potential for SCC unless a corrosion specialist deems it unnecessary. For repair welds in HF service piping, pressure vessels, and valves, a thermal stress relief treatment should be performed on Ni-Cu and Cu-Ni alloys regardless of whether or not the equipment or piping was originally PWHT'd. Pressure vessels that were not originally PWHT'd may require additional engineering assessment. Thermal stress relief is especially important in the dilute HF with water corrosion zone as well as in the HF regeneration system. When thermal stress relief is performed, procedures for the treatment should be specified by a qualified corrosion specialist as defined in API 510 and API 570. See G.2.5.2 for further information regarding heat treatment after welding.

#### **6.3.2.6 Dissimilar Metal Welds (DMWs)**

DMWs in HF alkylation units are typically between carbon steel and Alloy 400. In this section, DMWs pertain to pressure-retaining welds. DMWs can create areas of high weld hardness or less corrosion-resistant chemistry where the materials meet, which makes them highly susceptible to cracking and/or localized corrosion. As such, dissimilar metal pressure-retaining welds should be avoided wherever practical. DMWs associated with weld overlays are addressed in 6.3.2.7.

For pressure-retaining DMWs, weld procedures and associated PWHT procedures that reduce cracking susceptibility in the weld fusion zone and HAZ on the carbon steel side of the weld shall be developed. A nickel filler (e.g. ERNi-1 butter layer) should be used for the first layer on the carbon steel side of the weld. This aids in avoiding localized corrosion and weld fusion zone hydrogen cracking at the carbon steel to weld interface. Owner-operators should test the weld chemistry when qualifying their DMW procedures. See G.2.6 for additional information.

DMWs in HF service shall also be identified, inspected, and tracked as part of the inspection program and shall be documented in the inspection records (e.g. inspection isometric drawings). DMWs in HF service shall be specifically called out in the inspection plan for on-stream and, where accessible, internal inspection for

potentially localized corrosion and cracking, as DMWs have a significantly higher susceptibility to this damage compared to other welds. This is especially true if they did not have a nickel butter layer or do not have documentation of the weld procedure and are in HF service.

### 6.3.2.7 Weld Overlays and Cladding

When there is a need for a more corrosion-resistant alloy layer on any section of a vessel, cladding or weld overlay are the preferred methods. Strip-lining shall not be used. Weld overlays and cladding of corrosion-resistant alloys over carbon steel should extend to beyond where HF is normally present or likely to be present in upset conditions. Weld and associated PWHT procedures that limit hardness in the weld fusion and HAZs on the carbon steel side of the weld should be applied. The requirement and recommendations regarding weld chemistry in 6.3.2.6 apply to weld overlays and cladding. API 582 contains information specific to Alloy 400 weld overlays and back-cladding.

For weld overlays, the nickel filler is more likely to result in low iron levels at the surface of the Alloy 400 weld and thus minimize corrosion of the overlay. Subsequent weld layers should match the chemistry of Alloy 400 (e.g. E/ERNiCu-7). In addition to the other elements required for a standard PMI, Alloy 400 weld overlay on carbon steel should have a maximum iron content of 3 wt % at the surface of the weld exposed to the process. Above this level, the corrosion resistance of the Alloy 400 drops significantly. Control of the weld rod composition and layering of the weld are both needed to control the iron content at the surface in contact with the process. Owner-operators should test the weld chemistry when qualifying their dissimilar weld overlay procedures. See G.2.6 for additional information.

### 6.3.2.8 Quality Control and Inspection of New and Repair Welds

Pressure-containing welds in new and repaired piping and pressure vessels in HF service shall be inspected per applicable codes. Specific attention shall be given to the identification and removal of slag inclusions and other flaws (e.g. porosity) that may lead to accelerated HF corrosion. In particular, inspection for slag inclusions shall use more stringent acceptance criteria than required by the applicable construction code. For example, the owner-operator may use the ASME B31.3 severe cyclic service acceptance criteria for slag inclusions in piping welds. Inspection of the internal vessel surface at the weld, parent metallurgy, and HAZ using wet magnetic particle testing (WMT) or wet fluorescent magnetic particle testing (WFMT) should be performed to identify any fabrication flaws that could initiate in-service corrosion or cracking. Additional NDE (such as radiography or ultrasonic examination) may be valuable to provide a baseline condition of the equipment and piping prior to being put in service and to help interpret vessel flaws and changes that occur between internal inspections. PMI should be conducted on both weld consumables and pressure boundary welds.

### 6.3.2.9 Repair Welding of Carbon Steel Exposed to HF

Carbon steel that has been exposed to HF may become saturated with atomic hydrogen during service due to the corrosion reaction. For this reason, applying a hydrogen bake-out treatment and preheating prior to any repair welding should be performed to improve weld quality. Failure to perform a hydrogen bake-out treatment can result in a hydrogen-charged weld that is susceptible to cracking.

Thermal decomposition of iron fluoride may result from scale remaining on the internal surfaces of equipment and piping in the area of the bake out, PWHT, or welding. This can lead to personnel exposure to fluorine fumes or contamination to a weld area. To prevent contamination of the weld and base metal, the actual surfaces to be welded shall be prepared by grinding or an equivalent method to a bare metal surface condition. Removal of scale in the PWHT or bake out areas may also be considered, based on owner/operator experience. See (Annex H or Section 5)

All PWHT of repair welds shall be performed per 6.3.2.4 to control hardness and susceptibility to cracking. Repair welds performed on steels previously exposed to HF should be subjected to the appropriate NDE as specified by the owner-operator. Radiography, WMT or WFMT, and/or ultrasonic examination should be applied, based on the type and depth of repair. Repair welding of carbon steel should be performed with slag control as described in 6.3.2.3. Delayed hydrogen cracking of welds can occur on repair welds in HF service. Inspection for delayed hydrogen cracking should be performed either after PWHT or no earlier than 24 hours after weld completion if PWHT is not performed. Repairs or welded alterations to pressure vessels, piping, and heat exchangers shall meet the requirements of the most recent edition of API 510, API 570, ASME PCC-2, or other equivalent industry standards.

#### **6.3.2.10 In-service Welding**

Vessels and piping in HF service should not be welded or hot tapped while in service due to the potential for in-service cracking and corrosion. These activities could potentially expose personnel to HF.

If in-service welding or hot tapping is deemed necessary, a thorough technical and metallurgical review, including a risk analysis process, shall be conducted and documented with the appropriate HF alkylation personnel and other technical SMEs. The plan shall be approved by the appropriate level of authority prior to welding. Where approved, welding shall be performed in accordance with the current edition of API 510, API 570, API 577, API 582, ASME PCC-2, API 2201, NACE SP0472, or equivalent industry standards.

#### **6.3.2.11 Bending**

The bending of metals can introduce areas of high hardness and residual stresses, making the bends susceptible to corrosion and/or cracking. This applies to both heat exchanger tubes and nonstandard piping elbows made by cold bending or induction heating straight tube or pipe. These types of carbon steel elbows and heat exchanger tube U-bends in HF service should be stress relieved regardless of the amount of cold work and performed per requirements of 6.3.2.4. For Alloy 400, see 6.3.2.5. The furnace method of heat treating is believed by some owner-operators to be more effective than electrical resistance heat treating for reducing the potential for localized damage. HF-resistant alloy heat exchanger tubes can be bent using electrical resistance heating. This can reduce cold work stresses and remove the need for solution annealing.

#### **6.3.2.12 Temporary Repairs**

A documented management system (management of change or equivalent process) shall be in place, consistent with API 510 and API 570, which covers the installation, monitoring, inspection, maintenance, removal, and decontamination of temporary repairs installed in HF services.

Aspects that should be included in this management system include:

- a) HF-specific design requirements as well as those included in ASME PCC-2, Article 306;
- b) appropriate level of management authorization before the repairs are performed;
- c) verification that the repair matches its design prior to installation;
- d) documentation to track the temporary repair in service;
- e) management of change (or equivalent process) when any applicable temporary repair is repumped with sealing fluid so that the risks involved with repumping are understood and mitigated;
- f) the initial volume of sealant, the volume of sealant for repumps, and the maximum number of repumps;
- g) acid detecting paint applied to all repair clamps (see 6.5.13); and,
- h) removal of temporary repairs.

Refer to API 510 and API 570 for further information on temporary repairs.

The materials and fabrication practices used in temporary repairs that could be exposed to HF shall follow the materials requirements of this document. Polymeric wraps should not be used in HF service. The potential exception to this is as a structural reinforcement for external pipe thinning or external mechanical damage (e.g. dent, gouge) in non-leak situations until a properly designed mitigation can be installed. Where polymeric wraps are used, they shall meet the requirements of the ASME PCC-2, Article 400 series as applicable. The polymeric wrap should be confirmed and documented to be resistant to HF.

Sealant for temporary repairs should be confirmed and documented as HF-resistant. Where there is the potential for exposure to HF, the temporary repair shall be designed to maintain the equipment and piping integrity in the event that the material under the repair fails (e.g. designed for full line separation). For example, bolts in flanges that are partially or completely enclosed with clamps can be subject to hydrogen embrittlement cracking and potential failure. Clamps and wraps shall be supplied with engineering design calculations. The need for additional support for the weight of the clamp should be evaluated during engineering design.

Personnel who install temporary repairs in HF service should be trained on the use of leak-clamping and sealant-pumping equipment, including criteria for change-out of bolts exposed to HF before the repair is installed. Temporary repair installation procedures should include the replacement of all bolts that have been exposed to HF. Due to the potential for exposure to HF during installation, personnel who install temporary repairs in HF service should be trained on the use of appropriate PPE. All temporary repairs in HF service should be monitored on a scheduled basis by the appropriate group (e.g. operator rounds and scheduled inspections) and shall be removed at the next turnaround. A designated group should maintain a list of all temporary repairs in HF service. This designated group should be identified in the procedure. Section 6.4.6 contains further requirements for temporary repairs. Section 6.5.4.3.6 contains further requirements for hot bolting.

When designing temporary repairs for HF service, the potential separation/axial load of a line shall be taken into account in the design of any clamp in HF service and shall not rely on the adhesion of the sealant or surface friction to be the only method of preventing pipe separation. Temporary repairs of flanges connections in HF service that cannot be addressed by hot bolting should include a strongback as part of the design to hold the flanges together if the bolting fails.

### **6.3.2.13 Hot Bolting**

Hot (in-service) bolting is often considered when addressing flange leaks as a first attempt. Refer to 6.5.4.3.6 for additional information on hot bolting.

## **6.4 Inspection Programs**

### **6.4.1 Certification and Training of Inspectors and Mechanical Integrity Support Personnel**

Inspectors and mechanical integrity support personnel responsible for the HF alkylation unit shall be knowledgeable on Section 6 and Annex G and Annex H of this document. Inspectors shall be certified per API 510, API 570, and API 653 or other equivalent industry standards depending upon the equipment types for which they are responsible. NDE technicians shall be certified per applicable standards. Inspection of equipment and piping covered by this document shall be under the direction of an inspector and performed by qualified and certified personnel.

### **6.4.2 Inspection Planning**

#### **6.4.2.1 General**

The owner-operator shall develop comprehensive inspection plans for equipment and piping commissioned into HF service. These inspection plans shall be in accordance with API 510 and API 570.

NOTE Some inspection recommendations in this section are more stringent than those defined in the inspection codes.

Inspection plan development shall take into account the conditions affecting the performance of materials in HF service as indicated in Section 6 and Annex G. The information in Annex G should be used to help determine condition monitoring location (CML) placement and inspection intervals in HF service corrosion zones.

A corrosion specialist (as defined in 3.1.15) familiar with the damage mechanisms associated with HF service as indicated in this document shall be consulted for the development of inspection plans. The corrosion specialist should review and approve the individual inspection plans of all applicable components to assure the inspections have the highest probability of finding the damage mechanisms described in this document.

#### 6.4.2.2 Inspection Planning Specific to Pressure Vessels

Areas to be inspected in pressure vessels and heat exchangers should specifically include previous repair or alteration welds and portions of vessels that previously exhibited visible blistering, cracking, or significant corrosion. See 6.2.2.2 for additional information regarding inspection planning for cracking and blistering of carbon steel pressure vessels.

The internal inspection of the HF storage drum, or vessels used to store HF during turnarounds, is generally conducted outside of turnaround. Outages of acid deinventory vessels for inspection outside of turnaround should be risk-assessed (see 9.3). Maintenance and inspection activities performed on HF storage vessels outside of turnaround should be planned and executed to minimize their duration if the absence of the vessel would impact a unit mitigation plan/system.

#### 6.4.2.3 Inspection Planning Specific to Piping

##### Piping Localized Corrosion Inspection

Piping circuits in **some** phase change and dilute HF corrosion zones can be susceptible to localized corrosion along the length of the main piping. Refer to 6.5.3.2 for localized corrosion in phase change and dilute HF corrosion deadlegs. This localized corrosion can be subject to significant changes to either corrosion rates or location along the piping when a change in operation occurs (refer to paragraph 6.1.5 regarding IOWs.)

***All phase change and dilute HF corrosion circuits should be evaluated by a corrosion specialist to identify exposure to heating and cooling/condensing phase changes that can cause localized corrosion.***

These **identified** circuits should therefore be subject to a 100% volumetric thickness monitoring (e.g. ultrasonic testing (UT) scanning and profile radiography) program along the entire length of the piping to monitor for potential localized corrosion as spot UT measurements can miss highly localized corrosion (refer to 6.4.3.2 regarding onstream inspection for details.)

After the initial inspection, the CMLs for each piping circuit should include CMLs placed on any areas that have lower wall thicknesses and/or higher corrosion rates. These localized areas should be inspected at a maximum interval of half remaining life or 5 years whichever is less.

Regardless of the initial inspection findings, the entire 100% volumetric thickness monitoring program should be repeated at a maximum of 5 years to detect potential change in corrosion rates or location of lower wall thicknesses.

After a minimum of two complete 100% volumetric thickness monitoring programs for a given piping circuit with minimal localized corrosion detected, the owner/user *may* reduce the scope of inspection if a rigorous and compliant IOW monitoring program (refer to 6.1.5 and Annex G, G.5) is in place to detect operational



changes that can impact phase change or dilute HF corrosion. Regardless, dead-legs should be subject to ongoing repeat volumetric thickness monitoring for 100% of the length of piping (refer to 6.5.3.2.)

These requirements do not apply if the piping circuit has been upgraded to Alloy 400 where uniform corrosion CML coverage should be used.

See 6.5.4.1.3 for information on the inspection of ASTM A105 flanges for localized, preferential corrosion.

#### 6.4.2.3.1 Piping RE Inspection

Piping circuits in HF service that include high-RE components, mixed-RE components (high-RE and low-RE components in the same circuit), or components of unknown RE can have non-uniform corrosion rates, particularly in the phase change HF and dilute HF with water corrosion zones. Some owner-operators have reported having a significantly different corrosion rate between mixed-RE components in all corrosion zones. Relying on a limited number of representative CMLs to monitor corrosion rates in high-RE or mixed-RE circuits may not be sufficient to detect accelerated corrosion of individual components. Carbon steel piping components that do not meet recommended limits for low-RE content or where RE content is unknown should be monitored for corrosion more frequently and with appropriate techniques due to the higher potential for preferential corrosion. These RE inspection requirements should also be applied to welds, as well as the base metal. Refer to 6.2.2.1 for additional information regarding considerations for RE in carbon steel.

##### Piping Component InspectionA. General

Special emphasis inspection programs to evaluate the condition of all individual components and welds in piping circuits have been conducted by several owner-operators. Most of these programs have identified locations with significant corrosion rate variations and localized thinning of components, welds, and weld HAZs requiring repairs or replacement. Refer to 6.2.2.1 for additional information regarding considerations for RE in carbon steel.

##### B. Establishing the Initial Individual Component Inspection Program

A special emphasis inspection program shall be developed and implemented at least once to inspect all individual carbon steel piping components and welds to identify areas of accelerated corrosion. Aspects of the program shall include:

- i) the program shall be completed in all HF corrosion zones identified in Annex G,
- j) the program shall be prioritized by corrosion zone with phase change HF and dilute HF in water corrosion zones given priority based on known corrosion potential. After the initial inspection of all carbon steel components, the results should be used to adjust the ongoing inspection and repair plans and evaluate the frequency and/or need to inspect each component.

This special emphasis inspection program shall determine the wall thickness of individual components and welds throughout the unit. The program typically consists of:

- 1) identification of all the welds (and thus piping components);
- k) the use of radiographic and ultrasonic techniques to determine the thickness of the components on each side of the weld as well as the thickness at the weld.
- l) Some owner-operators have included PMI of individual components for RE as part of their special emphasis inspection program.

##### C. Expectations of data management

After the initial inspection of all carbon steel components, the results should be used to adjust the ongoing inspection and repair plans and evaluate the frequency and/or need to inspect each component.

The CMLs for each piping circuit should include CMLs placed on components that have lower wall thicknesses and/or higher corrosion rates.

Successive inspection programs can be implemented to track the findings, to address the impact of operational changes, or to address industry learnings.

Risk-based inspection can be used to evaluate inspection intervals.

#### D. Sustaining the Individual Component Inspection Program

The SE program may require a revalidation (or update) at some point. Guidance of when to revalidate the SE program includes, but is not limited to:

1. When process conditions have changed since the last overall inspection
  - a. IOWs have been triggered
  - b. MOC was initiated
  - c. Process rates have been increased
2. Industry has identified areas of concern with new information to reinspect

Additionally, when the initial program did not adequately establish CMLs, inspection monitoring, etc., then the SE inspection program may be revalidated at an interval as established by the Owner-User's program (e.g., not to exceed 10 years, or 2 turnaround cycles).

#### 6.4.2.4 Risk-Based Inspection (RBI)

RBI, as defined and described in API 580, is an optional technique for inspection planning that allows the owner-operator to determine inspection intervals and the type/extent of future inspection and examinations based on risk analysis. RBI as accepted in API 510, API 570, and API 653 may be used in HF alkylation inspection planning with the following limitations.

- m) RBI shall not be used to increase any inspection intervals for piping, piping components, and/or pressure vessels in the phase change HF and dilute HF in water corrosion zones above those required in this document. RBI may extend inspection intervals for Alloy 400 or C276, for Phase Change and Dilute HF up to 10 years with supporting inspection data
- n) RBI shall not be used to extend the external VT intervals of piping, piping components, and/or pressure vessels in any corrosion zones above those required in this document.
- o) RBI may extend the maximum on-stream inspection intervals of piping (and piping components) operating in the rich, fresh, and fractionator corrosion zones up to a maximum of 10 years, where also justified by inspection and operational data.
- p) RBI may extend the maximum on-stream inspection intervals for pressure vessels operating in the rich, fresh, and fractionator corrosion zones up to a maximum of 15 years, where also justified by inspection and operational data.
- q) RBI may extend the maximum internal inspection interval for pressure vessels operating in the rich, fresh, and fractionator corrosion zones up to a maximum of two turnaround intervals, where also justified by inspection and operational data.
- r) Consideration regarding sludge remaining in the unit – see 5.3.2.2.6.2

All RBI assessments should include the systematic evaluation of probability and consequence in accordance with API 580. Adjusting the inspection interval should only be done after a thorough data review because damage rates can change due to subtle changes in many different process variables (e.g. those parameters



shown in Table G.1). This section does not preclude the requirement for the implementation of requirements in 6.4.3.

#### **6.4.2.5 Vapor Pressure Suppression Catalyst Additives—Effect on Inspection Planning**

Vapor pressure suppression catalyst additives mixed with HF, aka MHF, can have different corrosion effects in some parts of the unit (e.g. in the HF regeneration tower, in the acid off-loading line) compared to units not using MHF. The impact of the additive should be reviewed with the licensor and a corrosion specialist. These corrosion effects should be addressed in the inspection program, including the injection point area.

### **6.4.3 Inspection Task Types and Intervals**

#### **6.4.3.1 External VT**

Each pressure vessel and piping circuit in HF service shall receive an external VT (per API 510 and API 570) at an interval that does not exceed 5 years. RBI shall not be used to extend external VT intervals beyond 5 years in HF service.

CUI is a particular concern in HF alkylation units because much of the equipment and piping operates at temperatures at risk for CUI and much of the process fluids in HF alkylation units have higher consequences if released. Insulated piping, pressure vessels, and support rings should be reviewed for CUI potential and to establish recommendations for CUI examinations. RBI can be useful in prioritizing the CUI risk of fixed equipment and piping. See API 510, API 570, and API 583 for more information on CUI and corrosion under fireproofing (CUF).

#### **6.4.3.2 On-stream Inspection**

Owner-operator inspection programs shall include provisions for obtaining on-stream thickness measurements (e.g. ultrasonic, radiography, etc.) for pressure vessels, storage tanks, and piping systems in HF service. The interval for these inspections shall comply with the limits of API 510, API 570, and API 653 or other equivalent industry standards and with the restrictions defined within this document.

Without the application of RBI, unless process changes, upsets, or other episodic events indicate that the interval should be shorter, the following requirements apply to on-stream inspection intervals:

- s) maximum of 5 years shall be used for piping in all HF corrosion zones; and,
- t) maximum of 5 years shall be used for pressure vessels in phase change HF and dilute HF in water corrosion zones; and
- u) maximum of 10 years shall be used for pressure vessels in the other HF corrosion zones.

The RBI extension of intervals is limited per the requirements of 6.4.2.4.

For carbon steel pressure vessels, exchangers, and piping components with either unknown or high-RE material, the owner-operator should consider shorter maximum initial inspection intervals than indicated above (or allowed by code) until consistent thickness measurements for corrosion rate data have been established. An increase or decrease of on-stream inspection intervals within the limits of API 510 and API 570, or other equivalent industry standards, shall be based on owner-operator data. Due to many variables affecting damage rates in HF alkylation units, any extension of on-stream inspection intervals shall be implemented only after the data has been thoroughly reviewed. A corrosion specialist should be consulted when reviewing the damage rates and adjusting the on-stream inspection interval. To satisfy the requirements for on-stream inspections per API 510 and API 570 (see sections on CMLs), a representative number of thickness measurements shall be established on each vessel and piping circuit in HF service. These measurements are intended to establish damage rates. The number and location of thickness measurements shall, in part, be based on results from previous inspections and unit operating history. However, a thorough

understanding of the different types of corrosion found in each HF corrosion zone as well as the effect of carbon steel RE content on corrosion rates and damage types is instrumental in CML placement. A corrosion specialist shall evaluate and adjust CMLs in HF service, as warranted, to identify the localized HF alkylation specific damage mechanisms referenced in Annex G.

In addition, a thorough understanding of the different types of corrosion found in each HF corrosion zone with the impact of operating changes, as well as the results of the RE inspection program per 6.4.2.3.2, are instrumental in CML placement.

Volumetric methods of thickness monitoring [e.g. ultrasonic testing (UT) scanning and profile radiography] as described in both API 510 and API 570 should be used for HF services, especially where the corrosion specialist determines that localized corrosion may occur. Spot UT measurements can miss highly localized corrosion.

On-stream inspection in lieu of internal inspection shall be prohibited in all HF-service corrosion zones. [Refer to API 510, Section 6.5.2.1(b)(6) for further information.]

#### 6.4.3.2.1 Piping On-stream Inspection

Carbon steel piping circuits in the phase change and dilute HF corrosion zone *should/shall* be subject to volumetric thickness monitoring using ultrasonic (UT) scanning and/or profile radiography along 100% of the length of circuit (refer to 6.4.2.3.2) and should/shall include:

- 1 Where piping size allows, *single* plane profile radiography preferred or,
- 2 A continuous automated ultrasonic (AUT) along *1 quadrant along piping, fittings, and welds* .
- 3 Close spaced (**3 to 12 in.**) spot ultrasonic (UT) along *1 quadrant along piping, fittings, and welds* .  
**The maximum spacing should be determined by a review by a corrosion specialist based on the degree of localized corrosion expected for the piping circuit.**
- 4 Horizontal runs of piping should/shall include top and bottom quadrant monitoring.
- 5 Long-range ultrasonic techniques have been used by some owner-operators for screening to identify indications of localized corrosion on individual pipe components and/or preferential weld corrosion.

Locations where lower wall thicknesses or higher corrosion rates are identified should/shall include placement of recorded CMLs at these locations.

In addition, a thorough understanding of the different types of corrosion found in each HF corrosion zone with the impact of operating changes, as well as the results of the RE inspection program per 6.4.2.3.2, are instrumental in CML placement.

On-stream inspection in lieu of internal inspection shall be prohibited in all HF-service corrosion zones unless the size or configuration makes vessel entry for internal inspection physically impossible. [API 510 6.5.2.1 a)

#### 6.4.3.3 Internal Inspection of Pressure Vessels

For pressure vessels or circuits thereof, in the phase change HF and dilute HF in water corrosion zones, an internal VT shall be conducted at every turnaround. For equipment in all other HF corrosion zones, each piece of equipment shall receive an internal VT at an interval not to exceed 10 years. A change of the internal

inspection intervals within the limits of API 510 shall be based on owner-operator history and corrosion data analysis.

When possible and practical, internal VTs on risers and acid standpipes should be performed on the same frequency as vessels.

For pressure vessels, the internal inspection interval may be extended using RBI on equipment only in the rich, fresh, and fractionator corrosion zones. Extending the inspection interval should be done only after thoroughly reviewing data and IOW history (including exceedances and/or stability of operations). Once a reliable corrosion history has been established, each piece of equipment in these three corrosion zones should receive an internal VT at an interval not to exceed one-half its estimated remaining life based on corrosion rate or two turnaround cycles (utilizing RBI), whichever is less.

If welded repairs or modifications to the pressure boundary are performed, the next internal inspection shall be during the next turnaround regardless of corrosion zone.

#### 6.4.3.4 Maximum Inspection Interval Summary

Table 3 is provided as an overview for maximum inspection interval requirements of piping (piping components) and pressure vessels without the application of RBI. The owner-operator shall be responsible for utilizing the document text (e.g. the impact of IOWs, use of RBI) and requirements to establish their specific inspection interval table, within the limits provided in the table.

**Table 3—Piping and Pressure Vessel Maximum Inspection Intervals – Time Based**

Corrosion Zone	Piping and Piping Components <sup>1</sup>		Pressure Vessels <sup>2</sup>		
	External	Thickness	External	Internal	Thickness
Phase change HF and dilute HF in water	5 years max	5 years max	5 years max	Not to exceed turnaround interval	5 years max
Rich, fresh, and fractionation	5 years max	5 years max <sup>3</sup>	5 years max	10 years max <sup>4</sup>	10 years max <sup>5</sup>
NOTE 1 Special emphasis inspections on 100 % components and weldments for low RE are not considered in this table.					
NOTE 2 On-stream in lieu of an internal inspection for pressure vessels is not allowed. See 6.4.3.2.					

Table 4 is provided as an overview for maximum inspection interval requirements of piping (piping components) and pressure vessels, with the application of RBI

**Table 4—Piping and Pressure Vessel Maximum Inspection Intervals – RBI**

Corrosion Zone	Piping and Piping Components		Pressure Vessels		
	External	Thickness	External	Internal	Thickness
Note 1: Phase change HF and dilute HF in water – carbon steel	5 years max	5 years max	5 years max	Not to exceed turnaround interval	5 years max
Notes 2 & 3: Phase	5 years max	15 years Max	5 years max	Two turna-	15 years

change HF and dilute HF in water – Alloy 400, C276				ound cy- cles	max
Rich, fresh, and fraction- ation	5 years max	5 years max	5 years max	10 years max	10 years max
<p>NOTE 1 RBI can be used in these cases to extend the fixed interval, with a maximum interval not to exceed 10 years.</p> <p>NOTE 2 RBI can be used in these cases to extend the fixed interval, with a maximum interval not to exceed two turnarounds.</p> <p>NOTE 3 RBI can be used in these cases to extend the fixed interval, with a maximum interval not to exceed 15 years.</p>					

#### 6.4.3.5 Other Inspection Intervals

Other specific equipment inspection intervals for HF service are set within this document. These include, but are not limited to, the following:

- a) flange faces—see 6.5.4.1.3,
- b) pressure relieving devices—see 6.5.9,
- c) storage tanks—see 6.5.12,
- d) small-bore piping—section 6.5.3.1,
- e) pumps—6.5.7,
- f) fired heaters—6.5.10.

#### 6.4.3.6 Hydrogen Damage Detection During Internal Inspection

A corrosion specialist shall evaluate the susceptibility of each pressure vessel in HF service being subject to environmental cracking and/or blistering damage, including a review of the impact of process changes to hydrogen charging. Further information regarding these damage mechanisms and inspection techniques can be found in Annex G, Annex H, and in API 571.

Environmental cracking can be the result of HSC-HF, HIC, or SOHIC (see 6.2.2.2). HSC-HF, HIC, and SOHIC damage shall be evaluated for inclusion into the inspection plan for the identified equipment. Additionally, when blisters are found, the inspection should be expanded to verify the presence, or lack thereof, of HIC/SOHIC cracking associated with the blisters. This should include a review of the susceptibility and historical inspections. Further information regarding these damage mechanisms can be found in Annex G and API 571.

HSC-HF is a form of environmental cracking that after being in HF service atomic hydrogen generated by corrosion, can embrittle localized zones of high hardness in the weld metal and HAZ. For this reason, the inspection of vessels or portions of vessels subject to environmental cracking that have not received effective PWHT shall be a part of the inspection plan. In this case, “not receiving effective PWHT” refers to equipment that lacks documented evidence of PWHT at 1175 °F ± 25 °F with adequate thermocouples and time at temperature. In general, when inspecting for HSC-HF:

- a) the areas of highest concern are pressure-retaining welds and internal attachment welds to the pressure boundary;
- b) surface-breaking cracks can be found by penetrant testing (PT), magnetic particle testing (MT), or WFMT. Of these methods, WFMT is the most common method used by refiners to locate this type of surface-breaking cracks;
- c) angle beam UT [shear wave ultrasonic testing (SWUT) or phased array ultrasonic testing (PAUT)] may also be useful for finding or determining the depth of cracks;
- d) alternating current field measurement (ACFM) can be used in lieu of WFMT for crack detection; however, it is more highly technician dependent.

In addition to HSC-HF, both HIC and SOHIC occurring from atomic hydrogen generation due to corrosion can result in internal cracking damage. Inspection for HIC and SOHIC follows similar approaches, which can include:

- e) HIC may reside at any location within the base metal where there are laminations or inclusions;
- f) SOHIC inspection typically focuses near weld seams and nozzles;
- g) visual techniques should be used to detect surface blistering that will indicate the potential for HIC or SOHIC adjacent to welds;
- h) automated UT can be used to identify sub-surface blistering and laminations;
- i) angle beam UT (manual or automated) or PAUT can be used for detecting and sizing cracks.

#### 6.4.3.7 Iron Fluoride Scale and Inspection

A layer of iron fluoride scale normally forms on the surfaces of carbon steel equipment in HF service. Thicker iron fluoride scales form as a result of higher corrosion exposures and can be used as an indication of surfaces that may need to be inspected more fully. The owner-operator shall establish the extent to which the internal surfaces of vessels and heat exchangers are to be cleaned of this scale for inspection purposes in accordance with the inspection plan.

In areas where damage is suspected or of concern, the scale should be removed for closer inspection. Heavy scale can mask deterioration of the underlying surface and prevent proper identification of the extent of damage. Many owner-operators have found that complete cleaning of the inside surfaces of the entire vessel to "bare metal" for the purpose of an internal inspection is not always necessary. Removal of scale does not necessarily reduce equipment life. On the other hand, removal of loose scale can increase equipment life by reducing the potential for under-deposit corrosion.

As a warning, when using inspection techniques that do not include A-scan capability, iron fluoride scale on inner process surfaces should be accounted for with the inspection technique and assessment of data.

#### 6.4.4 Unexpected Inspection Findings

Whenever an unexpected inspection finding occurs in HF service equipment and piping, efforts should be undertaken to determine the causes and appropriate monitoring and/or mitigation measures. The results of these efforts to determine the cause should be documented as part of the inspection findings. Accordingly, the inspection plans should be adjusted for all potentially affected equipment and piping systems. As an example of monitoring and/or mitigation measures, the owner-operator may evaluate changing the equipment or piping design, upgrading the metallurgy, reviewing and potentially changing or adding IOWs, updating the CCD, reviewing and/or changing inspection plans, and/or changing operating procedures. See API 585 for additional information regarding this topic.

## **6.4.5 Upgrading Metallurgy Due to Inspection Interval**

For equipment and piping in HF service with shortened inspection intervals, the owner-operator should evaluate upgrading the equipment and piping metallurgy (e.g. switching from carbon steel to Alloy 400) to extend the inspection interval to a more reasonable time frame.

## **6.4.6 Temporary Equipment**

Temporary equipment used during maintenance periods, operations, and process troubleshooting should be designed and constructed of materials suitable for HF service such as those provided in this document for the intended application and duration. Examples of temporary equipment include piping, tubing, blinds, hoses for neutralizing and/or draining equipment, heat exchangers, and pressure gauges.

For temporary equipment used for an extended period or reused, a program should exist to check the integrity of the equipment at appropriate intervals. Additionally, this equipment can be prone to SCC from repeated exposure to acid and air such as those constructed of Alloy 400 and copper. Temporary equipment in HF service shall be managed per 4.1.3 and 5.3.2.2.5 as applicable.

## **6.5 HF Service Equipment and Components**

### **6.5.1 Fireproofing and Insulation**

Fireproofing and insulation systems should be inspected and maintained using API 583 or other equivalent standards. Fireproofing of vessel and piping supports, critical valves, instruments, and electrical runs should be selected, designed, applied, and maintained as outlined in API 2218 or other equivalent standards. Insulation over flanges in HF service shall not be applied. Insulating over flanges can cover the gaps and flange perimeters and prevent monitoring for signs of leaks during operator rounds. Where fireproofing is used on valve flanges, the risk of covering the gap between the flanges against the risk of an undetected leak and potential CUI corrosion to the bolts should be considered.

### **6.5.2 Heat Tracing**

Where heat tracing is needed in HF services, either electric tracing with temperature control or tempered/jacketed steam tracing should be used. The goal is to provide heat but not overheat the process stream. Overheating is a cause of accelerated localized corrosion. Steam tracing should only be installed in HF service after consultation with a corrosion specialist. Where unjacketed steam tracing is used, standoffs shall be incorporated to avoid direct contact of tracing elements with process equipment and piping. If tracing is used to prevent condensation in dead-legs and low flow areas in HF service due to excessive corrosion rates, the tracing should be operated so the pipe wall temperature remains above the process temperature to avoid condensation and related corrosion.

### **6.5.3 Piping and Piping Components**

#### **6.5.3.1 Small-bore Piping and Threaded Connections**

Small-bore piping systems can have a higher vulnerability than most other piping systems to some deterioration mechanisms. Fatigue of threaded joints and other points of stress, as well as corrosion product accumulation in inactive branch connections, are more likely to occur in small-bore piping. Crevice corrosion can occur in both socket-welded and threaded connections. The small-bore piping mechanical integrity program outlined in API 570 and API 574 should be followed. Use of Class 3000 couplings and use of Schedule 160 and heavier walled piping are both common in order to increase strength and/or corrosion allowance in small-bore piping systems. The vibration of any piping components should be noted during operator rounds and reported to inspection or engineering for follow-up. Unions should not be used because of the susceptibility to vibration and other mechanical issues that can lead to leaks. Small-bore piping branched connections should be gusseted in two planes to reduce the chance of failure in vibrating service.



Piping systems that are too small to be butt-welded may be threaded or socket welded at the discretion of the owner-operator.

For the dilute HF in water corrosion zone, the metallurgy on both sides of threaded connections should be the same. Galvanic corrosion can be significant at these locations. If a dissimilar metal connection is necessary in this corrosion zone, it should be a flanged connection.

The majority of threaded piping in HF alkylation units is fabricated of carbon steel, and the impact of RE on threaded connections is the same as is experienced in other piping systems. Either PMI shall be used to determine the RE level of threaded piping components or threaded components shall be treated as being high RE and inspected accordingly based on corrosion zone and anticipated corrosion rates for high-RE components. If small-bore threaded carbon steel piping is seal welded, NACE SP0472 and ASME PCC-2, Article 203 shall be followed. When seal welding for threaded connections is used in vibratory service, all threads should be covered.

Threaded piping shall have a defined minimum thread engagement per ASME B1.20.1 or ASME B31.3. High-density PTFE tape should be used on threaded joints in HF service that are not seal welded.

Inspection programs should include NDE provisions to examine and determine the integrity of small-bore piping circuits on a frequency aligned with this section and API 570 considering their susceptibility to corrosion and fouling. Profile radiography should be used as the method of inspection per API 570 for small-bore piping. Inspection of small-bore piping should include looking for thread engagement and fouling in joints as well as thickness. A representative sampling of threaded joints and socket-welded joints based on corrosion potential shall be profile radiographed every 5 years to determine their condition, including thread engagement, and corrosion and fouling of joints. Where there are threaded connections that cannot be inspected by radiography, such as orifice taps and some instrumentation, disassembly of threaded connections is an alternative to radiography. The external VT should include seal-weld coverage of exposed threads in seal-welded joints.

#### 6.5.3.2 Piping Dead-legs

Sites shall have a documented system for the identification, inspection and management of all piping dead legs in HF acid service. A multi-disciplinary review team consisting of personnel from operations, inspection and mechanical integrity should be used to identify operational and corrosive dead legs. Dead legs shall be uniquely identified on inspection drawings and shall be inspected for localized corrosion and for fouling/scaling. Dead leg thickness data should be analyzed separately from the general piping circuit due to the potential for higher corrosion rates and differences in corrosion zones. Refer to API 570 6.6.2 for additional commentary on corrosion concerns associated with process dead legs. Refer to Annex G (3.5, 4.1 & 4.6.6) for additional information on dead leg corrosion mechanisms by corrosion zone/configuration.

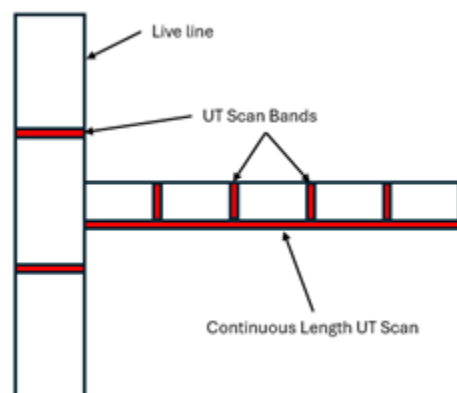
Due to the potential for accelerated localized corrosion in dead legs, the owner-operator shall have a documented dead leg corrosion inspection procedure that includes the required extent of inspection. Extensive inspection up to 100% of dead leg length should be considered with special emphasis given to low points where water or acid can accumulate (e.g. non-free draining dead legs, low point drains, bottom elbows on vertical sections). Two plane radiography is the preferred inspection method. When radiography is not practical due to pipe size/configuration, continuous ultrasonic scans along the length of the dead leg and circumferentially at defined intervals should be utilized (see below for examples).

Due to the potential for corrosion product buildup and plugging in carbon steel piping, the dead leg inspection program shall identify dead legs susceptible to fouling (i.e. PRV inlets/outlets). These dead legs shall be examined utilizing inspection techniques capable of identifying fouling (i.e. radiog-

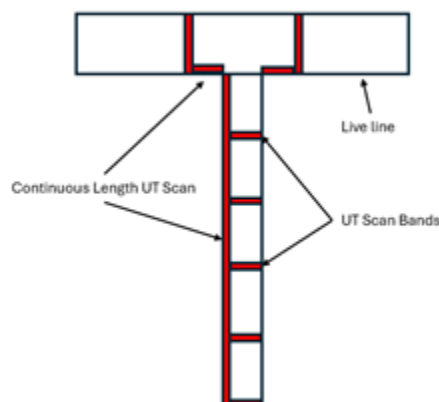


raphy, visual, thermography). Note that radiography can be utilized on larger pipe sizes for fouling inspections in conjunction with ultrasonic inspections for wall thickness.

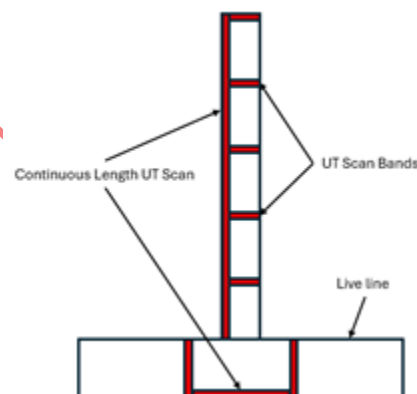
### Horizontal Dead Leg



### Vertical Dead Leg Extending Downward



### Vertical Dead Leg Extending Upward



During inspection, DLs should be checked for proper sloping to determine if they are free draining. Because sloping can change from the cold to hot state, this inspection should occur during normal unit operations. Thickness inspection scope for non-free draining DLs shall include the lowest points in the line. Additionally, sites should consider **correcting and verifying proper as installed** piping slope during the next planned maintenance event.

**Onstream thickness inspection intervals** of carbon steel dead legs in all HF acid corrosion zones shall not exceed 5 years. Dead legs with upgraded metallurgy (e.g. Alloy 400, C-276) shall be inspected at an interval not to exceed 10 years. Due to the potential impact of operational changes and/or lack of proper equipment drying/purging following operations and maintenance activities, RBI shall not be utilized to extend inspection intervals. Sites should consider shorter inspection intervals for carbon steel dead legs in the following scenarios:

- Operating temperature of the live line (or connected vessel) could result in a free second phase/dew point electrolytic corrosion condition
- Dead legs containing non-free draining horizontal sections

- Dead legs that cannot be confirmed to be water free after operations and maintenance activities. Note that corrosion in these circumstances can be extremely aggressive and may require inspection shortly after equipment startup

In addition to inspection, sites should implement multiple dead leg corrosion mitigation strategies including:

Regularly scheduled unit hazard assessments to evaluate existing dead legs for potential removal of non-essential dead legs.

Detailed operations procedures to dewater and nitrogen/helium purge dead legs following scheduled operations/maintenance activities per 5.3.2.2. Note: Due to the potential for extremely aggressive corrosion/cracking rates, inspection should not be considered a mitigation for insufficient purging of water and/or oxygen

Piping system design requirements that stress the importance of length minimization and proper free draining sloping for essential dead legs.

Metallurgy upgrade considerations:

Carbon Steel to Alloy 400 (Monel) for dead legs with a history of accelerated corrosion, plugging or an inability to sufficiently dewater following operations/maintenance activities

Alloy 400 to C-276, C-2000 or C-22 for dead legs with known exposure to oxygen with an inability to sufficiently purge following operations/maintenance activities. Note: although these alloys are more resistant to HF SCC than Alloy 400, they are still susceptible. Refer to Annex G.2.7.

#### **6.5.3.2 Piping Specification Breaks**

**6.5.4 Piping material specification breaks that are in HF service (e.g. carbon steel to Alloy 400) should be clearly identified on inspection isometric drawings. Piping materials specification breaks are typically shown on P&IDs, and may be used to update inspection isometric drawings and help plan general CML placement. CMLs should be located just upstream and downstream of each piping materials specification break in HF service. Flanged Joints**

#### **6.5.4.1 Flanges**

##### **6.5.4.1.1 Flange Corrosion Rates**

High corrosion rates have been experienced on some flanges, with the most concerning areas being on flange hubs as well as flange faces. Flange hub corrosion may be associated with both corrosion zone exposure and RE content. Some have observed that flange hub and flange crevice corrosion rates correlate. See further information in G.2.2.

##### **6.5.4.1.2 Flange Hubs**

ASTM A105 flange hubs have experienced accelerated corrosion on the hub portion of the forgings in some HF units. As such, these ASTM A105 flanges should be addressed in the inspection program, especially in the phase change HF and rich HF corrosion zones. Most owner-operators use profile radiography on piping sizes up to and including 6 in. and then use UT on the straight portion of the hub next to the weld on larger line sizes. Several owner-operators have carried out special emphasis programs on flange hubs and other forged components and have identified preferential corrosion.

## Flange Faces

Corrosion has been experienced on all types of acid service carbon steel flange faces. The gap and crevice between the inner ring of the flange gasket and the flange face is an inherent location for localized corrosion to occur. Over time, the corrosion of the flange face may extend into the gasket sealing area, potentially compromising the integrity of the seal leading to a flange leak.

The owner-operator shall have a documented flange inspection and QA/QC program. All flanges in acid service should be uniquely identified on the associated piping or vessel inspection drawing. Visual flange inspection is the preferred method to quantify corrosion, determine if sufficient gasket sealing surface remains, and recommend appropriate repairs as required. Tightly adherent scale, which can sometimes appear metallic, can mask corrosion. This scale shall be fully removed prior to visual flange face inspection to ensure any corrosion or mechanical damage can be properly assessed.

As an alternative to visual inspection of flange faces, advanced ultrasonic techniques such as PAUT may be used to evaluate flange condition potentially reducing the scope of visual inspection during turnarounds. Advanced ultrasonics shall be performed using qualified procedures and technicians who have validated their capability to identify this type of corrosion. A representative sampling of flanges shall be opened and visually inspected at the next opportunity to validate the results of the NDE method. Representative sampling should be no less than 10% of flanges inspected and should include the potential for both false positives and false negatives.

Several factors should be considered when determining flange face inspection intervals including acid classification and process circuit, documented flange corrosion/leak/repair history, calculated gasket sealing surface requirements, flange assembly practices, and gasket type used.

Regardless of acid classification, flanges without a documented inspection history that have not been assembled according to the flange assembly procedures listed in 6.5.4.4 should be inspected at an interval not to exceed the greater of 10 years or two (2) turnaround cycles. In this interval classification, findings from one flange inspection should not be applied to other flanges in the same process circuit regardless of similarity in size or age.

Inspection intervals for flanges with a documented inspection history that meet the assembly requirements of 6.5.4.4 can be determined with a documented RBI process but should not exceed the greater of 20 years or four (4) turnaround cycles. In this interval classification, flanges within the same process circuit can be considered a common corrosion environment such that inspection findings from one flange can be applied to other flanges.

If a flange has experienced any indication of a leak, the flange shall be disassembled, separated, cleaned of all scale, and visually inspected at the next opportunity, regardless of inspection history.

#### 6.5.4.2 Gaskets

For raised face type flanges, spiral-wound or metalcore gaskets are typically used in HF service. Gasket dimensions should be in accordance with ASME B16.20 unless customized and optimized gasket designs specific to HF service are used.

Spiral-wound gaskets in HF service shall have metal outer rings and either metal inner rings or alternate means to prevent inward buckling of the spiral windings. These rings prevent the spiral winding from collapsing under compressive stress. HF-resistant metal should be used for the inner rings. The inner ring may also be encapsulated with PTFE, expanded PTFE, and/or flexible graphite. Encapsulation of the inner ring serves two purposes. One is to fill the crevice between the flange faces, thus minimizing HF intrusion and flange face crevice corrosion. The other is to protect the inner ring from being exposed to HF, especially if fabricated of carbon steel. Bare metal carbon steel inner rings should not be used in HF-resistant alloy flanges (e.g. Alloy 400).

Some sites have had success with metalcore gaskets (grooved metal gaskets with covering layers) to improve the sealing of some difficult to seal flanges. Where these gaskets are applied for pipe flanges, they shall have a metal core and centering ring made of HF-resistant material and covering layers of graphite or other HF-resistant material. Metalcore gaskets may also include an expanded PTFE inner ring or a metal inner ring composed of HF-resistant material and encapsulated in PTFE, expanded PTFE, or flexible graphite.

If ring type joint (RTJ) gaskets are used in carbon steel flanges, the soft iron rings should meet ANSI/ASME specifications and have a maximum hardness of 90 HB. When ring grooves have become damaged, several owner-operators have had success by using conversion gaskets, either spiral-wound or metalcore, which seal on the face of the ring joint flange.

Gaskets for both PRVs and rupture disc holders in HF service shall be made of HF-resistant materials.

New gaskets shall be used for all bolted joint assembly and reassembly, including metal ring gaskets for RTJ flanges. Gaskets shall not be reused.

#### 6.5.4.3 Bolting

##### 6.5.4.3.1 B7 vs B7M Bolting

All HF-service studs should be ASTM A193, Grade B7 or B7M. All HF-service nuts should be ASTM A194, Grade 2H or 2HM. Hereafter, a "bolt" refers to the assembly of B7+2H ("B7 bolt") or B7M+2HM ("B7M bolt") components. There are pros and cons of either bolt assembly for HF service. The choice of the bolt should be based on achieving the in-service compressive stress for the type of flange gasket used, including whether the gasket design utilizes a PTFE, expanded PTFE, or flexible graphite-covered inner ring. The gasket manufacturer can provide in-service compressive stress targets.

B7M bolts have a lower hardness than B7 bolts and may therefore provide better resistance to cracking on exposure to HF in some circumstances, especially if a flange joint leaks and exposes the bolts to HF acid. Owner-operators may check a representative sample of B7M bolts to verify they meet specifications.

B7M bolts also have a lower yield strength and therefore have a higher potential of being work-hardened and yielding if overtightened. For some flange and gasket designs (e.g. heat exchangers), B7M bolts may not have sufficient yield strength to develop adequate initial gasket stress to allow for flange material relaxation and internal pressure. For these flanges, B7 bolts should be considered. B7 bolts have higher yield strength and reduced risk of bolt yield during tightening but are more susceptible to hydrogen stress cracking than a properly torqued B7M. However, B7 bolts can rotate or warp the flanges if overtightened, which increases the risk of a flange leak.

#### **6.5.4.3.2 Bolt and Gasket Stress**

ASME PCC-1 provides details and guidance for determining the target assembly bolt stress and bolt torque. Specialty HF service gaskets will typically require a different target bolt stress as compared with standard spiral-wound flange gaskets. The gasket manufacturer should be consulted to determine target gasket stress. The initial assembly bolt stress should be high enough to maintain minimum gasket compression stress during operations while accounting for gasket material relaxation and internal process pressures, yet low enough to not overtension the bolts or cause flange rotation (bolt or flange yielding). After initial flange bolt tightening, the bolt tension and gasket compressive stress decreases. This happens to the greatest extent within the first few days after initial bolt tightening. This is caused primarily by soft materials in the gasket (PTFE or flexible graphite filler or cover) slowly moving and conforming to the flange sealing surfaces. This slow movement of soft materials is referred to as relaxation or cold flow. It has been noted that the higher the initial gasket stress, the greater the relaxation, with up to a 25 % reduction of initial bolt and gasket stress possible. For flanges that have sufficient initial bolt and gasket stress to account for relaxation, a follow-up retorque is unnecessary. In rare cases where sufficient initial bolt tightening cannot be achieved, then a follow-up retorque of the bolts may be needed at 100 hours or longer after the initial bolt tightening.

#### **6.5.4.3.3 Lubrication for Bolting**

Lubrication should be applied to all bolting and nut-bearing surfaces before tightening when a torque-tightening method is used. Applying lubrication allows a more predictable k-factor (also referred to as nut factor or friction factor) for achieving the target bolt and gasket stress. Lubricants should not contain any material that will react with HF (e.g. silicone). See 6.2.4.1 for more information.

#### **6.5.4.3.4 New vs Reused Bolting**

For flanged joint reassembly in HF services, when using the torque method of controlled bolting, the reuse of studs can significantly reduce accuracy and the resulting stud loads. For this reason, new bolting (nuts and bolts) shall be used for all bolted joint reassembly in HF services if a torque-tightening method is used. If a bolt tension method is used, and the bolts show no indications of HF exposure or corrosion, then bolting hardware may be reused if approved by the owner-operator.

#### **6.5.4.3.5 Bolting Exposed to HF**

All bolts that have been exposed to HF vapors and have indications of corrosion (including scale or crystal precipitation on the bolts) shall be replaced. This is due to their susceptibility to hydrogen embrittlement cracking. Bolts that have indications of corrosion shall not be re-tightened to attempt to stop a leak. See 6.5.4.3.6 for in-service bolt replacement. Flange covers may hinder the dissipation of the released HF and can therefore exacerbate corrosion and cracking of the underlying flange and bolting. For flanges that show evidence of leakage (such as acid detecting paint changing color) but the bolts have no indications of corrosion, some owner-operators perform a risk assessment to enable bolt retightening in an attempt to stop a suspected leak. Those flanges that are re-tightened shall have the surface neutralized, the acid detecting paint restored, and ongoing monitoring to verify no leakage.

#### **6.5.4.3.6 Hot Bolting**

Special procedures and caution should be followed when replacing bolts on flanges that are in service and under pressure, referred to as "hot bolting." Refer to ASME PCC-2, Article 311 for additional guidance and precautions for hot bolting of flanges. Clamps or strongbacks across the flanged joint may be considered as an additional precaution to maintain sufficient gasket compression during hot bolting of flanges or as a temporary repair until bolts can be replaced.

#### 6.5.4.4 Flange Assembly Procedures

A comprehensive bolting and gasketing management program shall be in place that covers specific issues pertaining to the bolted joint assembly for HF alkylation units. Elements that should be included in the program include the following.

- a) All flanged joints in HF service use controlled torquing or tensioning in accordance with ASME PCC-1.
- b) Flanged joints that do not have sufficient initial bolt stress (i.e. some heat exchanger body flange joints), to account for relaxation and process pressure, will have a retorque applied (during start-up or at least 100 hours after initial bolt tightening).
- c) Flange mating surfaces are carefully cleaned and dried before being inspected and assembled, as rust is rapidly attacked by HF and other residual debris can result in a flange leak.
- d) Careful inspection of flange gasket surfaces for proper condition (flange face corrosion within acceptable limits, no scale buildup, and no gasket remnants) after cleaning.
- e) Machining gasket surfaces to the proper roughness per ASME B16.5, or other applicable standard, if repairs are needed.
- f) The use of specified gaskets, specifically including the type and materials that will be used in HF services, including specialty gaskets where needed.
- g) The use of specified bolts (e.g. B7 or B7M with 2H or 2HM nuts).
- h) Correct lubrication of bolts, nuts, and flange bearing surfaces, including avoiding getting lubricating material on the gasket surface of the flange face (lubricant on the gasket surface can react with HF and lead to flange leakage).
- i) Proper flange alignment.
- j) Achieving uniform compression of the gasket.
- k) Appropriate flanged joint assembly training for all personnel that will be assembling flanged joints in HF service (see ASME PCC-1, Appendix A).

QA/QC procedures shall be in effect to verify that all joints are leak-free before the reintroduction of process fluids. These procedures should include the following.

- a) Contractor QA/QC steps before turning the flanged joint over to the owner-operator.
- b) Owner-operator QA/QC steps before turning the flanged joint over to operations for testing and inspection.
- c) Operations QA/QC and leak testing steps before the reintroduction of process fluids

#### 6.5.5 Valves in HF Service

At each turnaround, a representative number of valves in each corrosion zone should be internally inspected for corrosion or other forms of damage. Profile radiography has shown to be an effective option for on-stream evaluation of thinning and corrosion, especially for smaller valves. Alternatively, smaller valves can be replaced in lieu of inspection. The selection of valves for internal inspection should be based on process conditions as well as on-stream inspection data from adjacent piping spools. Gate, globe, plug, check, and control valves should be included in the representative sampling and be removed from their adjoining spool pieces prior to inspection.



Owners should have a designated and pre-qualified approved manufacturing list for valves in HF service.

Valve repairs should be conducted by manufacturer-certified repair shops. Repair shop standard practices should include the inspection of stuffing box bores for enlargement due to corrosion and for the condition of flanged joints.

Critical check valves, as defined in accordance with the definition in API 570, are those that need to operate reliably to avoid the potential for hazardous events or substantial safety consequences if reverse flow occurs. Critical check valves in HF service piping systems and HF safety systems shall be identified, inspected, and maintained in accordance with API 570 and API 574. Radiography alone typically will not detect a flapper stuck in the open position. Examples of potential critical check valves can be found in H.3.

Some valves in HF service are equipped with grease fittings in the valve packing area, and the owner-operator can add grease to the valve packing to prevent iron fluoride scale from getting into the packing. A documented program to periodically grease these valves per manufacturer's recommendations should be in place. Valves made of HF-resistant alloys have less need for grease fittings than those made of carbon steel. In lieu of maintaining a valve greasing program, some owner-operators have chosen to either not use or eliminate valves with grease fittings in the valve packing area.

For valves with liners, some owner-operators have experienced potential flow path restrictions due to liner rotation and have added them to turnaround inspections.

## **6.5.6 Instrumentation**

### **6.5.6.1 General**

Instrument parts, including valves and associated process connections, that are wetted by process fluids and that either contain HF or can contain HF shall be constructed of HF-resistant materials. Pressure boundary bolting for instrumentation should be B7/2H or B7M/2HM assemblies, per 6.5.4.3.1. In addition, stainless steels, Cu-Ni, and Ni-Cu alloys shall not be used for pressure boundary bolting in HF services, including instrumentation and control valves in HF service. It is a good practice to use HF-resistant materials on body parts such as pressure boundary closures that are not exposed to the process.

Incorrect material of construction is a particular concern in instruments such as pressure gauges, transmitters, and control valves. Experience has shown that instrument suppliers/rebuild shops (including pump seal system instrumentation) have sometimes shipped their standard materials of construction instead of paying close attention to the specified materials of construction for HF service in the requisition. Hence, the MVP covered in 6.2.5 should be applied to all instruments including analyzers and valves. Instrument specifications for HF services should be written to identify their specific use in HF service. Instruments that have been hydro tested with water should be thoroughly dried out before being put into service.

### **6.5.6.2 Level Indication**

Vapor-liquid level monitoring in HF services is typically measured by the use of displacer, differential pressure (DP), nuclear, ultrasonic, magnetic float, and/or radar devices. HF/hydrocarbon interface level monitoring is typically measured by the use of nuclear, DP, and/or magnetic float devices. A general precaution is that magnetic level instruments made of Alloy 400 components can exhibit magnetic properties, especially at temperatures below about 60 °F/16 °C. Other HF-resistant nickel alloys (e.g. Alloy C-276) do not have this magnetic issue. See G.2.5.3 for more information on the magnetic properties of Alloy 400.

Due to their silica content, gauge and ratio glasses shall not be used in HF services. Glass shall not be used in new and replacement seal pots for pumps in HF service or in normally non-HF services that can be exposed to HF where an upset or failure could occur (e.g. fractionator tower bottoms). Existing glass in these services, even with CTFE shielding/coating, shall be risk assessed for the need to proactively upgrade to HF-resistant materials. See 6.2.4.1 and G.2.11 for further information on silicon-based components.



Trycock valves shall not be installed in HF service. Existing trycock valves shall not be operated and shall be planned for removal.

When pressure-based devices are used for level indication, the requirement and recommendations in 6.5.6.3 apply.

#### **6.5.6.3 Pressure Indication**

The internal process wetted parts of pressure indication instruments in HF service shall be made of HF-resistant materials. Where available, non-process wetted transmitter internal sensor housings and capillary tubes should also be made of HF-resistant materials (e.g. Alloy 400 or Alloy C-276), even when an isolating diaphragm is used. A diaphragm between the process fluid and pressure-sensing device (e.g. bourdon tube) should be used for both pressure gauges and DP gauges in continuous HF service. Process wetted surfaces of diaphragms in pressure transmitters and DP instruments in HF service should be gold-plated Alloy 400 or gold-plated Alloy C-276. This is to minimize distortion due to hydrogen permeation through the diaphragm. For diaphragm-protected pressure instruments in HF service, new and replacement capillary lines should use a fill fluid that is not reactive with HF (e.g. a halocarbon that is both inert to the materials and normally in the liquid phase at atmospheric pressure).

Cracking of some bourdon tubes made of HF-resistant material in pressure gauges in HF service has been reported. In some cases, this cracking is thought to be due to residual water and/or air in the bourdon tube coming in contact with HF.

Where mercury (Hg) is present, cracking as well as gold plating corrosion may occur.

#### **6.5.6.4 Flow Indication**

Regardless of corrosion zone, orifice plates in HF service should be Alloy 400 or another HF-resistant nickel alloy. Because of the potential to trap water behind concentric type orifice plates in horizontal lines, the line should be free draining. Eccentric-type orifice plates may be used to avoid trapping water in horizontal lines to allow for the ability to fully drain the line. Alternatively, sites can use administrative controls to facilitate draining. When pressure-based devices are used for flow indication, the requirement and recommendations in 6.5.6.3 apply.

#### **6.5.6.5 Temperature Indication**

Thermowells shall be constructed of HF-resistant alloy material in all corrosion zones.

Owner-operators should implement a thermowell integrity program for thermowells in HF service. When implemented, that program should include the following elements.

- a) Thermowells receive examination prior to installation to confirm the design and dimensions are as specified per the datasheet.
- b) Thermowells are periodically removed for inspection to assess integrity including cracking related to vibration.
- c) Nozzles associated with thermowells are examined for any damage, including cracking related to vibration.
- d) Threaded connections and dissimilar metal connections are examined for any crevice corrosion or galvanic corrosion.

All welds on thermowells shall follow the heat treatment requirements of this document for the material of construction.

Design parameters for thermowells are addressed in ASME PTC 19.3 TW.

Thermowells shall be included in the MVP (see 6.2.5).

#### **6.5.6.6 Impulse Lines and Tubing**

Impulse lines for instruments in HF service should be as short as reasonably possible to minimize the potential for scale accumulation and to minimize the potential reading error caused by an accumulation of a lighter phase in the high point of the lines. They should be free draining back to the process piping or equipment root valve to prevent the accumulation of a heavy liquid phase or scale in the lines. They should be designed with minimum connections to minimize the potential for leaks. Piping should be used for impulse lines between the process and the instrument root valve. Tubing may be used between the root valve and instrument.

Instruments and/or impulse lines should be evaluated for risk from mechanical impact. Those that are at risk for impact should have protective measures implemented to minimize the potential for damage from external forces (i.e. maintenance activities or falling objects).

Instrumentation impulse lines should be properly aligned and provided with independent support of the instrument or analyzer to minimize line stress. QA/QC should be performed on impulse lines and fitting assemblies before being put into service.

Provision of a clean, acid-free flushing medium to allow periodic flushing of problematic instrument impulse lines is one method that has been successful in preventing scale buildup, thus improving instrument reliability. Bidirectional flushing capability has been found to be of particular help. Instrument tubing and fittings in HF services shall be made of HF-resistant alloys (e.g. Alloy 400 or Alloy C-276) and shall be assembled per the compression fitting manufacturers requirements. Instrument tubing in HF service should be replaced any time a leak occurs or if the system cannot be purged to remove oxygen prior to putting it back in service rather than the tubing being repaired and reused. Tubing may be reused as long as it still meets the compression fitting manufacturer's assembly requirements. See 6.2 for additional information on the management of HF SCC.

#### **6.5.6.7 Analyzers**

Analyzers in HF service shall have their process-wetted components constructed of HF-resistant polymer, Alloy 400, Alloy C-276, or another HF-resistant alloy. Some owner-operators have switched to Alloy C-276 over Alloy 400 if the sampling system is subject to oxygen during servicing.

Some analyzers on HF alkylation units are not in HF service and therefore are not subject to the degradation mechanisms of materials in HF service [e.g. continuous emission monitoring system (CEMS) on unit furnaces and gas chromatographs in process streams that do not contain HF]. While analyzers for non-HF services do not need to be made of HF-resistant materials, using only analyzers with HF-resistant material inside the HF unit battery limits reduces the risk of accidentally using materials not suitable or not resistant to HF service.

#### **6.5.6.8 Control Valves and Remotely Activated Valves**

HF-resistant materials shall be specified for control and remotely operated isolation valves. Carbon steel, Alloy 400, and Alloy C-276 have been used with success depending on the corrosion zone. Some sites have also required valve actuator tubing to be of HF-resistant materials to preclude any likelihood of a mix-up with process tubing.

#### **6.5.7 Pumps**

Pumps in rich HF, fresh HF, and phase change HF services shall either have dual seals or be of sealless design. Pumps in the other HF corrosion zones should either have dual seals or be of sealless design.

All dual seal pumps in HF service should have some means of detecting leakage from the primary (inboard) seal. All sealless pumps in HF service should have a “dual containment” design and have some means of detecting a leak from the primary containment shell.

Pumps in rich HF, fresh HF, and phase change HF services shall have monitoring for early indication of bearing and seal failures. This monitoring should be performed remotely. All other HF corrosion zone pumps should have monitoring for early indication of bearing and seal failures. Monitoring for early indication of bearing and seal failures should include both pump and driver vibration and bearing housing temperatures. All monitoring for early indication of bearing and seal failures should be tracked and trended. Enhanced lubrication systems, such as oil mist systems, have been successfully used in reducing bearing failures that could result in seal failures. All pumps in HF service, including all internal components, shall be constructed of HF-resistant materials. New and replacement pump seal pots in HF service and associated piping/tubing, instrumentation, and components shall be constructed of HF-resistant materials. Existing pump seal pots and associated piping/tubing, instrumentation, and components shall be risk assessed for the need to proactively upgrade to HF-resistant materials. See 6.2 and G.2 for information regarding materials.

The case and rotating parts of pumps in HF service should be inspected for corrosion and other forms of deterioration. In addition to VT for general corrosion, pump casings should be checked for porosity and cracking. PT or WFMT can detect cracks at or near the surface. Photography can be useful to help understand wear pattern development.

New pumps, new pump casings, or pressure boundary weld repairs to pump casings can contain flaws not detectable at the time of fabrication or repair but can propagate during service. Regardless of prior pump operating and inspection experience, new or repaired pumps should have an internal inspection after at least 2 years of service but not to exceed 5 years of service or one turnaround cycle, whichever is greater. Repairs that should have follow-up inspection include weld buildup or overlay to restore corrosion loss and crack/porosity repair to the pressure boundary. For pumps with 10 or more years of operating experience and documented inspection findings, the frequency of internal inspection should be based on corrosion history and in-service condition monitoring. If internal corrosion is typical of prior service experience and there is no evidence of cracking or porosity, then the frequency of future internal inspections can be based on operating and inspection experience. Weld repairs and/or machining with the purpose to restore mechanical fits and clearances are not considered pressure-boundary repairs for follow-up inspection as described herein. See 6.3.2 for further information as well as recommendations and requirements for welding in HF service.

Pump hydraulic modifications (such as impeller diameter changes or an increase in pump rotational speed above historical experience) that affect the design discharge pressure or flow rate by more than 5 % can induce changes to internal turbulence and localized internal erosion/corrosion compared with prior operating and inspection experience. An internal inspection should be performed after at least 2 years of service but not to exceed 5 years or one turnaround cycle, whichever is greater, after a pump hydraulic modification.

#### **6.5.8 Heat Exchanger Bundles**

Seamless tubes should be used in new and replacement heat exchanger bundles in HF service, regardless of metallurgy. Where U-tubes are used, refer to the bending requirements in 6.3.2.11.

To reduce the possibility of leakage, some owner-operators use welded tube-to-tubesheet joints in HF service bundles. See Annex G for further information. Tube-to-tubesheet welding procedure qualification should be in accordance with QW-193 per ASME *BPVC* Section IX.

During turnarounds, owner-operators have experienced difficulty pulling bundles with an iron-fluoride scale on the shell side. Some owner-operators specify double the maximum Tubular Exchanger Manufacturers Association (TEMA) shell-to-baffle clearances during design for carbon steel shells and/or bundles in shell-side HF service to allow easier bundle pulling.

**6.5.9 For tubes in HF service that have been plugged, both ends should be cut, pierced, or drilled behind the tubesheet before the plugs are installed. This applies regardless of tube metallurgy. Plug use shall be in accordance with ASME PCC-2, Article 312, which specifies maximum service pressure for non-welded tapered plugs as 200 psig on the shell side, among other requirements. Pressure-relief Devices (PRDs) and Systems**

#### **6.5.9.1 PRD Materials of Construction**

PRVs in HF service shall be constructed from HF-resistant materials (e.g. carbon steel or Alloy 400) for the body and bonnet, depending on corrosion zone. HF-resistant alloy materials (e.g. Alloy 400 or C-276) shall be used for the nozzle, disc, and seat. Stems shall be Alloy 400, Alloy K-500, or Alloy C-276. Bellows-style PRVs in HF service shall be supplied with HF-resistant alloy bellows. For example, Alloy C-276 has been found by many owner-operators to have better cracking resistance than Alloy 400 for bellows. See G.2.5.4 for Alloy K-500 hardness limits and G.2.7 for Alloy C-276 considerations.

Rupture disks and holders used in HF service shall be constructed of HF-resistant alloys.

#### **6.5.9.2 Pilot-operated Relief Valves**

Pilot-operated relief valves should not be used in HF service. This is due to their mechanical complexity, which results in several fail-open failure modes, as well as the fact that their smaller parts are sensitive to potential plugging from particulates and/or corrosion products (see API 520, Part 1 and API 576).

#### **6.5.9.3 PRD Testing and Maintenance**

A written procedure based on API 510, API 570, and API 576 (as applicable) should be developed for the testing and maintenance of PRDs. The procedure should address how to safely remove a relief valve while the unit is online and offline. Alternate relief protection considerations per API 576 should be followed.

#### **6.5.9.4 PRV Inspection Intervals**

Owner-operators should have a program that addresses setting inspection intervals. This program should include information on the pop testing inspection of PRVs, as described in API 576. For owner-operators without unneutralized pop testing inspection data, a maximum inspection interval of 5 years shall be used (for the purpose of as-pulled pop testing, unit decontamination is considered neutralization). Surface decontamination of Alloy 400 exposed to HF (ie spraying with an ammonia based solution) is considered acceptable and does not affect the validity or interval of the as-pulled pop-test.

The initial inspection intervals for new valves can be set based on the inspection history of the valve it is replacing, provided the valve is a replacement-in-kind and is in the same service and functional location.

Where owner-operators have a pop testing inspection program, the results of these tests shall be documented. For owner-operators with active pop testing inspection programs (typically, in the unit), the test results can be used to establish or modify the inspection interval. Within the HF alkylation unit, the testing interval shall not be extended without as-received pop testing data. For example, selected PRVs may require shorter testing intervals based on owner-operator testing data.

To reduce the inspection frequency and determine the actual relief pressure, the as-received pop testing of PRVs shall be performed before any cleaning, neutralizing, and disassembly is performed. See API 576. This can be conducted on a test stand built on site. In order to accomplish the initial as-removed pop testing for HF unit PRVs, some sites have built dedicated test stands with a neutralization bath on the pressure relieve valve outlet within the HF unit battery limits. Others may hire qualified service contractors to bring a portable test stand on site during the turnaround. Both of these options allow for testing of the valves in the as-received condition prior to any cleaning and neutralization.

The testing interval may be shortened but shall not be extended without as-received pop testing data. Even with as-received pop testing data, the inspection interval:

- e) shall not be extended beyond 10 years in phase change HF and dilute HF in water corrosion zones; and,
- a) should not be extended beyond 10 years in the other corrosion zones.

Extending inspection intervals beyond the 10-year limit shall require a review by a corrosion specialist familiar with the damage mechanisms in the HF alkylation unit and a risk analysis.

Any failure of the PRV to function as specified (e.g. leaking by, popping early, failure to pop within the allowable range for the relief setting) should call for:

- a) an evaluation to be performed to determine the cause;
- b) the valve to be repaired or replaced if necessary; and/or,
- c) use of the results to adjust the testing frequency as needed.

#### 6.5.9.5 Other Areas for Inspection Related to PRDs

To determine if PRD isolation valves are open, radiography or another verification method should be performed each time an isolation valve in the relief path is opened. For larger gate valves, radiography of the cross-section of the bonnet before and after the gate is opened has been found to be successful for some owner-operators.

Due to the potential for corrosion product buildup and plugging in carbon steel piping, the inspection program shall include either radiographic or internal visual examination of HF service carbon steel PRV inlet and outlet lines. This problem can be significant near high points and stagnant inlet lines where HF condensing may cause corrosion. The inspection program shall include periodic examination (i.e. radiography, visual, thermography, or other methods) for fouling to verify HF service carbon steel PRV outlet lines and common headers from the PRVs to the acid neutralization scrubber are not fouled. If an on-stream thickness examination is showing metal loss, a follow-up inspection should be performed to look for possible scale buildup. Profile radiography is typically the method chosen for these inspections.

Regardless of line metallurgy, relief valve discharge lines downstream of KOH treaters/aqueous caustic treaters and relief header lines upstream of the acid neutralization scrubber may be susceptible to fouling due to salt accumulation and should be periodically inspected using RT (or other method) for pluggage. Relief header lines downstream of the acid neutralization scrubber should be inspected for fouling. These inspections are meant to give assurance that system relief paths both upstream and downstream of the acid neutralization scrubber are not restricted. Any restrictions found shall be given high priority for mitigation measures.

Purging of relief valve inlet lines or upgrading the metallurgy should be evaluated if significant corrosion occurs or if an accumulation of scale significantly restricts the area available for relief flow. Corrosion has been reported in the inlet lines to PRVs where HF vapors accumulate and condense. Failures have occurred at various locations of inlet lines from localized corrosion therefore the full length of inlet lines should be examined. Examples include PRV inlet lines in the following locations:

- a) lower parts of fractionator columns due to thermal defluorination HF vapor accumulation (see G.3.6),
- b) superheated iC4 stripping vapor due to thermal defluorination HF vapor accumulation (see G.3.6),
- c) top of propane and nC4 defluorinators due to dilute HF in water condensation (see G.3.5).

See 8.1.1 for information and further recommendations related to relief valve outlet systems.

### **6.5.10 Fired Heaters**

Fired heaters should be inspected in accordance with API 573. Where applicable, the following areas should be emphasized:

#### **A. Fireside Corrosion**

For heaters burning unneutralized ASO, the flue gas surfaces of heaters and stacks should be inspected at each turnaround.

#### **B. Tubeside Corrosion**

For fired heaters with reboiled process streams on the tube side - due to the thermal defluorination of organic fluorides inside the tubes in the fired heater, HF will be present, and HF-resistant materials should be used for process wetted parts such as heater tubes, coil outlet piping, and the associated instrumentation and piping, and these components shall be part of the inspection plan.

#### **C. Areas susceptible to thermal defluorination**

### **6.5.11 Sample Containers**

#### **6.5.11.1 Sample Container Materials of Construction**

HF sample containers shall be constructed of HF-resistant alloy materials such as Alloy 400 or Alloy C-276. See section 6.2 for generally accepted materials of construction.

Fabrication of sample containers should avoid welded construction where possible. However, if welded containers are used, the sample container shall utilize recommended practices for materials of construction, fabrication, heat treatment (e.g. solution annealed), regular inspection frequencies (e.g. RT of the welded area, inspection for cracking), and sample handling in order to minimize the likelihood of oxygen-induced SCC.

#### **6.5.11.2 Sample Containers Inspection and Testing**

Inspection and testing of sample cylinders shall be sufficient to assure leakage from deterioration or damage does not occur. Each sample container shall be inspected and tested on an established frequency no greater than 12 months. The procedures should include retirement/replacement criteria that are based on the inspection and testing results.

### **6.5.12 Product Runtowns and Storage**

#### **6.5.12.1 Alkylate Tank Water Phase Drainage IOW**

An IOW should be in place on alkylate tank water-phase drainage for low pH. See G.4.5 and Table G.1 for further information on IOWs.

#### **6.5.12.2 Tank Bottom Corrosion Protection**

Some owner-operators have installed a coating on the alkylate tank bottom to protect it from acidic water. Coatings may not work for various reasons (e.g. coating composition or inadequate installation QA/QC). Coatings for alkylate tank bottoms should not contain any materials that are readily attacked by HF (e.g. silica or glass fibers).



### 6.5.12.3 Storage Tank Inspection Intervals

API 653 internal inspection intervals should not exceed 20 years unless one or more of the conditions listed below are met and a corrosion specialist has completed an evaluation:

- a) a caustic heel is used, the water phase is monitored for pH, and an IOW for low water-phase pH is in place,
- b) the tank has a double bottom per API 653,
- c) an aqueous caustic treater is used to treat the alkylate before running down to tankage, or
- d) a properly specified coating (i.e. resistant to HF service) has been applied to the tank bottom with proper QA/QC and remains intact between tank internal inspections.

In all cases, the maximum inspection interval shall not exceed the requirements in API 653.

### 6.5.12.4 Propane and Butane Treater Systems

Historical operating conditions of the butane/propane product treatment (e.g. HF breakthrough from the caustic treater) and potential hydrogen and corrosion damage shall be taken into account when developing the inspection plans for propane/butane rundown piping and storage vessels. An effective communication process shall be in effect between operations and inspection when a breakthrough occurs. See also the IOW table in Table G.1 in Annex G. Refer to 8.2.4 for details on operating these systems.

### 6.5.12.5 Rundown Piping

The propane and butane rundown streams from an HF alkylation unit are normally HF-free. However, when the upstream solid-phase KOH treater becomes spent, the process stream can contain either AHF or dilute HF in water and potentially cause corrosion in rundown piping and/or downstream pressure vessels.

See 8.2.4 for potential ways to minimize such damage from HF in the product streams.

For aqueous caustic treaters, including alkylate treaters, monitoring the base solution for strength and replenishing the solution either in a batch-wise or continuous manner is typically performed.

Many owner-operators experience corrosion in ASO rundown piping. This is most likely due to:

- a) not neutralizing the HF regeneration system bottom stream;
- b) having incomplete neutralization of the HF that is contained in the HF regeneration system bottom stream;
- c) having caustic flow upstream when the ASO stream is not flowing; or,
- d) having incomplete neutralization of the HF that is contained in the HF regenerations system bottom stream.

Caustic carryover can be experienced in the neutralized product. These potential effects should be taken into account when developing the inspection plan for ASO rundown piping. If heat tracing is used on ASO rundown piping, the guidance on heat tracing in 6.5.3 applies.

### 6.5.13 Equipment Exposed to Low Temperature

Due to the presence of light hydrocarbons in an HF alkylation unit, some equipment and piping in the unit may be exposed to low temperatures, such as during start-up conditions and from auto-refrigeration. Such equipment and piping should be identified in various technical/hazard reviews and should be checked to make sure that the minimum design metal temperature (MDMT) specifications for the materials of construction are included in the analysis to avoid any potential for brittle fracture in service. For example, iso-butane boils at 11 °F, n-butane at 31 °F, and propane at -44 °F. Risks associated with this damage mechanism are typically managed with procedures and/or operator rounds. Some standard refinery equipment and piping may not be able to withstand low temperature excursions without the risk of brittle fracture. API 579-1/ASME FFS-1 can be used to assess the potential for brittle fracture.

## 6.6 Maintenance and Related Work Practices

### 6.6.1 General

Maintenance programs apply to all processes and systems within an HF alkylation unit. However, there are other related work processes that do not fit the previous sections and/or topics yet affect equipment and piping mechanical integrity. The intent of this section is to bring these items into one area that provides the operator-user information and requirements to successfully maintain the mechanical integrity in an HF alkylation unit.

### 6.6.2 Maintenance Program

; maintenance management system shall be in place for HF Alkylaton units to include a process to prioritize and complete required repairs that are identified during inspection and testing activities and that are necessary to maintain unit mechanical integrity. The maintenance management program should include qualifications and training of maintenance personnel working on pump sealing devices, flanged joints, tubing connections, and instrumentation

The program should also include a continuous improvement process to identify and address HF service equipment, piping, and instruments with reliability issues. As part of this process, a list of equipment and piping with reliability issues should be established and maintained. Some owner-operators refer to this as a "bad actor list" or the "top 10 reliability list." Examples may include but are not limited to:

- a) PRV inlet lines that experience fouling and pluggage;
- b) piping with short-interval inspection schedules because of episodic corrosion acceleration;
- c) valves and flanges with a history of corrosion/leaks;
- d) pump seals that fail more frequently than seals in similar service;
- e) instrumentation that is out of calibration more often than similar instrumentation; and,
- f) mitigation equipment and piping that is frequently out of service because of improper functioning.

The continuous improvement process should include identifying the root cause(s) for the frequent and/or chronic issues and corrective actions to mitigate.

### 6.6.3 Pressure Testing

Pressure testing should be conducted per API 510, API 570, and ASME PCC-2, Part 5, Article 501. When pressure testing HF service equipment and piping, there are advantages to use a nontoxic hydrophobic liquid as the testing medium, such as kerosene or diesel. This minimizes getting water into small crevices in heat exchanger bundles and valve packing and helps remove water that may already be present in the equipment

or piping being tested. When water is used as the testing medium, a detailed review should be conducted before the test to determine that all affected equipment and piping can be completely drained and dried. All affected equipment and piping should be drained and dried after the test, before reintroduction of HF-containing process fluids, or a nontoxic hydrophobic liquid should be used for pressure testing.

#### **6.6.4 Fabrication and Repair Shop Surveillance**

Because specifications for HF service equipment and piping normally go beyond typical construction codes for other refinery equipment and piping, new construction or repairs to HF service equipment and piping should be in accordance with the practices outlined in API 588. The owner-operator should determine the criticality of equipment and piping being fabricated and assign the appropriate level of shop inspection/surveillance to be conducted. The goal is to assure design specifications and QA practices are adhered to prior to delivery. A non-exhaustive list of specific issues includes PMI for materials of construction, welding QA/QC and use of techniques to avoid slag inclusions, DMW fabrication procedures, heat treatment soak times and temperatures, completion of specified NDE, the quality of cast components, and bolting and gasketing materials. Additional information is located in Annex G.

## **7 Transportation and Inventory Control**

### **7.1 Refiner/Shipper Cooperation**

#### **7.1.1 General**

During shipping of fresh HF, the carrier's equipment is not protected by the refinery safety and leak-mitigation systems. The refinery owner-operator, the HF supplier, and the carrier should actively cooperate to ensure that shipping operations are performed safely.

#### **7.1.2 Shipping Containers**

HF suppliers and carriers shall use equipment designed, inspected, and maintained in accordance with U.S. Department of Transportation (DOT) regulations (49 *CFR* Parts 100 to 185) or other applicable regulations for non-U.S. jurisdictions. Shipping containers, including highway tank trailers, rail tank cars, and portable ISO tanks should be dedicated to AHF service.

#### **7.1.3 Shipping Practices and Routes**

The HF carrier should plan a route to the refinery that will minimize risk and should adhere to the planned route. Containers and/or the powered vehicle shall be closely tracked while in transit. Tracking systems should be used to allow improved communication and improved security of and accountability for the load during transit. The HF carrier's emergency response program shall comply with local and federal regulations.

Routes within the refinery should be jointly planned between the carrier and the refinery owner-operator and have a minimum clearance of 13' 6". Further, the refinery owner-operator shall designate a secure holding area for early deliveries within the refinery property. In addition, the refinery owner-operator shall establish a communication system between the carrier and the authorized refinery representative once the carrier is on site or inside the holding area.

#### **7.1.4 Unloading Systems**

A carefully designed unloading station can greatly reduce the risk of an HF release during the unloading operation. Nitrogen-pressured unloading is the most common method, although other procedures are also used. Unloading piping shall be designed to minimize dead-legs where HF could accumulate.

Where access to the transport/ISO container is from a top platform, egress should be possible in at least two directions. Operations for the portable ISO tank should not commence with individuals on the ladder or standing on the rear deck of the chassis.

Unloading hoses shall be an approved HF compatible hose with adequate pressure ratings that has a suitable outer cover and have a PTFE inner liner. The hose should be crush and collapse resistant. These hoses shall be dedicated solely to HF service as the hoses are designed for general corrosive chemical service. A mechanical integrity program shall be established by the hose owner that includes, at a minimum, periodic testing, retirement protocol, and permanent marking with the last inspection date (see 6.4.6 for additional information). The hose shall have a maximum working pressure greater than the maximum operating pressure of the nitrogen supply or motive force.

A grounding/bonding cable connected to the shipping container shall be used during the unloading process if required by refinery policies. If required, the grounding/bonding cable shall be provided by the refinery.

Tank trailer, portable ISO tanks and rail tank cars shall have air-to-open remotely activated valves on all connections. Crossover provision between the HF unloading and nitrogen pressurizing lines shall be provided to allow an inert gas leak test prior to HF transfer and sweep after the HF transfer, prior to disconnecting. All transport container root valves shall be enclosed in a protective housing. Portable ISO tanks and rail tank cars may not have pneumatically actuated valves mounted permanently.

The emergency stop system that controls the containers remotely activated valves, and the emergency stop system for the refinery that controls the actuated unloading system valves should have the capability to be connected. Portable ISO tanks and rail tank cars may not come equipped with such systems.

At some sites the simultaneous closure of the actuated valves on the transport container as well as the refinery valves will occur whether the transport driver or the refinery operators activate the emergency shutdown system. This has been demonstrated as best practice.

The refinery owner-operator shall install a vent line to the neutralization section for depressurizing the HF transport container. Sites may add remotely activated valves to route the HF unloading line to both the tank and to the flare header. Personnel should not be at elevation during liquid acid transfer unless equipped with breathing air. Provisions shall be made to monitor the pressure in the HF storage vessel during unloading. The vessel pressure should be visible from ground level or in the control room.

Safety relief valves on HF transport containers may be set at different pressures. To avoid venting HF-laden gas to the atmosphere, the refiner's nitrogen safety relief valve should be set at least 20 % below the setpoint of the transport vessel's HF safety relief valve and at least 10 % below the transport vessel nitrogen safety relief valve, if so equipped. To avoid venting HF-laden gas to the relief flare system, the refiner's nitrogen pressure regulator shall be set below the HF storage vessel safety relief set pressure and below the test pressure of the unloading hoses.

The unloading system, including any hoses, flanges, gaskets, valves, and other equipment for HF, shall be visually inspected and tested for leaks prior to each use. The leak test should be recorded to document the test was complete.

### **7.1.5 Personnel and Clothing**

For driver involved offloading, the carrier shall provide two qualified drivers for unloading each shipment of HF. The carrier shall provide safety equipment and clothing for their drivers (see 5.6.2 for information on PPE) and the carrier shall define requirements for decontamination of their PPE. If site decontamination requirements differ from that of the supplier, the site should provide means to comply with those requirements.

Site procedures shall dictate the number of backup personnel needed during unloading and an outline of the responsibilities of each participant in case of an upset or emergency.

### 7.1.6 Training and Emergency Procedures

Driver training should include HF hazards, first aid, security measures, PPE, typical refinery practices, unloading procedures (if applicable), and operation of the safety features of the shipping container. Training, testing, and certification of the individuals performing the work should be consistent with the refinery training policies and transportation requirements. Certification of such training should be made available to the refinery owner-operator upon request.

The HF carrier shall have an emergency response plan, and the drivers shall be trained on the plan. The HF carrier emergency response plan should be compatible with the refinery site's emergency response plan. The refinery owner-operator shall review with the drivers the appropriate refinery unit safety, and evacuation procedures, including mitigation system response in the event of a release. This review should include familiarizing the drivers with their roles and responsibilities in the event of any refinery incident that may affect HF offloading operations.

## 7.2 HF Unloading

The safe unloading of HF into the unit is of utmost importance to the success of the refiner's hazards management program. A clearly written operating procedure for HF unloading shall be in place, and a process shall be in place to ensure that all steps in the unloading procedure are performed for each delivery.

The unloading procedure shall address the need to remove non-essential personnel from the unit and surrounding areas during the acid unloading process, post warning signs, and restrict access to the unloading facility. The unloading facility or transportation vehicle shall include means for chocking the vehicle wheels to prevent movement during unloading. The connecting hoses or lines from the unit's unloading manifold to the transport container shall allow for enough slack to ensure the hoses do not become taut during unloading.

For each delivery in which the driver(s) participates in HF unloading, refinery personnel shall review with the driver(s) the unit-specific HF unloading procedure, so the various task responsibilities are clearly understood.

Annex I of this document lists certain procedural options for tank trailer transport unloading. At a minimum, the HF unloading area shall be equipped with the following.

- g) Remotely activated valves. A manual valve may be the last connection on the manifold.
- h) Located on the unit's unloading manifold as close as practicable to the HF hose connection.
- i) Having an emergency stop system linked to them so the valves can be closed in an emergency from a remote area.
- j) Being accessible from the unit or the control room.
- k) Having the unit activation station both a minimum of 50 ft away and within line-of-sight of the unloading station if it cannot be activated from the control room.
- l) Water mitigation systems that provide coverage of the unloading facility and transport container.
- m) Remote visual surveillance (e.g. camera or dedicated observer).
- n) Check valve on nitrogen supply to the transport container.
- o) Emergency eye wash and shower shall have a clear path within 50 ft of the unloading operations.
- p) Water available for gross decontamination of the unloading facility.

- q) Valves to allow nitrogen tightness testing of the connections from the unloading manifold to the transport vessel.
- r) A manifold pressure indicator to facilitate testing and monitoring during unloading.
- s) A drain/vent valve installed at the unit's unloading manifold to permit final depressurization after unloading is complete.

A remotely activated valve shall also be provided on the nitrogen connection that is connected to the emergency shutdown system. A manual valve may be the last connection on the manifold.

## 8 Pressure-relief, Product Treatment, and Utility Systems

### 8.1 Pressure-relief and Flare Systems

#### 8.1.1 General

Overpressure vents, relief valves, and hard piped vent lines from equipment and piping in Rich HF, Fresh HF, and Phase Change HF corrosion zones, shall be routed through an acid neutralization scrubber to neutralize the HF before the hydrocarbons are released to the flare. Pressure Relief Devices located in the fractionator corrosion zones may relieve minute amounts of HF that have accumulated in the lower portion of the tower due to thermal decomposition of organic fluorides to the non-acid flare header, however these minute amounts are not expected to impact flare system integrity. In the acid neutralization scrubber, the HF flare gas is neutralized with a circulating caustic stream. Refiners can and have used both an NaOH circulating stream (typically < 5 % by weight NaOH to prevent plugging from salt formation) or a KOH circulating stream (can be as high as 45 %). The KOH solution has the advantage of allowing for higher strengths, and greater neutralizing capacity, without concerns of salt deposition.

The capacity of the acid neutralization scrubber shall be reviewed whenever significant process changes are made that could increase relief or vent rates in the unit. Consideration should be given to the minimum allowable caustic circulation strength when calculating the neutralizing capacity of the system. The flow and temperature of the circulating neutralization solution shall be continuously monitored, and its strength for neutralizing HF should be routinely checked. The change in pH of the caustic circulation should not be used as a primary indication of the solution's neutralizing capacity, because the pH will not change until the solution is spent. Caustic strength should be determined using titration. Also, low flow and low strength IOWs should be established to mitigate corrosion effects. 1

When the alkylation unit and acid neutralization scrubber are taken out of service and if HF is stored in the unit, then there should be temporary routing of the HF storage relief to a location other than the acid neutralization scrubber (e.g. atmosphere, neutralization pit, non-acid flare). If relief is going to the atmosphere, consideration should be given to the use of a rupture disk under the relief valve, and the appropriate instrumentation associated with it (see 6.5.9.6).

If rupture disks are used below PRVs, in addition to the requirements specified in ASME BPVC Section VIII and API 520, a means of continuous detection for disk leakage shall be included with each installation. A common means used is a high-pressure alarm or notification on the control panel. Rupture disks shall be replaced whenever leakage is detected or the PRV is removed for servicing.

#### 8.1.2 Acid Neutralization Scrubber

Venting of water-containing streams (i.e. streams in the dilute HF in water corrosion zone) to the HF flare header upstream of the acid neutralization scrubber should be avoided. A continuous dry and clean gas purge (e.g. natural gas, dry gas, or nitrogen) should be utilized to minimize stagnant pockets and corrosive



atmospheres in the flare header. Main and sub headers purge gas rates should be at least 0.1 ft/sec and can be determined by delta pressure calculations or direct flow measurement. The basis for the flow rate is to provide a minimum 1 ft/sec velocity of the purge gas to the entrance nozzle of the acid neutralization scrubber, to prevent moisture from the acid neutralization scrubber system from intruding back into the "dry" acid relief header/piping, which would promote a corrosive condition. During normal operations, neutralizing chemicals (e.g. ammonia) shall not be continuously injected into either the acid or non-acid flare header to neutralize any HF because of potential neutralization reaction solids forming and plugging the header. Ammonia used for occasional equipment preparation for maintenance may be swept to the flare as the volume of the material and duration of the activity limits the potential plugging of the header. ASO neutralizer/washer vent gas and KOH treater brine streams will be saturated with water and should not be piped into the dry acid flare header. Some sites have piped these directly into the acid neutralization scrubber vessel with a dedicated nozzle.

There is freezing potential in the acid neutralization scrubber due to auto-refrigeration of liquid LPG range hydrocarbon entering the vessel and could restrict flow from the acid neutralization scrubber to the flare system. Sites should evaluate the various streams that relieve to the acid neutralization scrubber to determine the risk associated with this phenomenon. Temperature and pressure indication on the acid neutralization scrubber outlet can identify this issue and steps can then be taken to alleviate the condition, such as heating up the circulating caustic or adding temporary heat to the acid neutralization scrubber outlet. More rigorous design solutions could also be considered, such as a liquid knock-out pot prior to entering acid neutralization scrubber. The design of the acid neutralization scrubber should allow for rapid mixing of the acid with the caustic solution to prevent localized corrosion from occurring where mixing occurs.

## **8.2 Product Treatment and Neutralization of Byproducts**

### **8.2.1 General**

Alkylation unit materials, unit products, vented streams, and unit byproducts may contain trace or dissolved HF and should be treated to reduce the potential for downstream corrosion. Any release or exposure to these materials or streams presents the possibility of injury and should be treated accordingly. Each operating unit should have facilities to control, neutralize, or otherwise mitigate any hazards from these sources. In addition, product streams should be treated as required by product specifications to remove organic fluorides. Untreated or insufficiently treated residual organic fluorides can revert to HF via thermal defluorination when burned as a propane/butane product.

Sampling of product tanks should have provisions in place to account for the possibility of acidic liquid. See 6.5.12.5 for mechanical considerations of rundown piping and IOW Table G.1 in Annex G for IOWs associated with product rundown.

For aqueous caustic treaters, including alkylate treaters, monitoring the base solution for strength and replenishing the solution either in a batch-wise or continuous manner is typically done.

### **Neutralization of Regeneration Bottoms / ASO**

Since HF may be present in the byproducts of the regeneration process, operating and maintenance procedures should reflect that ASO or polymer from the regeneration system may contain a small amount of free HF, an HF/water mixture, or both, and therefore be hazardous and corrosive.

ASO or polymer that leaves the unit boundary shall be neutralized, washed, or otherwise treated to minimize personnel exposure and potential corrosion problems. The method of treatment should be covered in operating procedures. ASO shall be neutralized even when disposed of via burning as fuel within furnaces and incinerators because unneutralized HF in this fuel can result in severe fouling and corrosion within the furnace convection sections. Furthermore, burner piping in that service can develop leaks and can cause personnel exposure issues. Neutralization of regeneration bottoms should be performed in a closed system.

## 8.2.2 Alkylate

Alkylate storage tanks may collect water from leaking tank seals. The alkylate rundown stream from the fractionation section can contain particles of iron fluoride. When iron fluoride contacts liquid-phase water, it can hydrolyze to form HF and iron oxide. The HF formed, along with normally non-detectable levels of HF in alkylate, absorb into the water, making the water acidic and more corrosive. The use of protective coatings or the addition of alkali to the water heel in the tank should be evaluated as a means of reducing corrosion of the tank floor. See 6.5.12.3 for additional tank inspection details. Some units operate an aqueous caustic treater or alkylate water wash system (e.g. MHF) that can reduce the probability of sending hydrolyzed iron fluoride to tankage.

## 8.2.3 Propane and Butane

Propane product should pass through a KOH treater, to dry the stream and/or neutralize any remaining HF. It is normally treated by first being passed through defluorinators to decompose organic fluorides before being sent through the KOH treater because KOH does not decompose organic fluorides. Butane product may be passed through a defluorinator to remove organic fluorides if required to meet product specifications, and it normally will be treated with KOH to remove any residual HF, with or without being defluorinated.

Fluoride monitoring should be conducted on the inlet to the LPG defluorinators in order to manage defluorinator bed life and/or corrosion in the equipment between the condenser and the KOH / caustic treater. A change in inlet fluorides can indicate that there has been a shift in operation. An increase in inlet fluorides increases the water produced in the defluorinators, which shifts the dewpoint of water in the defluorinator product. The defluorinator product is expected to contain trace HF acid, so as the temperature decreases to the dewpoint between the condenser and the KOH treater or aqueous caustic treater, acidic water corrosion occurs. Hydrogen damage has also been observed with this corrosion method within the system exchangers and defluorinators. See Annex G.3.5 for more details on these corrosion mechanisms.

Potential hazards that should be considered when operating procedures are written for this part of the process include the following.

Operational issues in the unit may allow significant quantities of HF into a defluorinator and/or KOH treater. In a defluorinator, the heat of reaction may be high enough to cause vessel damage and potential loss of containment due to excessive vessel wall temperature. In a KOH treater, product vaporization can increase pressure at a rate or amount that exceeds the equipment design and relief valve capacity. Safety instrumented systems to stop the flow to the treater(s) upon indications of significant HF intrusion shall be installed. The scenarios used to develop these systems shall be documented. Procedures should be in place to clear piping and/or upstream equipment of HF before reintroducing feed to the treatment system; see Annex J for information on scenarios to consider and how these systems may be designed.

For sites designed to operate with propane and/or butane defluorinator(s) upstream of a solid bed KOH treater, operation of the solid bed KOH treaters shall not be allowed without at least one active defluorinator in operation. A spent defluorinator will still catalyze the reaction of combined fluorides to HF, leading to an increase of HF in the outlet stream to the KOH treater, which can increase corrosion in the system and accelerate the spending of the KOH treater. Fluoride testing should be performed, and/or a bubbler system installed (where allowed), on the LPG leaving the primary propane and/or butane defluorinator, in order to minimize the potential for operation with a spent treater. Inlet fluoride testing may also be used to predict the remaining life of the primary treater. LPG fluoride sample systems should be designed to minimize pluggage and/or have a routine preventative maintenance plan.

- t) Drying the LPG stream and the reaction of HF with KOH in the treater vessel form thick brine that can spatter when drained. A disengaging device that is connected to the flare header should be used to reduce this risk and also contain any release of propane or butane.

- u) Salts may form in the KOH treater and trap some HF. This may cause KOH treater drainage to have low pH during normal operation or after injection of steam or water to remove the salts. If LPG is released while testing for pH, it can contain HF.
- v) In order to prevent corrosion in the product rundown line and tankage, there should be a method in place to identify when the KOH treater bed is spent or no longer effectively treating the product stream. Methods may include:
  - w) monitoring pH or quantity of the brine that is drained from the treater,
  - x) testing for the presence of HF in the product stream,
  - y) copper strip corrosion testing of the product, or
  - z) valve freeze testing for moisture in the product.

See Table G.1 for related information.

- aa) If carbonyl sulfide is present in the unit feed, it can hydrolyze to form hydrogen sulfide ( $H_2S$ ) in the alumina treater. This  $H_2S$  can react in the KOH treater to form sulfides that in turn can release the  $H_2S$  if the brine goes below 7 pH. Unit procedures for handling, treatment, and disposal of KOH brine should take precautions to account for potential sulfidic caustic. The pH of the drained KOH brine may have a low pH [see Item c)].
- bb) If arsenic is present in the unit feed or fresh acid, it can cause hydrogen blistering of carbon steel components of the unit. Defluorinator alumina in the unit will trap arsenic leaving with the LPG products. Arsenic may deposit on the defluorinator alumina and can present a hazard when spent alumina is handled. Operations and maintenance procedures should reflect this possibility to ensure the proper handling and disposal of the material. Inspection should be notified of the presence of arsenic because of the potential effects on carbon steel (See Annex F.2.1.c).

#### 8.2.4 Process Drains and Neutralization

Process draining of HF or acidic hydrocarbons to the atmosphere or atmospheric systems should be avoided. Process drainage may contain HF and should therefore be monitored to determine the need to neutralize the drainage before it is released to the wastewater treatment plant. Units should have a neutralization basin or pit for HF area drains. Certain alkali neutralization (e.g. calcium-based or sodium-based) may result in insoluble fluoride salts, which may cause plugging. If HF acidic drainage is allowed to mix with sulfidic drainage from other areas, a release of  $H_2S$  can result. An area  $H_2S$  monitor/alarm should be considered near acid sumps or neutralization pits. Operating procedures should address these possibilities, as well as the proper handling of fluoride salts.

#### 8.2.5 Process Byproducts

The following are examples of process byproducts that should be managed to minimize risk to the environment:

- a) constant-boiling mixtures or HF/water mixtures;
- b) ASO or polymers;
- c) neutralization pit and caustic regeneration solids;
- d) defluorinator solids;
- e) HF-area surface water drainage;

- f) potassium fluoride (KF), KOH, sodium fluoride (NaF), or NaOH drained material from treater operation;
- g) neutralizing and cleaning chemicals from turnarounds;
- h) runoff from water mitigation systems; and,
- i) product tank drainage.

### **8.3 Utility Systems**

#### **8.3.1 General**

Unexpected contamination of the process by utility waters (cooling water, steam, or condensate) can have a significant impact on unit corrosion and safety. Conversely, contamination of the utility systems including nitrogen with HF may spread HF hazards beyond unit limits. Procedures shall be in place that define the design criteria for utility connections to process streams and methods to prevent backflow from the process stream into the utility stream. Single check valves should not be used as positive isolation for utility connections. Permanent utility connections to process streams should be minimized.

#### **8.3.2 Cooling Water**

Operation with the cooling-water pressure higher than the process pressure should be avoided where possible. Cooling water leaking through exchangers into the process can quickly increase unit HF corrosivity. HF sampling and equipment inspection frequencies should reflect this possibility. Procedures for transient operations, such as start-up or shutdown, should include steps to minimize the duration of cooling water exchangers operating when cooling water pressure is higher than process pressure.

Operating with the cooling-water pressure below the process pressure is preferred but risks leakage of HF into the cooling-water system. A dedicated cooling-water system for the HF alkylation unit can isolate this problem to the unit. Cooling water shall be monitored for pH, fluoride ion, or hydrocarbon daily to provide a warning of this occurrence. Because of the presence of buffering chemicals and the large inventory of water in the cooling tower basin, monitoring the cooling water return from the HF Alkylation Unit will react much faster than sampling the water in the cooling tower basin. Fluoride ion monitoring is an excellent technique to use due to the ability to detect incipient leaks prior to a change in pH or hydrocarbon detection. If continuous monitoring is used, then operating procedures should include manual testing for verification.

#### **8.3.3 Steam Systems**

Operation of high-pressure steam exchangers with steam pressure higher than the process pressure should be avoided whenever possible. Where high-pressure steam exchangers are used, the possibility of water leakage into the process should be considered. As with cooling water, this possibility should be considered when schedules for circulating HF sampling and equipment inspection are set.

#### **8.3.4 Condensate Systems**

If condensate from exchangers in HF service is used outside of the unit boundary, on-stream pH, conductivity, fluoride ion, or other monitors shall be installed in the condensate system to provide an early indication of HF leakage and prevent exposure to those outside of the alkylation unit. All other condensates in HF service should be tested on at least a daily basis. Fluoride ion monitoring is again an excellent technique to use due to the ability to detect incipient leaks prior to a change in pH or hydrocarbon detection. Operating procedures should include manual testing for verification.

### 8.3.5 Nitrogen Systems

Nitrogen used in the HF alkylation unit should be periodically monitored for oxygen by testing, supplier certificate of analysis, or other means of oxygen analysis. The maximum oxygen specification for nitrogen used in the HF alkylation unit should be less than 100 ppm to avoid accelerated corrosion.

Special care should be taken to avoid leakage of HF into the nitrogen or purge gas system used to unload fresh HF.

Nitrogen is soluble in LPG. Using nitrogen as a blanket in iC4 makeup and olefin feed storage can lead to excess venting of non-condensable gas from fractionation system overhead systems.

### 8.3.6 Instrument Air Supply Systems

Backup systems shall be provided for critical air-powered systems that do not fail-safe. Refer to 4.7 for safety systems requirements.

## 9 Risk Mitigation—Options and Techniques

### 9.1 Background

The HF alkylation process has been commercially operated since the early 1940s. As technology enhancements have been developed, HF alkylation plants have incorporated risk mitigation technologies into their operating philosophy.

Generally, risk reduction options include active mitigation systems that involve the ability to detect and respond to a release, passive mitigation systems that reduce impacts without requiring action, or a combination of the two. This section provides an overview of the available systems and associated procedures as well as protocols to help support decision making, emergency response planning, and protection of plant workers and the surrounding public.

### 9.2 Risk Assessment Approach, Scenario Selection, and Evaluation

A quantitative assessment (consequence-based or risk-based) shall be performed at each site to evaluate the potential for off-site HF impacts. This assessment shall involve the calculation of the distance to a hazard endpoint.

The quantitative assessment shall be conducted using dispersion models that have been validated with experimental data. The dispersion model impacts should allow for time-varying release rates and the effects of HF and water interactions to generate an integrated dosage profile based on the selection criteria of either of the approaches below.

Sites with HF Alkylation Units shall also follow guidance in API RP 752, API RP 753, and API RP 756 regarding the analysis and management of credible fire, explosion, and toxic risks associated with the unit to onsite process plant permanent buildings, portable buildings, and tents that are intended for occupancy.

#### 9.2.1 Risk Assessment Approach

For the required quantitative assessment, the owner-operator shall choose at least one of the following two approaches.

- j) A consequence-based approach, which takes into consideration the impact of an HF release and is based on maximum credible events (MCEs) for rich HF equipment. The RMP (risk management plan) worst-case scenario required to be reported by the EPA shall not be used as the MCE as it is an extreme case and not representative of MCEs.

- k) A risk-based approach, which takes into consideration numerical values for both the consequences and the frequencies of a range of potential HF releases.

An experienced analyst who is competent in the selected analysis method, the behavior of HF, hazard identification, scenario development for hypothetical toxic releases, and frequency assessment should conduct the study.

The owner-operator shall document the following elements used to evaluate the potential hazards and/or risk exposure of an HF alkylation unit:

- a) assessment approach,
- b) scenario selection (see Section 9.2.2),
- c) analysis methodologies,
- d) data sources used in the analysis of the potential hazards,
- e) detection and mitigation systems used, along with availability and response time for each system,
- f) evaluation criteria (see Section 9.2.3), and
- g) results of the analysis.

Additional information regarding risk assessment approaches is provided in Annex K.

### 9.2.2 Scenario Selection

A critical input to either quantitative assessment approach is HF release scenario selection. The scenarios considered for selection should be primarily based on operations-specific releases and loss of containment events due to equipment-related failures. Also, consideration should be given during scenario selection to known industry and site or company loss of containment incidents on other HF alkylation units as well as known HF-specific hazards (e.g. corrosivity and reactivity). For each scenario selected, information such as equipment design, process stream compositions, and operating conditions should be included as part of the quantitative assessment. Further information on scenario selection is given in K.2.

The quantitative assessment should take credit for both active and passive mitigation systems available on the unit, considering (1) the time for detection of the release and (2) activation of relevant components in the active mitigation systems that limit event duration.

#### Evaluation Criteria

##### 9.2.2.1 Consequence-based Approach

Evaluation criteria for the consequence-based approach shall be expressed in terms of an exposure dosage at the location of the receptors of concern (see K.2.2). The elapsed time for meeting the evaluation criteria shall be within 15 minutes of the event occurrence. The results from a consequence-based approach are typically expressed in terms of distance to the chosen evaluation criteria. Owner-operators can compare the results to either their fence line distance or to the closest off-site receptor.

##### 9.2.2.2 Risk-based Approach

The evaluation criteria for a risk-based approach shall address the risk to the population as a group (aggregate risk) and the risk to an individual (geographic risk). An owner-operator may choose to establish a single risk criterion that addresses both individual and aggregate risk. The evaluation criteria may be expressed as numerical values of individual, aggregate, or exceedance values. They can also be expressed



as graphical formats that include cumulative frequency vs consequence, geographic risk contours, or matrices with numerical axes.

### 9.2.3 Revalidation

The HF alkylation unit's quantitative assessment (consequence-based or risk-based) should be revalidated under the following circumstances.

- a) After a significant change in the public population is noted, including increases due to the development of:
  - l) residential communities,
  - m) areas of potential concentrations of people (e.g. schools, stadiums, churches, other large gathering events),
  - n) areas with people who have limited ability to evacuate (e.g. nursing homes, hospitals, jails).
- b) Prior to implementing unit modifications that will significantly change the following QRA parameters for the controlling scenario:
  - 1) increase in total HF acid inventory,
  - o) increase in the equipment count in rich acid service (vessels, piping, pumps),
  - p) increase in the pressure at potential release points,
  - q) permanent changes in risk mitigation systems as required by 9.2, which could reduce the effectiveness of the system,

NOTE: Refer to 4.1.3 on managing temporary changes.

- r) an increase in connections in rich acid service.

The decision to revalidate a quantitative assessment is a complex process requiring review of many variables. Each site should perform a documented revalidation of the QRA basis at least every census cycle, nominally every 10 years, accounting for the cumulative impact of all the above changes and update the QRA if the basis has changed.

## 9.3 HF Mitigation Systems

An effective mitigation system detects an HF release of consequence and provides means to both mitigate the event and manage its duration such that both on-site and off-site impacts are minimized. Mitigation systems or combination of systems deployed to manage the risk exposure associated with the HF alkylation process shall be designated as safety systems and managed in accordance with 4.7.

Response time is critical in any HF release scenario; therefore, procedures shall be in place or facilities installed to rapidly start the mitigation system(s) upon detection of HF releases of consequence. The response time shall be consistent with the criteria used in the quantitative assessment. Operating procedures for mitigation systems shall indicate how the system is activated and associated critical steps. Operations shall perform drills on the operating procedures for manually activated mitigation systems at a frequency sufficient to ensure they will meet the response time criteria.

### 9.3.1 HF Mitigation System Fireproofing

Equipment in the HF Alkylation unit and HF storage areas shall be evaluated for fireproofing needs consistent with API RP 2218 or comparable international standard, including:

- a) Identification of key equipment associated with HF mitigation systems described in section 9.4 thru 9.6 that can be functionally disabled if damaged due to fire exposure such as electrical power systems, control systems and wiring, key remotely activated valves, and structural steel supporting vessels and piping.
- b) Identification of the Fire Resistance Rating (See API RP 2218 for information on Fire Resistance Rating) required for equipment identified above to perform long enough to complete its intended function (i.e., isolation of HF large HF inventories, completion of acid de-inventory, start HF water mitigation, etc.).

#### **9.3.1.1 Electrical, Instrument, and Control System Fireproofing**

Components of electrical, instrument and control systems used to activate HF mitigation systems needed to mitigate the consequences of an HF release located in identified Fire Scenario Envelopes (See API RP 2218 for information on Fire Scenario Envelopes) shall be protected from fire damage unless they are designed to fail safe during a fire exposure. If the control wiring used to activate HF mitigation systems during a fire could be exposed to the fire, the wiring shall be rated for a 15-to-30-minute fire exposure.

#### **9.3.1.2 Remotely Activated Valve Fireproofing**

Power and signal lines connected to key remotely activated valves of HF mitigation systems in Fire Scenario Envelopes shall be protected from fire consistent with 9.3.1.1. The valve's operator (motor or pneumatic) and associated components (i.e., backup air reservoirs, etc.) shall be sufficiently fire protected to provide enough time for the valve to complete its intended function. Valves that fail to the safe position need not be fireproofed. Procedures should be in place to periodically remove fireproofing to inspect valves for potential leaks.

#### **9.3.2 Electrical Power Reliability for HF Mitigation Systems**

Power supplies for HF Mitigation shall be designed, maintained, and tested to meet local applicable codes and standards. A backup power supply shall be provided for the critical electrically powered instruments and control systems.

The need for emergency and essential power supplies for HF Mitigation Systems, including associated control systems, described in sections 9.4 through 9.6 shall be assessed and documented. The assessment should include, but is not limited to, the following considerations:

- a) site-specific HF risk as documented in the required quantitative assessment (Section 9.2),
- b) ambient conditions likely to be experienced at the site (seismic activity; weather conditions such as tornadoes, hurricanes, thunderstorms, or lighting; etc.)
- c) credible emergency scenarios such as fire and explosion,
- d) duration of need for backup power (time required for unit shutdown and/or successful activation of HF mitigation systems),
- e) range of tolerable outage time,
- f) reliability of primary and secondary power supplies (redundancy and/or hardening of primary power such as segregated routing of incoming feed)

### **9.4 Detection Systems**

#### **9.4.1 General**

The objective of HF detection systems is to provide timely information of a leak that can be used to assist in the decision-making process regarding activation of mitigation systems and enactment of emergency

procedures. The open environment of a unit with many siting variables does not support using a detection system for HF exposure monitoring. In addition, detection systems may include hydrocarbon detection and other technologies deemed appropriate for the unit.

#### 9.4.2 HF Sensors

All HF Alkylation units shall have a continuously operating HF detection system with feedback to operations in the control room with following design elements:

- a) Provide coverage for all process areas that contain equipment in Rich HF or Fresh HF service, including storage and loading/unloading areas.
- b) Include both point sensors and open-path perimeter sensors that do not share a common failure mode.
- c) Include backup power source capable of supplying power for short-duration power loss.

The HF detection system should also have the following design elements:

- a) Provide coverage for all process areas that contain equipment in Phase Change HF, Fractionation HF, and Dilute HF service.
- b) Based upon a review of the areas on the unit that have a higher leak probability and consequence, such as areas with flanged piping manifolds, pumps, and areas commonly frequented by personnel.
- c) HF sensors selected and located based on dispersion analysis such that they detect potential HF releases of concern per quantitative assessment criteria under varying weather conditions (including all wind directions, not just prevailing wind directions), release rates, potential leak sources, and elevation.
- d) HF sensors capable of responding effectively under ambient conditions likely to be experienced at a given site.
- e) HF sensor components that are designed and selected to minimize interference from other compounds that may be present in the facility due to potential releases from adjacent units.
- f) Alarm setpoints chosen to provide as early a warning of an HF release as practical without being a nuisance alarm due to detector sensitivities.
- g) Used to automatically activate other mitigation systems to increase the speed of response to the event.
- h) HF sensors used to auto-activate another mitigation system should be designed to minimize the possibility of false activation.

Additional information regarding HF sensor design is provided in K.3.2.

#### 9.4.3 Remote Surveillance

Video cameras shall be placed to provide a view of all process areas that contain equipment in rich HF and fresh HF service, including storage and loading and unloading areas. A bird's-eye-view camera of all HF acid equipment shall be included in this system. Video cameras should have remote pan and zoom capability with a home position pointed at a designated higher-risk area and immediate record/playback capability at the board operator station.

Video monitors shall be located in the control room where operators can readily use them for directing and observing the effects of mitigation measures. When used in conjunction with the HF sensors, video cameras can improve the operator's ability to assess a potential emergency and determine its exact location and scope.

#### 9.4.4 Acid Detecting Paint

Early detection and response to incipient leaks from flanges and threaded connections through the use of acid detecting paint has been proven to prevent larger releases. Acid detecting paint shall be applied to all components as listed in 6.5.13 prior to the introduction of HF acid into the equipment. Refer to 6.5.13 for additional recommendations relating to the application and maintenance of acid detecting paint and 5.3.5.1 for recommendations relating to operations response to acid detecting paint changes.

### 9.5 Water Mitigation Systems

Properly designed water mitigation systems address the leak scenarios by significantly reducing airborne HF. The Industry Cooperative Hydrogen Fluoride Mitigation/Assessment Program (ICHMAP) demonstrated that applying high volumes of water to any release of HF will significantly reduce the airborne fraction of the HF released and provide an effective tool for mitigating the effects of an HF release. The higher the volumetric ratio of water that is in contact with the HF cloud, the larger the reduction in airborne HF (e.g. a 40:1 volumetric ratio of water to HF can achieve a 90% reduction in airborne HF under favorable conditions).

All HF Alkylation units shall have a water mitigation system with the following design elements:

- a) Remotely activated from the control room and at least one other location.
- b) Remotely controlled if movement is a necessary function of the design (e.g., aim-and-shoot system).
- c) Specifically designed for HF mitigation (e.g., nozzle placement, design, and flow suitable for HF vapor mitigation).
- d) Provide coverage to all areas of the unit that contain equipment in rich HF and fresh HF service (e.g. the reaction loop, HF regeneration system, acid boots, fresh HF storage, HF unloading, etc., both elevated and at grade).
- e) Provide continued mitigation for a defined credible HF release scenario until either the HF release is stopped, or the remaining bulk HF inventory has been secured in a safe location.

The amount of time the water mitigation system volume available will last during a credible release scenario shall be documented. A contingency plan for reduced availability of the primary source of mitigation water should be developed. Design considerations for HF water mitigation systems are provided in K.3.3.

Procedures shall address how to operate and optimize the system under different release scenarios and weather conditions. A weather station with feedback to operations on wind speed and direction should be installed to aid in effective water deployment.

If an automated system is used, the activated components should be kept operating until the operator can visually determine which components will provide the most direct and effective mitigation and then should allow the operator to select those appropriate components and turn off those no longer needed.

### 9.6 Mitigation Systems that Limit Event Duration

#### 9.6.1 General

HF Alkylation units shall have a mitigation system that limits the duration of the event to the user-defined evaluation criteria (see 9.2.3). This can be accomplished with remotely activated block valves for HF isolation and/or a rapid acid transfer system (RATS). The quantitative assessment should drive the selection of the item(s) below (remotely activated block valves for HF isolation and/or RATS) that are most appropriate for the site.

### 9.6.2 Remotely Activated Block Valves for HF Isolation

The magnitude of an HF release from an HF alkylation unit can be reduced if remotely activated valves are in place that can quickly isolate the major HF inventories. These remotely activated block valves should be located so that large HF inventories and credible potential leak sources can be safely isolated from each other. If remotely activated block valves are being installed on an existing unit, the overpressure protection systems for impacted equipment shall be reviewed for relief path and relief capability. These remotely activated block valves should be able to be remotely activated from at least two different locations. Remotely activated block valves may be automatically triggered from a detection system, such as for isolating an HF regenerator system or acid pump.

#### Remotely Activated Block Valve for HF Pump Isolation

Pumps in HF service with mechanical seals shall have remotely activated isolation systems with following design elements:

- a) Remotely activated isolation valves on pump suction lines for pumps in Rich HF and Fresh HF services.
- b) A downstream critical check valve (see 6.5.5) if no remote isolation valve exists on the outlet pump discharge.
- c) A means of remotely stopping the pump driver.
- d) Activation of the pump stop and isolation system available in the control room.

These remotely activated systems should also have the with following design elements:

- a) Remotely activated isolation valves on pump suction lines for pumps in Phase Change HF, Dilute HF, and Fractionation HF services.
- b) Remotely activated isolation valves on pump discharge lines.
- c) Activation of the pump stop and isolation system accessible to operators in the unit a safe distance away from the affected pump (approximately 50 ft or more).

Design considerations for remotely activated block valves for HF isolation are provided in K.3.4.

### 9.6.3 Rapid HF Acid Transfer Systems

The duration and thus the magnitude of an HF release in the reactor/settler system of the unit can be reduced by rapidly transferring the HF to a safe location. Systems that do this are termed rapid acid transfer systems (RATSs) or rapid acid deinventory systems (RADSSs). If the required quantitative assessment at an HF Alkylation unit indicates a credible HF release from the reaction circuit can result in a significant HF exposure to member of the public, a RATS system shall be installed. If installed, the critical functions (including transfer of HF from the reaction circuit to the RATS drum) and timing of a RATS shall be verified at least every turnaround cycle.

If installed, a RATS should contain the following features:

- a) A remote method to initiate the system (either manual or automatic).
- b) Isolation of the olefin feed from the reactor/settler system.
- c) Isolation of the acid inputs to the reactor/settler system.

- d) Opening of a flow path for the acid to the safe location. This includes any motive forces required to make the transfer.
- e) If the safe location is vented, the vapors vented during the movement should be sent to an HF gas scrubbing system, which is either adequately sized for the flow and composition of the vented vapor or the limitations of the scrubbing system understood and a mitigation plan for any breakthrough developed.
- f) A remote or automated method to end acid transfer.
- g) Isolation of the acid in a safe location.

For a system to be considered RATS, the total duration from when a leak is first detected to when the HF acid inventory is secured in a separate vessel(s) shall not be more than 15 minutes. This duration should include:

- a) the time required to notice that an HF leak has occurred.
- b) the time required to decide to activate the system,
- c) the time required to activate the system,
- d) the time for all the valves to move to the proper position once the system is activated,
- e) the time required to transfer the HF to a secure location,
- f) the time for the system to recognize that the deinventory process is complete,
- g) the time to close the valves to isolate the inventory.

If a RATS is being installed on an existing unit, the overpressure protection system for new and impacted equipment shall be reviewed for relief path and relief capability, including thermal expansion in piping. Additional design considerations for a RATS system are provided in K.3.5.

## 9.7 Passive Mitigation Systems

Passive mitigations may also be applied to the evaluation criteria for the required quantitative assessment. Passive mitigation systems do not require human or mechanical interaction to function. Examples of passive mitigation systems include flange covers, physical barriers around equipment to provide a coalescing surface for released HF acid and/or direct the release towards water mitigation components, catch-pans, settler compartments, vessel design to minimize HF inventory, vessel baffles to segment HF inventory, minimizing dead-legs and flanges as potential leak sources, dual seal or seal-less pumps, and vapor suppression additives. See 5.3.5.1 and 6.5.4.3.5 for more details around managing flange covers.

For HF storage drums, inventories should be minimized to levels adequate for unit operation, considering the time required to order and receive HF.

The advantage of passive mitigation systems is that they are always available to function as there are no failure-to-activate mechanisms associated with them.



## Annex A (informative)

### PHA Scenarios for Consideration

This annex provides supplemental information to aid in determining potential cause/consequence scenarios when conducting an HF alkylation unit PHA. Table A.1 is intended to act as a point of reference for a qualified PHA team. It is not intended to be a canned PHA nor is it considered to be exhaustive. Not all scenarios will be applicable to all units as the specific equipment and unit configuration will dictate exact cause/consequence scenarios.

This annex is purely informative and is not intended to be included within the scope of API 751 audits.

**Table A.1—PHA Scenarios for Consideration**

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
1. Product treating	Exotherm in KOH treater/defluorinator caused by excessive acid neutralization from acid boot carryover	Rapid pressuring of KOH treater/defluorinator from vaporization of propane or butane. Possible vessel failure, LOC, fire, and personnel exposure.	High acid boot level, reverse flow, misdirected flow, loss of heat to propane stripper	Procedure for proper HF stripper operation. The riser/high hat on the fractionator reflux pump suction. Coalescer on defluorinator outlet. A trip system with EIVs tied to the KOH treater differential temperature (DT). A high-level alarm on depropanizer/overhead accumulator acid boot. HF stripper DT alarm and bottoms low-temperature alarm.
	Depletion of defluorinator alumina material. Defluorinator not operating at high enough temperature to react the organic fluorides. Defluorinator bypass open or leaking.	Loss of LPG containment from corrosion caused pinhole leaks in equipment downstream of product treaters. Increased corrosion rate due to untreated LPG product fluorides.		Calculation of alumina usage to plan for vessel reloads. Sampling for a breakthrough of the defluorinator. Monitoring LPG products for fluorides. Defluorinator inlet low temperature alarm.
2. Feed treatment	High water content of HF acid from poor feed drying or from steam leaking into the process from steam-heated exchangers. Increased water content in HF will lead to increased phase change corrosion in the fractionation section due to the formation of a water-rich phase that will create hydrated iron fluoride scales that are less protective, leading to loss of hydrocarbon	Loss of hydrocarbon and HF containment through pinhole leaks caused by increased corrosion from lost FeF <sub>2</sub> protective layer. Water in acid > 2 wt % causes the formation of a loose FeF <sub>2</sub> scale that does not effectively adhere to the metal.		Moisture analysis on feed driers. Design pressure of process to be greater than the pressure of utility systems. Mitigation safeguards. Online acid analyzer with routine lab test verification. Post release mitigation systems as described in Section 9.

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
	containment.			
	Reverse flow of HF into the Feed Dryers	Exotherm, Equipment damage	"Loss of Feed to the Unit (various causes) - with RV Loss of Feed to the Unit (various causes) - with SIS"	"Relief Device on the dryer (sized such that it can handle the vaporization rate caused by the exotherm). If relief device is not adequate, then may need an added safety system (such as a HIPPS -High Integrity Pressure Protection System)"

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Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
3. Low acid strength : Potential acid runaway condition	Feed treatment—High feed sulfur caused by low caustic quality or poor caustic contacting	Loss of LPG containment from corrosion caused pinhole leaks in equipment downstream of product treaters. Corrosion from high organic fluorides, formed from low acid strength, not treated due to over loading of the treaters.		Design specifications for the caustic contactor and water wash system. Lab analysis on caustic quality and feed sulfur.  Flow meters with alarms on caustic regenerant to ensure good quality of caustic. Online acid analyzer with routine lab test verification.
	Reactor—Feed contaminants, high water content, low ic4/Olefin ratio, low reactor temp, low reactor acid level, low acid circulation, or misdirected caustic from the ARN getting into the acid circuit			Defined operating window for acid strength and feed contaminants. Procedures for acid strength monitoring and control.
	HF regeneration system column—Poor HF regeneration system column operations from low flow to the HF regeneration system column overstripping bottoms and contaminants go overhead and not removed from acid, or column flooding			Online acid analyzer with routine lab test verification. Product treating safety trips.

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
4. Acid and caustic handling	Incorrect use of sulfur-containing caustic that may be processed with acid	Release of H <sub>2</sub> S		Training and procedures for caustic handling and neutralization. Personal H <sub>2</sub> S monitor. Fixed H <sub>2</sub> S monitors with alarms, caustic treating flow rate alarms, and level alarms.
	HF unloading hose failure or human error during unloading leading to HF exposure	Loss of HF acid containment during acid unloading with possible acid burn to an employee, potential on-site or off-plot personnel exposure to HF, and environmental impact.		Procedures, training, and disciplined use of PPE. Controlled unit access during acid unloading. Standby operator. Emergency shutdown (ESD) on the acid trailer and unloading station. Mitigation safeguards.
	Failure to follow unloading procedures. Overpressure of HF acid truck with nitrogen.			Nitrogen supply pressure regulated and controlled by PRV.. Post release mitigation systems as described in Section 9. Connecting HF truck ESD to plant unloading shut down system (per API 751 rev 5 recommendation)
	HF exposure during sampling	A leak of HF acid during acid sampling with possible acid burn to an employee		Procedures, training, and disciplined use of PPE. Controlled unit access during sampling activities. Mitigation safeguards. Area HF detection with alarms. Water sprays.
	Improper draining of KOH treater	Possible caustic burn to an employee from splashing caustic. Possible HF or H <sub>2</sub> S exposure if KOH is spent or presence of COS Possible LPG release if drain is left open too long		Procedures and training for draining KOH treaters including disciplined use of PPE. Enclosed drain systems. Spring operated valves on atmospheric drains
	Overfilling Storage Tank (RAT/RAD)	"Storage tank liquid overflow will result in tank pressure equilibrating to reactor/settler operating pressure. For COP Units this will not result in hitting MAWP of tank but for UOP Units the MAWP will be exceeded resulting in potential overpressure and release of HF acid	Level instrument malfunction, results in operator initiating filling of the tank. (2 Truck drivers and 2 operator would be there, but personnel presence credit	Independent high level alarm; Pressure control valve on the Storage (Rapid Acid transfer) tank Pressure relief device design for liquid overflow, going to a safe location (acid header) Inventory control procedures

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
			is assuming that the unloading station is not next to the acid storage tank.)"	
	Overfilling Storage Tank (fresh truck)	<p>If HF acid trailer unloading was initiating event for high level there is the potential to overfill the vessel and increase backpressure on the transfer truck. If trailer unloading motive force supply pressure is greater than trailer PSV setpoint there is the potential to lift the trailer PSV and release HF to the atmosphere. Ensure that the PSV on the nitrogen supply is set 20% lower than the trailer's HF PSV.</p>	Human error	<p>"HF Acid Loading procedure HF acid detectors and alarms (mitigation, not prevention) Independent high level alarm with operator response Pressure relief device design for liquid overfill Inventory control procedures Water curtain automatically activated by HF detectors or by operations (mitigation). Check valve on the discharge of the Fresh Acid Pump</p>

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
5. ASO neutralization (with NaOH or KOH)	Poor ASO neutralization from low caustic strength or low caustic circulation.	Corrosion in other refinery units from processing unneutralized ASO		Specification on maintaining caustic strength. Caustic circulation low flow alarm. Caustic level alarm.
	Blocked flow downstream of static mixer or Plugging in the static mixer causing loss of pressure differential between HF regeneration system (Rerun column) and caustic injected into ASO Neutralization system	Reverse flow of caustic from ASO/polymer/constant boiling mixture treatment into HF regeneration system vessel. Violent reaction when caustic is added to concentrated HF. Potential HF regeneration system vessel failure, LOC, fire, and personnel exposure.	Plugging in the static mixer causing loss of pressure differential between HF regeneration system and caustic injected into ASO/polymer/ constant boiling mixture treatment	Car Seal open any manual block valve in caustic circulation path. Limit pump discharge pressure to prevent backflow (making scenario not credible) Post release HF Mitigation system. (Note that Dual Critical check valves are recommended but should not be counted as IPLs since this is a potentially fouling service)
	Caustic carryover (due to High caustic level in caustic treater or process rates above design).	Potential catalyst poison from caustic carryover when processing ASO in some units. Possible cracking (both KOH caustic cracking and fluoride stress corrosion cracking) leading to loss of containment if downstream disposal sites have metallurgy susceptible to stress corrosion cracking.		Conductivity probe with alarm on the ASO material. Level alarms. Procedures to check for and drain caustic before transferring Appropriate metallurgy to prevent cracking
6. Improper venting of light hydrocarbon from atmospheric storage tanks	High rundown temperatures (insufficient cooling).	Potential hydrocarbon LOC and fire. Potential to sink a floating roof.		Product heat exchanger designed for end-of-run and summer operating conditions. High rundown



				temperature alarm.
	Low tower bottoms temperature with high RVP material rundown to an atmospheric storage tank			Operating procedures and training. Column bottom temperature alarm.
	Low tower bottoms level with LPG material rundown to an atmospheric storage tank			Operating procedures and training. Column bottom level alarm.
	Storage Tank overpressure	For UOP Units where the motive gas is the isostripper overhead, if the isostripper overpressures during the deinventory event it is possible to exceed the MAWP of the storage tank result in tank failure and a HF acid release. Severity is based on the assumption of a major HF acid release.	Acid deinventory logic malfunction such that hydrocarbon is dumped to the acid storage vessel (only applies during dumping) Deinventory tank has high initial level so there is not room for complete deinventory volume which could be due to leaking valves or malfunctioning level instrument."	High level alarm in the acid tank with operator response High deinventory vessel level interlock that isolates the tank High level alarm in the acid tank with operator response High deinventory vessel level interlock that isolates the tank
	Sending LPG/HF acid to the alkylate treater (if one exists) and to the alkylate storage tank.	Potential to sink floating roof storage tanks and release of LPG and HF acid to the atmosphere resulting in fire and personnel exposure.	Iso-stripper bottoms level control valve fails open	Independent low level alarm
7. Vessels	Liquid fill of acid settler that normally has a vapor space in the vessel, due to blocked outlet	Potential overpressure of acid settler [if feeds (recycle iC4/olefin feed stream) can supply enough pressure]. Potential LOC of LPG followed by HF, fire, and on-site personnel exposure to toxic (HF).	Trip of main fractionator/isostripper feed pump or fail or malfunction close of feed valve to main fractionator/isostripper	PRD rated for liquid fill case, high level trips, high pressure trips, alarms.
	High pressure flow source to an acid settler designed for a vapor space	Potential overpressure of acid settler	Failed check valve on a split feed style fractionation system (depropanizer over pressures settler)	Identify critical check valves

	Sending Acid to Alkylate	Potential personnel exposure to HF Acid when dewatering or sampling. These would be operators not used to HF Acid and they may not recognize the Acid burn, If there are glass components, loss of containment within a short time after exposure to HF Acid.  Corrosion at the Alkylate Storage Tank, Loss of containment, release of Alkylate. Potential for tank fire."	Low bottoms temperature / loss of reboiler	"Caustic Heel in Alkylate Tank will neutralize HF Acid. Independent Low bottoms temperature alarm on upstream tower
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Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
8. Acid relief neutralization (ARN)	ARN low caustic strength during active venting of HF containing stream. (Assumes normal starting concentration is 30-45% in KOH systems. Assumes normal starting concentration is <5% in NaOH systems. Break through can be more rapid in NaOH than in KOH systems but with same consequence severity.)	An HF acid leak to the atmosphere through the flare, most likely accompanied by burning hydrocarbon leading to a well-dispersed and diluted atmospheric acid release		Specifications and procedures on maintaining caustic strength. Submerged vent gas absorber (VGA) inlet to ARN. Caustic circulation low flow alarm.
	PRV release of HF-containing stream that enters the ARN with low caustic strength, low caustic circulation, or poor caustic contact. (Assume low caustic strength typically occurs once per week. Also, assume PRV release is due to a blocked-in case.)			
	A blocked outlet of the acid settler vessel upstream of the ARN along with a high caustic level in the ARN. Wet caustic carryover fouling the flare line.	Overpressure of ARN from blockage of outlet due to auto-refrigeration of caustic solution or fouling of the flare line leading to loss of containment of HF acid and LPG with possible fire from an ARN vessel failure		Submerged VGA line into the ARN. Knock out drum upstream of ARN. RT of flare line for deposits. Mitigation safeguards. Temperature alarms on ARN caustic. Caustic high-level alarm. Rupture disk bypass around the ARN. Post release mitigation systems as described in Section 9.
	High liquid hydrocarbon flow to ARN/RGS freezes caustic in the upper trays due to LPG flashing	Blocked flow within ARN, potential overpressure of piping and equipment. A potential LOC of LPG and trace HF, a potential on-site personnel exposure to toxic (HF), or a potential fire.	High liquid relief rate from misalignment; inadvertent routing of high flow of LPG to ARN from a liquid full vessel such as a fractionator overhead total condensing systems or receiver/surge drum	Temperature alarms on ARN caustic. Caustic high-level alarm. Rupture disk bypass around the ARN. Post release mitigation systems as described in Section 9.

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
<b>HF Alkylation Specific Pump Scenarios</b>				
9. Pump failure	Acid circulation pump seal failure (some pumped acid units) from loss of seal flush flow rate and/or seal reservoir level or pressure	HF acid release from pump seal leak (high volume pump)		Mitigation safeguards. Dual seal pumps with barrier fluid IPL alarm system and/or seal flush flow/IPL Alarm, use of sealless pumps. Post release mitigation systems as described in Section 9.
	HF regeneration system pump seal failure from loss of seal flush flow rate and/or seal reservoir level or pressure	HF acid release from pump seal leak (modest volume pump)		Vibration monitoring system with shut down capability. Evaluate use of Seal-less pumps.
10. Pump Seal Failure on Deprop Feed, Deprop Reflux, or Frac Feed pump	Loss of seal flush from low HF/propane stripper tower level (mechanical or operational)	Pump seal failure and possible fire on depropanizer/isostripper reflux pump, HF/propane stripper feed pumps, or unit fractionation feed pump		Operating procedures and training. Adequately designed surge volume on stripper bottom with level indication. Mitigation safeguards. Dual seal pumps with barrier fluid alarm system. HF/propane stripper tower bottom level alarm. Post release mitigation systems as described in Section 9. Dual seal pumps with barrier fluid alarm system. HF/propane stripper tower bottom level alarm. Post release mitigation systems as described in Section 9. Alternative flush system or evaluate self-flushing of pumps
<b>HF Alkylation Specific Fixed Equipment Scenarios</b>				
11. Global LOC of HF	1 in. or greater leak of HF acid from concentrated HF service equipment or piping	Loss of containment of HF, potential on-site personnel exposure to toxic (HF)	Piping or equipment failure in concentrated HF service equipment or piping, 1 in. or greater in size	Post release mitigation systems as described in Section 9. Activate an idling, standby or shut down control strategy
12. Flange or gasket leak	Poor flange face condition, poor flange fit-up, or poor bolt torquing	Small, wisping leak of HF and/or hydrocarbon from flanges; fire is not likely	A consequence of interest if the unit history indicates repeated flange leaks	Torque procedures and craftsmanship with routine auditing. Hot bolting practice. Mitigation safeguards. Post release mitigation systems as described in Section 9.

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
13. PRV and PRV piping	Inadequate unit dry-out, oxygen removal inadequate or piping dead-legs causing corrosion and deposits in the PRV piping	Reduced PRV capacity from pipe fouling. Potential vessel overpressure and flange leak.		A design specification for PRV inlet piping purge of the dead zone and free-draining piping. Operating procedures and training. Insulate depropanizer/isostripper and defluorinator PRV inlet piping to minimize acid condensation. RT of headers. Mitigation safeguards. Post release mitigation systems as described in Section 9.
	Misplacement of depropanizer/isostripper PRV—Liquid relief if placed too low in the tower	High-pressure transition when liquid relieves through a vapor relief system. Potential vessel overpressure and flange leak.		A design specification for PRV placement. Mitigation safeguards. Post release mitigation systems as described in Section 9.
	Misplacement of depropanizer/isostripper PRV—Valve corrosion if placed too higher in the tower	Diminished PRV operation from valve corrosion. Potential vessel overpressure and flange leak.		A design specification for PRV placement. Purge on PRV inlet. Mitigation safeguards. Post release mitigation systems as described in Section 9.
14. Furnace tube failure	Furnace tube overheat or coking from low process flow rates	Potential for tube rupture and alkylate or LPG fire contained in the firebox		Tube metal temperature monitoring. Routine infrared inspection. Operator response to low process flow alarm. Auto spare pump startup.

Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
15. Corrosion	Exceeding temperature limits; > 160 °F for carbon steel, > 300 °F for Alloy 400	Loss of containment of hydrocarbon and HF acid in the depropanizer/isostripper feed line, acid vaporizer, or HF regeneration system column caused by temperature accelerated corrosion – longer term		Temperature limits on material selection. Process temperature monitoring with an appropriate follow-up inspection. Mitigation safeguards. API 751 audit checklist to verify adequacy and use of management safeguard systems. Process temperature alarms with operator response. Post release mitigation systems as described in Section 9. Online corrosion monitoring probes
	Operating the unit at feed rates in excess of the design rate reduces the settler residence time and increased acid carryover from the settler to the depropanizer/isostripper	Loss of containment of LPG and HF acid through pinhole leaks in the top of the depropanizer/isostripper caused by acid corrosion – longer term		Monitoring depropanizer overhead acid boot level control valve position to detect additional acid flow. Monitor settler velocity/flux rates or residence time and fractionator acid boot collection/flow rates to detect a change in entrained acid flow. Mitigation safeguards. Unit feed rate standard operating level (SOL). Post release mitigation systems as described in Section 9.
	Use of carbon steel material in an Alloy 400 service	Loss of containment of hydrocarbon and/or HF acid through leaks caused by accelerated corrosion from wrong metallurgy use		QC, PMI practices, and retro-PMI inspections to verify proper metallurgical use. Mitigation safeguards. Post release mitigation systems as described in Section 9.
	Metal with REs greater than 0.15 wt %	Loss of containment of hydrocarbon and/or HF acid		QA and PMI practices to verify



Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
		caused by accelerated corrosion from poor metal quality.		metallurgical content. Mitigation safeguards. Post release mitigation systems as described in Section 9.

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Initiating Category	Causes	Consequence	Initiating Event	Possible Safeguards
Corrosion (continued)	Acid condensation corrosion from excessive process cooling	Loss of containment of LPG and HF acid in the HF regeneration system column overhead line or product cooler outlet line (between the defluorinator and caustic treaters) from accelerated corrosion		Insulate HF regeneration system overhead line to minimize cooling. The line is to be free draining. Mitigation safeguards. Product cooler outlet temperature indicator with operator response to low temperature. Post release mitigation systems as described in Section 9. Alternative metallurgy
	Failure to PWHT caustic containing equipment	Loss of containment of process material, as a result of SCC		Standards for PWHT of all carbon steel in caustic service. Use of nitrogen rather than steam for vessel purging. Process temperature limit based on caustic strength if not PWHT (see NACE SP 0403). Verification of PWHT.
	Acid leaks to the cooling water or steam condensate system. Exposure to all equipment sharing the same cooling water or condensate system.	Loss of hydrocarbon containment to the cooling water caused by accelerated corrosion from low pH water or low pH condensate	Exchanger tube leaks	The design pressure of utilities (steam and cooling water) is less than process pressure. Dedicated cooling water tower for the unit. Cooling water fluoride or pH monitoring. Condensate pH, fluoride, or conductivity monitoring with alarm, special procedures to manage pressure during transitional periods
	Iron fluoride hydrolyzing with alkylate tank bottoms water causing a low pH solution and accelerated corrosion of the tank floor	Alkylate storage tank floor leak with potential for a pool fire	Tube leak in main fractionator/isostripper feed/effluent exchanger, tower upset, or purposeful slumping	Routine testing of water draws for pH. Caustic heel in the alkylate storage tank with routine testing for pH. Tank coating. Product rundown treatment.

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## **Annex B**

### **(informative)**

## **Elements of a Comprehensive Audit**

This annex provides supplemental information to aid in the creation of a comprehensive audit for HF alkylation systems and procedures. This annex is purely informative and is not intended to be included within the scope of API 751 audits.

The following audit approach provides elements that are merely examples for illustration purposes only. Refer to 4.2 for the requirements pertaining to audits of HF alkylation systems and procedures.

### **Example Comprehensive Audit Approach**

- a) A checklist for the site to fill out prior to the audit comparing the site's operations to the recommendations of API 751. The checklist should be used by the audit team as one input to planning the audit strategy.
- b) An audit team with a diversity of skills related to HF alkylation. Skills to be considered, depending on the systems and procedures to be audited, include:
  - c) inspection/corrosion,
  - d) mechanical/maintenance,
  - e) operations,
  - f) process engineering,
  - g) process hazards management,
  - h) emergency response,
  - i) instrumentation/analyzers, and
  - j) process control.
- k) Walkthrough(s) of the unit to look at the following items:
  - l) firefighting access, escape routes, location of emergency discharge vents, housekeeping, isolation of surface drains, and access to potential leak sites;
  - m) condition of and care of process equipment, including operations and maintenance duties;
  - n) conduct/permitting of activities on the unit;
  - o) validation of compliance with procedures and applicable law;
  - p) labeling of lines, key valves, instrument settings, alarm and trip systems, emergency shutoffs, and unit access limits and warnings;
  - q) safety equipment, including fire extinguishers, hydrants, hoses, respiratory gear, PPE (use, condition, care, cleaning), grounding provisions, emergency communications systems, safety showers, eyewash stations, mitigation and detection equipment, and first aid equipment.

- r) A systems review that includes the following items:
- s) review of process control for the specification of normal control ranges, alarm management, system software and backup, instrument and equipment redundancy, up-to-date piping and instrumentation diagrams, and instrument reliability history;
- t) review of detection systems for mechanical condition, testing and repair history, calibration frequency, and frequency of nuisance trips; and,
- u) review of mitigation systems for mechanical condition, repair history, fire protection, and testing.
- v) Unit Safety Systems and how they are activated for
- w) Water mitigation systems
- x) Acid evacuation or rapid acid transfer / deinventory systems
- y) Preventing significant HF quantities entering Product treaters
- z) Remote isolation devices
- aa) Moving the unit to a safe operating state (safe park) in the event of an emergency
- bb) Preventing an overpressure of HF service equipment in addition to Pressure relief valves
- cc) A review of operating procedures for all appropriate activities that cover technical correctness, clarity, the ease with which the procedures can be followed, and completeness. The date of the last review should be checked, and the inclusion in the review of all changes to the unit should be verified. Logbooks, checklists, work and entry permit procedures, training manuals and materials, and other records should also be reviewed.
- dd) A review of preventive and predictive maintenance procedures and maintenance records covering mechanical equipment, piping, trip systems, vessels, interlocks, safety relief valves, detection devices, mitigation systems, equipment neutralization, and use of PPE in the shop area.
- ee) A review of inspection procedures, methods, and schedules. Records should be up-to-date and should reflect the current condition of the unit. Reports of inspection findings and the status of recommendations should also be reviewed.
- ff) Interviews with key operating, engineering, emergency response, medical, maintenance, and inspection personnel concerning maintenance, QC, safety, training, operating procedures, management of change, emergency procedures and simulations, and other matters not easily found in unit records. The interviews should be structured to elicit any concerns that people may have, to determine that they are familiar with applicable operating and maintenance procedures and safety and emergency plans and to assess the effectiveness of training programs.
- gg) A review of the emergency response plan, the site's Toxic Refuge Facility siting plan in the event of an HF release and the documentation of emergency drills to determine the plan's effectiveness. Such matters as notification procedures, response, agency interaction, and community outreach should be considered, as should visits to first aid and medical-response sites. First aid kits should be checked to ensure that they contain up-to-date materials. It should also be verified that personnel have been trained in the use of the kits.
- hh) A review of the latest PHA and recent management of change records to validate compliance with site and regulatory requirements.

- ii) A review of any injuries (notably any HF injuries) or incident investigations (notably any HF releases) that occurred on the unit since the last audit. This review should be conducted to ensure that any agreed-upon action items from injury and/or incident investigations are complete.
- jj) Other audit activities appropriate to the specific site.

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## Annex C (informative)

### HF Exposure Limitations and Guidance Criteria

#### C.1 General

The limitations and guidelines listed below (Table D.1, Table D.2, and Table D.3) were in effect at the time of publication. Users of this recommended practice need to consult the most recent edition of the source for each limitation or guideline to confirm whether or not the information listed below is current.

Refer to 5.2 for guidance in using this annex.

#### C.2 HF Exposure Limitations and Guidelines

Table D.1—Occupational Exposure Limitation

Organization	Reference	Level	Duration	Concentration (ppm)	Notation
OSHA	<sup>a</sup>	PEL TWA	8 hours per day	3	N/A
ACGIH <sup>®</sup>	<sup>b</sup>	TLV <sup>®</sup> ceiling <sup>c</sup>	N/A	2	Skin, BEI <sup>®</sup>
ACGIH <sup>®</sup>	<sup>b</sup>	TLV <sup>®</sup> TWA	8 hours per day	0.5	Skin, BEI <sup>®</sup>
ACGIH <sup>®</sup>	<sup>b</sup>	BEI <sup>®</sup>	Prior to shift End of shift	2 mg/L 3 mg/L	Fluoride in urine, B, Ns
NIOSH	<sup>d</sup>	REL TWA	8 hours per day	3 (2.5 mg/m <sup>3</sup> )	N/A
NIOSH	<sup>d</sup>	STEL ceiling	15 minutes	6	N/A
NIOSH	<sup>d</sup>	IDLH	≤30 minutes	30	N/A

<sup>a</sup> OSHA 29 *CFR* 1910.1000, Table Z-2.

<sup>b</sup> ACGIH<sup>®</sup>, TLV<sup>®</sup>, and BEI<sup>®</sup> are registered trademarks of the American Conference of Governmental Industrial Hygienists. 2019 ACGIH<sup>®</sup>, TLVs<sup>®</sup>, and BEIs<sup>®</sup> are based on the *Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*.

<sup>c</sup> A ceiling is a concentration that should not be exceeded during any part of the working exposure.

<sup>d</sup> NIOSH *Pocket Guide to Chemical Hazards and Occupational Health Guideline for Hazardous Chemicals: Hydrogen Fluoride*.

BEI<sup>®</sup> = Notation for "Background"—The determinant may be present in biological specimens collected from subjects who have not been occupationally exposed, at a concentration that could affect the interpretation of the result.

B = BEI<sup>®</sup> notation for "Background"—The determinant may be present in biological specimens collected from subjects who have not been occupationally exposed, at a concentration that could affect interpretation of the result.

Ns = BEI<sup>®</sup> notation for a nonspecific determinant that may be observed after exposure to other chemicals.

Skin = TLV<sup>®</sup> designation indicating for the potential significant contribution to the overall exposure by the cutaneous route, including mucous membranes and the eyes by contact with vapors, liquids, and solids.

**Table D.2—AIHA™ Emergency Response Planning Guidelines (ERPG™) in ppm <sup>a</sup>**

	≤10 Minutes	≤60 Minutes
ERPG-1	2	2
ERPG-2	50	20
ERPG-3	170	50
<sup>a</sup> 2018 Emergency Response Planning Guidelines (ERPG™) and Workplace Environmental Exposure Levels (WEEL™) Handbook. AIHA™, ERPG™, and WEEL™ are trademarks of the American Industrial Hygiene Association.		

**Table D.3—Acute Exposure Guideline Levels (AEGLs) for HF, in ppm <sup>a</sup>**

	10 Minutes	30 Minutes	60 Minutes	4 Hours	8 Hours
AEGL-1	1.0	1.0	1.0	1.0	1.0
AEGL-2	95	34	24	12	12
AEGL-3	170	62	44	22	22
<sup>a</sup> EPA website: <a href="https://www.epa.gov/aegl">https://www.epa.gov/aegl</a> .					

### C.3 Emergency Response Planning Guidelines (ERPG™)

As defined by AIHA™, the ERPG™ values are intended to provide estimates of concentration ranges where one reasonably might anticipate observing adverse effects as described in the definitions for ERPG-1, ERPG-2, and ERPG-3 (listed below) as a consequence of exposure to the specific substance.

The ERPG™ definitions are as follows.

- ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.
- ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
- ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing or developing life-threatening health effects.

### C.4 Acute Exposure Guideline Levels (AEGLs)

AEGLs are used by emergency planners and responders worldwide as guidance in dealing with rare, usually accidental, releases of chemicals into the air. AEGLs are expressed as specific concentrations of airborne chemicals at which health effects may occur. They are designed to protect the elderly, children, and other individuals who may be susceptible.

### C.5 AEGLs Assigned 1, 2, or 3 According to Severity of Effects

AEGLs are calculated for 5 relatively short exposure periods—10 minutes, 30 minutes, 1 hour, 4 hours, and 8 hours—as differentiated from air standards based on longer or repeated exposures. AEGL “levels” are

dictated by the severity of the toxic effects caused by the exposure, with Level 1 being the least and Level 3 being the most severe.

All levels are expressed as parts per million or milligrams per cubic meter (ppm or mg/m<sup>3</sup>) of a substance above which it is predicted that the general population could experience, including susceptible individuals.

- a) *Level 1*: Notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
- b) *Level 2*: Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- c) *Level 3*: Life-threatening health effects or death.

## C.6 Below AEGL Level 1

Airborne concentrations below the AEGL-1 represent exposure levels that could produce mild and progressively increasing but transient and non-disabling odor, taste, and sensory irritation or certain asymptomatic, non-sensory effects. With increasing airborne concentrations above each AEGL, there is a progressive increase in the likelihood of occurrence and the severity of effects described for each corresponding AEGL.

AEGL values represent threshold levels for the general public. As mentioned, that includes susceptible subpopulations, such as infants, children, the elderly, persons with asthma, and those with other illnesses. However, it is recognized that individuals, subject to unique or idiosyncratic responses, could experience the effects described at concentrations below the corresponding AEGL.

## C.7 Use of “Dose” and Probit Equations

For consequence and risk-based studies, it is helpful to conduct the analysis utilizing a dose (the combination of exposure concentration and duration) instead of an exposure concentration. The use of dose allows evaluation of the benefit of mitigation options that address the duration of the release (exposure). Probit equations provide a way to define the relation between dose (exposure concentration, exposure duration) and lethality probability. The general form of the probit equation is provided below:

$$Pr = a + b \ln(C^n T)$$

where

a, b, and n are constants;

*C* is the exposure concentration (ppm);

*T* is the exposure duration (minutes).

Several probit equations have been developed for HF exposure and probit tables are found in AIChE Center for Chemical Process Safety's *Guidelines for Chemical Process Quantitative Risk Analysis*. See Table D.4.

**Table D.4—Probit Constants**

Probit Source	Probit Constants		
	n	a	b
Mudan <sup>1</sup>	1	-26.36	2.854
TNO Purple Book <sup>2</sup>	1.5	-8.4 mg/m <sup>3</sup> (-8.62 ppmv)	1
U.S. Coast Guard (1980) <sup>3</sup>	1	-25.87	3.354
World Bank (1988) <sup>4</sup>	1	-26.4	3.35
<p>Sources:</p> <ol style="list-style-type: none"> <li>1. Lees, F.P., <i>Loss Prevention in the Process Industries</i>, Second Edition, Elsevier, 1996. Mudan, K.S., "Use of Toxicity Data in Quantitative Risk Assessment of HF Alkylation Units," paper presented at <i>AIChE Summer National Meeting</i>, 1989, Philadelphia, PA.</li> <li>2. TNO Purple Book, prepared for the Committee for the Prevention of Disasters, "Guidelines for Quantitative Risk Assessment, CPR18E. SDU," The Hague, 2005.</li> <li>3. Perry, W.W., and W.P. Articola (1980), "Study to Modify the Vulnerability Model of the Risk Management System," U.S. Coast Guard, Report CG-D-22-80, February 1980.</li> <li>4. World Bank's manual, <i>Techniques of Assessing Industrial Hazards: A Manual</i>, Technical Paper No. 55, Washington, DC, 1988 (Section D.2, Table D.2, Toxic Properties of Some Materials).</li> </ol>			

## Annex D (informative)

### An Approach for HF Leak Tracking and Management

#### D.1 Scope

The purpose of this annex is to provide an example of how to establish a program to effectively detect, track, and manage incipient leaks on the HF alkylation unit. The intent of the program is to ensure that a timely repair can be made before the magnitude of a leak increases significantly.

The requirements for this program are specified in 5.3.5.

#### D.2 Definitions

The following definitions are unique to Annex E and the example leak tracking and management program described herein:

- a) *active leak*—a leak that has been identified, and not yet addressed;
- b) *mitigated leak*—a leak that has been temporarily repaired (e.g. bolt change-out, engineered clamp, etc.);
- c) *permanent repair*—a permanent repair is defined by:
  - d) new piping,
  - e) new valve,
  - f) new gasketing.

### D.3 Category 1 Leak: Paint Discoloration

Category 1 leaks are defined by a color change on the acid detecting paint, from yellow to red. No visible fluoride scale or HF smoking or dripping are observed. See Figure E.1



Figure E.1—Examples of Category 1 Leaks



#### D.4 Category 2 Leak: Fluoride Scale Buildup

Category 2 leaks are defined by the presence of visible buildup of fluoride scale. No visible HF (smoking or dripping) is observed. Fluoride scale can be described as a crusty buildup inside flanges, around valve packing, at plugs on bleeder valves, around channel heads or tubesheets on exchangers, etc. Green fluoride scale results from HF contact with Monel® in the presence of oxygen. See Figure E.2.



Figure E.2—Example of Category 2 Leak



## D.5 Category 3 Leak: Visible HF Acid Leak

Category 3 leaks are defined by the presence of visible HF (either smoking or dripping). HF forms a white cloud similar in appearance to a steam leak when released to the atmosphere. Small leaks may be seen as a wisp or puffing out from a flange, valve packing, around a plug on a bleeder valve, or around the channel heads or tubesheets on exchangers, etc. See Figure E.3.



Figure E.3— Example of Category 3 Leak

## D.6 Surveillance Program

A key factor in the success of this program is the effectiveness of conducting routine surveillance of all HF unit connections covered by the program. Establishing the frequency of various surveillance tasks helps ensure the effectiveness of the program.

An example frequency of conducting surveillance is provided here for informational purposes:

- a) all HF unit connections and temporary enclosures covered by the program checked monthly by process operators;
- b) all active leaks checked each shift by process operators;
- c) all mitigated leaks checked on the same frequency as the original active leak, for a specified period of time following the repair attempt (2 weeks minimum);

- d) all personnel entering unit trained to identify leaks, both active or new, and how to respond;
- e) unit inspector does quarterly checks of all temporary enclosures (i.e. clamps).

## D.7 Priority of Addressing Leaks

Setting the appropriate priority on addressing incipient leaks is a key factor in the effectiveness of this program, as higher severity leaks require action to be taken more urgently than less severe leaks.

An example priority of repair of leaks under this program is provided here for information.

- a) Category 1 (paint discoloration).
- b) Assessed by inspection within 72 hours of initial detection.
- c) First repair attempt made within 7 days of initial detection.
- d) Category 2 (fluoride buildup).
- e) Assessed by inspection within 24 hours of initial detection.
- f) First repair attempt made within 48 hours of initial detection.
- g) Category 3 (visible HF smoking/dripping).
- h) Immediate response, inspection, and first repair attempt.
- i) Permanent repair to be provided as soon as practical, never to exceed next turnaround or design life of the temporary repair.

## D.8 Leak Tagging

The use of uniquely numbered physical tags installed at the leak site serves several key functions in this program. In addition to providing a visual cue to all personnel in the area that an active or mitigated leak is present, it also enables full tracking of each and every leak as a separate, independent entity when determining repair priorities, maintenance activities, etc. Finally, it helps identify and track repeat leaks following initial repair.

Examples of the key features of an effective leak tagging program are provided here for information.

- a) Tags constructed of metal and attached with metal wire to ensure durability.
- b) Tags are numbered so that each leak has a dedicated unique number assigned to it.
- c) Two tag system employed using distinctly different colors:
- d) one set of tags to denote active leaks—this tag stays on the leak until 2 weeks past the mitigated repair,
- e) a different set of tags to denote mitigated leaks—this tag stays on the leak until the permanent repair is completed,
- f) tag number for mitigated leak matches tag number used for an active leak, but in a different color.
- g) All leak tags without a permanent repair addressed at next planned turnaround.

## D.9 Leak Tracking

A leak tracking system serves two main functions:

- h) helps ensure permanent repairs are completed on equipment that has leaked during the next planned major outage or turnaround; and,
- i) helps identify long-term or system-wide issues.

Leak tracking programs can vary in complexity and scope. The most basic form can be a simple spreadsheet containing a running log of leaks that have occurred on the equipment in HF service. Examples of basic data that can be tracked includes:

- a) date leak identified;
- b) leak tag number/date applied;
- c) leak severity/category (e.g. Category 1, Category 2, or Category 3);
- d) leak location (e.g. exchanger: E-001 tubesheet/shell flange; control valve: CV-001 inlet; plug valve: E-001 inlet isolation valve, etc.)—detailed description recommended;
- e) equipment type (e.g. exchanger, valve, piping, pump, etc.);
- f) equipment sub-type (e.g. plug valve, gate valve, centrifugal pump, exchanger shell, etc.);
- g) equipment manufacturer;
- h) equipment circuit (e.g. acid regeneration, isostripper overhead, depropanizer feed, etc.);
- i) equipment materials/metallurgy (e.g. carbon steel, Monel®, Hastelloy®, PTFE);
- j) dead-leg/stagnant zone;
- k) repair description (e.g. machined flange, replaced gasket, installed engineered clamp enclosure, etc.);
- l) repair completion date.

Database tools have been used for more complete programs or multi-site leak tracking. Some companies have developed data entry forms with dropdown menus to drive easy and consistent data entry. Users can enter more details, such as equipment manufacturer or operating conditions, in a short period of time. These details can help identify trends and underlying causes. Databases can store additional types of data, such as photos of leaking equipment for future clarity and repair documents all in one location. Database tools equipped with workflow functions can be used for automatic notification of unit personnel, supervision, and inspection personnel and drive approval processes for recommended repairs. Reports and lists of active leaks can be quickly produced as tools for routine checks, along with comprehensive reports for turnaround work planning.

## Annex E (informative)

### Examples of Tasks for Each Clothing Class

#### E.1 Clothing Classes

Following are some examples of planned work, not emergency response activity, for each of the four classes of personal protective clothing and equipment defined in this recommended practice.

- a) *Traditional Class A Protective Clothing and Equipment (Corresponds to OSHA Level D)*—Examples of routine work include but are not limited to reading meters and gauges in the field, visually inspecting the unit, unloading or dumping alumina (not exposed to HF); repairing equipment that has been opened, disassembled, and neutralized so that no HF can be trapped within; working on non-HF-containing equipment in an HF area if there is no other HF-area work going on nearby; reassembly of thoroughly cleaned HF equipment; welding on equipment that has been properly prepared for welding; and painting.
- b) *Traditional Class B Protective Clothing and Equipment (Corresponds to OSHA Level C)*—Examples of routine work include but are not limited to operating valves in main or trace acid service, greasing of valves, washing down, collecting samples of non-HF-containing materials, pump work after blinding has been completed and the cover plate removed, reboiler work (after column manways have been opened), dismantling safety relief valves (when there is no potential for trapped HF), and disassembling HF equipment that has been opened and neutralized, including exchangers and condensers with HF-containing tubes that are known to be unplugged.
- c) *Traditional Class C Protective Clothing and Equipment (Corresponds to OSHA Level B)*—Examples of routine work include collecting samples that contain a potentially harmful quantity of HF, changing pressure gauges in HF areas, blinding and opening of lines where equipment has been depressured, working on any HF equipment that is not blinded at the first flange, the initial opening of equipment after blinding (including exchanger heads, manways, and flanges), working on small piping manifolds before it is established that no HF can be trapped inside attached equipment (including work on meters and meter manifolds and valves, disassembly of pumps, and disassembling exchangers and reboilers that contain HF before tubes are unplugged); and connecting and disconnecting HF loading hoses (see 7.1.4 for further details).
- d) *Traditional Class D Protective Clothing and Equipment (Corresponds to OSHA Level A)*—Examples of work include repairing failed pump seals and valve packing and working in close proximity to leaks that require lines or equipment to be isolated.

## **Annex F**

### **(informative)**

## **Corrosion and Materials Considerations Specific to HF Alkylation**

### **F.1 General**

This annex provides discussion for the various corrosion mechanisms in different HF services (corrosion zones), materials that are and are not used in HF alkylation units, and the use of IOWs, all of which are based on published information and owner-operator experience. Additionally, MTI MS-4 and NACE 5A171 are useful references that provide a summary of published information on materials commonly used and to be avoided and corrosion data for a wide range of HF services including services found in HF alkylation.

### **F.2 Materials of Construction Considerations**

#### **F.2.1 Carbon Steel**

##### **a) General**

Carbon steel is the most common material of construction in HF alkylation units due to its relatively low corrosion rates in HF alkylation services. When exposed to HF, it typically forms a protective iron fluoride layer that reduces corrosion rates relative to carbon steel with no fluoride protective layer. However, the effectiveness of the protective layer can be either reduced or lost by operating outside design boundaries, especially with respect to flow velocities and HF water content. The other product of the corrosion reaction between HF and carbon steel is atomic hydrogen. When operating outside of design boundaries, accelerated corrosion and increased hydrogen charging of the steel are common effects.

The process conditions of temperature, HF water content, and velocity can impact carbon steel corrosion rates in HF. Carbon steel has demonstrated satisfactory resistance to corrosion in free HF or concentrated HF (such as in acid storage, reactors, and settlers) up to approximately 120 °F (49 °C) and in dissolved HF or vapor phase HF (such as settler effluent and iC4 recycle systems) up to approximately 160 °F (71 °C).

In some cases, carbon steel has shown satisfactory corrosion resistance up to approximately 170 °F in column overhead vapor lines and up to approximately 180 °F in column feed lines where the HF content is well below the solubility limit. In these cases where the temperatures are above 160 °F, corrosion rates tend to be higher and may warrant increased inspection frequency. Corrosion rates may be reduced by minimizing free HF entrainment from upstream equipment and keeping the water content of the circulating HF below about 1.5 wt %.

##### **b) Environmental Cracking of Carbon Steels**

Carbon steel and HF react to form iron fluoride and atomic hydrogen. The atomic hydrogen from this reaction can diffuse into the steel and result in various forms of damage. These include blistering, hydrogen embrittlement, hydrogen stress cracking in hydrofluoric acid (HSC-HF), hydrogen-induced cracking (HIC), and stress-oriented hydrogen-induced cracking (SOHIC). HSC-HF, HIC, and SOHIC are forms of environmental cracking damage.

HSC-HF in HF service is typically managed by limiting hardness in carbon steel and welds. Blistering, HIC, and SOHIC base metal hydrogen damage is typically managed by specifying requirements for steel making cleanliness controls and PWHT. See 6.3.2.1 for further details.

Atomic hydrogen from the HF-carbon steel corrosion reaction can enter the steel and can cause various forms of environmental cracking such as HSC-HF, HIC, hydrogen blistering, and SOHIC. Steels with high inclusion content and laminations are more susceptible to hydrogen blistering and HIC damage. This is the result of hydrogen buildup at nonmetallic inclusions and void areas from welding slag, lack of fusion, etc. Cleaner steels manufactured with special processing and chemistry controls to provide lower inclusion content, such as those referred to as HIC-resistant steels, can provide improved resistance to hydrogen blistering and HIC damage in HF service but may be more susceptible to SOHIC. Some refiners also specify HIC testing of HIC-resistant materials to better determine how resistant it is to damage. Base metal, weld deposits, and weld HAZs with high hardness are susceptible to HSC-HF. These types of damage are most commonly experienced in equipment and piping manufactured from plate.

Susceptibility to HSC-HF can be reduced by controlling CE and/or by PWHT. They all act to limit weld and HAZ hardness. Areas of high residual stress adjacent to welds are susceptible to SOHIC, which can be reduced by the use of clean steels and PWHT. NACE SP0472 provides guidance on the prevention of in-service environmental cracking of carbon steel welds in corrosive service. Rather than relying on the control of CE to manage hardness, some users specify PWHT for all carbon steel piping and equipment exposed to HF service, especially in the rich HF and phase change HF corrosion zones. Some refiners require all carbon steel flanges to be normalized in addition to the above measures. See 6.4.4 for additional information related to carbon steel cracking and blistering, and 6.3.2.3, 6.3.2.7, and 6.3.2.8 regarding carbon steel material specifications, welding, and hardness control to reduce the risk of environmental cracking and blistering.

NACE SP0472 contains information on alternative thermal methods for weld and HAZ hardness control (e.g. CDW) to avoid in-service environmental cracking. For HF service, users only apply these methods to seamless piping welds and other locations where temper bead welding has been approved by a corrosion specialist. Welds in seamless piping are usually made by single-sided welding, where the heat from multi-pass welding tempers the root and fill pass regions of the weld to acceptable hardness levels, thus minimizing the need for PWHT to control hardness. Temper bead welding for hardness control has been applied to multi-pass girth welds and multi-pass branch connection welds from the outside surface only. Temper bead welding for hardness control has also been applied to multi-pass seal and socket welds. However, as with carbon steel CE control above, some refiners require PWHT regardless of how the welding was performed.

#### **c) Role of Arsenic in Environmental Cracking of Carbon Steel**

Arsenic can play a role in promoting hydrogen charging of carbon steel by inhibiting the hydrogen recombination reaction on the metal surface in all corrosion zones. Arsenic can enter the unit through fresh HF supplied by the vendor and/or unit feedstocks. Many HF vendors limit the arsenic content of fresh HF to not more than 10 parts per million by weight. Most refiners have adopted the arsenic limit of the vendor from the certificate of analysis that accompanies each batch of HF received. Additionally, arsenic in certain crudes may carry through the upstream process units and end up in the HF alkylation unit feedstock. It can be especially important for units that run incremental propylene feed. This is due to arsenic concentrating as arsine in the propylene by distillation. Two monitoring points for arsenic are the incremental propylene feed when this stream is part of the alky feed and the propane defluorinator spent catalyst. The analysis for arsenic in spent propane defluorinator alumina/bauxite may be available through the site environmental group, if it is part of the analysis required for its disposal. Testing would typically be performed every time it is changed out. The arsenic on spent defluorinator solids can indicate total unit arsenic loading. Using arsenic level in spent propane defluorinator solids as an IOW may be used to adjust the inspection plan for hydrogen damage.

### **F.2.2 Carbon Steel Residual Element Contribution to Corrosion in HF Alkylation Units**

#### **d) General**

Carbon steel composition can also influence corrosion rates in HF. It has been shown that certain REs in carbon steel contribute to higher corrosion rates. The primary REs of concern are chromium (Cr), nickel (Ni), and copper (Cu). However, the amount of carbon (C) can also influence the corrosion rate. Accelerated



corrosion due to RE has been reported on individual carbon steel components containing high RE and on welds containing high RE in HF service. Occasionally, accelerated corrosion has been reported on carbon steel components with low RE that are welded to carbon steel components containing high RE in the dilute HF corrosion zone.

ASTM standards for typical carbon steel specifications such as ASTM A516, ASTM A106, ASTM A333, ASTM A960, and ASTM A961 now include supplementary requirements for HF service that provide limits on the maximum allowable RE content. It may be beneficial to verify that the RE content of the carbon steel meets the recommendations in these ASTM supplementary requirements. See NACE 5A171 and NACE 03651 for further details. Also, Section 6 of this document contains requirements and recommendations regarding the RE content of carbon steel.

It is not unusual to find differences in measurement RE vs that shown on the MTR. This can be due to several factors including but not limited to the following:

- a) differences in analyzer operators,
- b) how the analyzers are calibrated,
- c) type and manufacturer of analyzer,
- d) analyzer technology,
- e) difference between field and laboratory results,
- f) challenge managing MTR on commodity components,
- g) surface prep and cleanliness,
- h) chemical composition changes through a "heat" of metal.

Handheld analyzers are typically thought to be less accurate than lab-based instruments. Typically, an amount of metal is melted and cast as a "heat." Parts of that heat may be rolled, formed, or shaped into "lots." There may be small differences in the heat from the start of the cast to the end of the cast. This is due to the casting process itself. Thus, a lot may be different in composition than the heat by a small margin. ASTM A20/A20M and ASTM A751 provide guidance on evaluating the variation between heats, lots, etc., and the analysis thereof.

As an example, the heat may be tested for vanadium. It may be 0.08 wt % in the heat. However, when checking the lot toward the end, it may have dropped to 0.05 wt %. If the acceptable range by ASTM specifications is 0.06 wt % to 0.10 wt %, this particular variation in composition would be acceptable. More information on the types of material identification instruments can be found in Annex H.

Corrosion in HF alkylation units has been found to be strongly affected by carbon steel composition. In general, the higher the base corrosion rate, the more significant the impact RE has on corrosion rate. Also, local corrosion rates can be subtly affected by local carbon steel composition. Discussed below is the impact of RE content in carbon steel for certain services. This information can assist the owner-operator in focusing their inspection programs for potential localized corrosion due to carbon steel chemistry.

Inspections that have been done on all the carbon steel components have found significant corrosion on flange hubs. Most of those cases reported have been directly attributed to RE issues. There have been some issues that have been reported as "not fitting the typical pattern seen with RE." However, since no information has been published on the unique failures that have been reported, no conclusions can be drawn around the cause of the preferential corrosion on the flange hub. Regardless of the cause of the corrosion, this points out the importance of monitoring the thickness of the flange hub as part of the inspection program in HF service.



A number of owner-operators have noted that the Cr content, as well as Cu and Ni content, of low-RE carbon steel components (especially piping components) with  $\geq 0.18$  wt % C has been increasing over time. This increase in Cr level has led to a concern that when the weld is made with the low carbon ( $<0.18$  wt % C) welding electrode, the Cu+Cr+Ni content of the completed weld could exceed the 0.15 wt % limit because of the dilution that occurs during the welding process. Some refiners have reported information on testing done on completed welds that indicate there can be enough Cr, Cu, and/or Ni from the dilution effects that the completed weld no longer met the specification for low-RE carbon steel. With the completed weld being high RE, the corrosion rate on the weld would be different from the low-RE base metal. Based on these reports, some owner-operators have started testing the RE content of the finished weld. Unfortunately, with the increase in Cr, Cu, and Ni content in carbon steel materials with  $\geq 0.18$  wt % C being relatively recent, coupled with the lack of published data on the RE composition of the completed welds, there is no industry consensus on how to manage the RE content of the completed welds.

However, two things are clear, as follows.

- i) When the RE level on carbon steel base metal with  $\geq 0.18$  wt % C meet the requirement to be low-RE carbon steel and the weld electrodes ( $<0.18$  wt % C) meet the requirement to be low-RE carbon steel, the resulting weld may not meet the low RE requirements.
- j) 6.4.2.3.2 and 6.4.2.3.3 would apply to any components that are high RE.

**e) RE Contribution to Phase Change HF Corrosion**

NACE 03651 indicated that the combination of C and RE content could increase non-uniform corrosion by up to five-fold compared to baseline measured corrosion rates. Another conclusion of the study was that the optimum specification for low-RE carbon steel would be  $C \geq 0.18$  wt % and  $Cu + Ni \leq 0.15$  wt % for base metals and  $Cu + Ni + Cr \leq 0.15$  wt % for the weld itself due to carbon levels being intentionally  $< 0.18$  wt %. The study also concluded that at HF/water ratios of 60:40 and higher, corrosion is dominated by diffusion effects and galvanic effects are expected to be less significant. The study also demonstrated that welds made with SMAW E6010/6011 filler metal can preferentially corrode. This has been experienced by owner-operators as well. The increased corrosion of higher RE components is a primary concern in phase change HF services.

**f) RE Contribution to Dilute HF in Water Corrosion**

In services where dilute HF in water can be generated, it has been found that the interaction of lower RE components galvanically coupled to higher RE components at welds will cause higher localized corrosion losses to the lower RE components. This is due to galvanic potential differences between materials. The presence of a free water phase is necessary for this corrosion to occur. A common thought that low RE is to be avoided in the dilute HF in water corrosion zone, however, is incorrect. In fact, the use of low-RE components can minimize the differential RE between components and thus minimize the potential for this galvanic corrosion effect in this corrosion zone.

**g) RE Contribution to Rich HF Corrosion**

Several sites reported at the NACE TEG 205X minutes and NACE REFIN-COR™ (latest revision) (Houston, TX; NACE International) database concerning corrosion of high-RE welds as well as base metal in both the iC4 recycle from the main fractionator/isostripper, where there can be high levels of entrained rich HF, and all rich HF areas in reactor/settler and fractionator acid recovery systems. While the corrosion rates on these components were not excessive in general terms, they were 3 to 4 times higher than the corrosion rate in low-RE components in the system. This corrosion has resulted in failures as well as the replacement of piping and equipment after long-term service. Several sites have reported at industry forums finding corrosion of higher RE welds and base metal components in rich HF services, including circulating reactor/settler rich HF, fractionator recovery rich HF, and in systems with entrained rich HF such as effluent, iC4 draws and fractionator overhead accumulator hydrocarbon systems. The literature report also noted that when weld RE was low and base metal RE was high, the base metal preferentially corroded. Note that some treat the accelerated corrosion experienced in the iC4 draw from the depropanizer as phase change HF rather than rich

HF due to their experience with corrosion in this system. Most owner-operators are specifying low-RE carbon steel for rich HF and fresh HF corrosion zones.

#### **h) Challenges in Purchasing Low-RE Components**

There continues to be challenges in purchasing and validating RE content of low-RE carbon steel for owner-operators (see 6.2.2.1 and 6.2.5). With ASTM standards for typical carbon steel specifications now including supplementary requirements for HF service applications, improved availability of some components has been reported. Most discussions on owner-operator experience with the issue indicate that a significant lead time may be required for some components, especially when significant quantities, special requirements, and/or special configurations are involved. Some owner-operators have entered into agreements with suppliers to ensure more reliable stock of materials.

### **F.2.3 Other Carbon Steel Base Metal Considerations**

#### **i) Clean Carbon Steel Plate**

Clean carbon steel plate (that which is melted and cast to reduce the formation of oxides and inclusions) can provide enhanced resistance to hydrogen damage (blistering/HIC/SOHIC). The following are examples of specifications used to improve resistance to hydrogen damage.

- a) Sulfur limited to 0.005 wt % maximum.
- b) Steel to be vacuum degassed.
- c) Steel may be calcium treated for inclusion shape control at the discretion of the material manufacturer. Calcium treatment of ultra-low sulfur steel (sulfur < 0.001 wt %) is not considered to be necessary. Some owner-operator's experience has set the calcium content to not exceed 3 times the sulfur content.
- d) Each plate can be 100 % ultrasonically examined in accordance with ASME SA-578 Supplementary Requirement S1.1 with Acceptance Standard—Level C.

#### **j) Forgings/Flanges Base Metal Cleanliness**

Some users also have some additional requirements for *forgings/flanges base metal cleanliness*. The following are examples of specifications used to improve hydrogen damage resistance in forgings.

- a) Forgings and flanges used in the equipment are vacuum degassed and manufactured to fine-grain control.
- b) Forgings may be calcium treated for inclusion shape control at the discretion of the material manufacturer. Calcium treatment of ultra-low sulfur steel (sulfur < 0.001 wt %) is not considered to be necessary. Some owner-operator's experience has set the calcium content to not exceed 3 times the sulfur content.
- c) Forgings can be examined per ASME BPVC Section VIII, Division 2, Paragraph 3.3.4 for UT requirements.

### **F.2.4 Stainless and Low-alloy Steels**

For AHF (as received from supplier) at less than 400 ppm water, stainless steel may be used without significant corrosion and is what most vendors use for transporting HF. However, in the alkylation unit where the HF water content is typically significantly higher than this, it results in very high corrosion rates and the propensity to stress corrosion crack if oxygen is present. Even in the fresh acid tank, stainless steel is not used because of

the real potential of increasing the HF water content (e.g. when storing unit acid in the fresh acid tank during turnaround). Duplex stainless steels are considered to have the same drawbacks as austenitic stainless steels.

Low-alloy steels have been found to corrode at rates significantly higher than carbon steel, including those low-alloy steels with increased Ni and Cu content intended for atmospheric corrosion resistance. The higher hardness of low-alloy steels also increases the potential for hydrogen stress cracking. Most owner-operators have extended this to areas of the unit that are not normally in HF service but could be if another component either leaked or failed. Excluding low-alloy steels from the HF alkylation unit helps avoid incorrect material installation in HF service.

Because most instruments used in the refining industry are fabricated using stainless steel, it is common to find stainless steel bolting and tubing in instrumentation. Some manufacturers use stainless steel closure bolts on Alloy 400 instrument bodies unless specified otherwise. There have been reported failures of stainless steels used for these components in HF service.

## **F.2.5 Ni-Cu, Cu-Ni, and Copper Alloys HF Acid Damage**

### **k) General**

In general, Alloy 400 is highly resistant to all forms of HF acid in HF alkylation units up to about 300 °F (149 °C). Above this temperature, corrosion rates have been known to increase significantly with increasing temperature. Because of this concern, an operating limit of 300 °F (149 °C) in the presence of HF in Alloy 400 services is often set and IOWs are typically used around the HF regeneration system to flag for potential increased corrosion.

### **l) Oxygen Effects on Alloy 400**

The other major vulnerability that can lead to Alloy 400 corrosion is when it is simultaneously exposed to both HF and some form of oxidizing agent, most commonly oxygen. Alloy 400 being simultaneously exposed to both HF and oxygen causes cuprous fluoride to be oxidized to cupric fluoride, which leads to intergranular corrosion, and in some cases, SCC. This vulnerability increases if the Alloy 400 contains high residual stresses resulting from either cold work or weld fabrication and the HF is vapor phase. Simultaneous exposure to HF and oxygen can happen in many ways. Some typical ones include:

- a) unit nitrogen or blanket gas that contains excessive oxygen,
- b) purge/vent practices that create a vacuum that can draw air into the system,
- c) improper/insufficient purging when bringing equipment online,
- d) failure of relief valve bellows due to a bellows gasket leak,
- e) insufficient neutralization practices when preparing equipment for maintenance,
- f) failure to purge the unloading hose and associated piping when receiving fresh acid.

The presence of oxygen at higher temperatures (above 300 °F) has been noted to lead to rapid pitting attack as well as denickelification. For example, denickelification has been experienced in the acid vaporizer bundle in the HF regeneration system.

There is quite a bit of confusion in the industry about SCC in general, and SCC of Alloy 400 in HF service is probably at the top of that list. For SCC to occur, the material must be stressed. However, that stress does not have to be a residual stress from forming or welding. If the material is stressed in service, it can crack just as readily, even if it is fully stress relieved prior to service. Finding HF SCC on Alloy 400 tubing after a leak has been found is common. Oxygen-related SCC has also been reported in acid relief headers that have been upgraded to Alloy 400, particularly at PRV locations where piping becomes exposed to air during maintenance

activities. Alloy 400 valve stems are particularly vulnerable to simultaneous exposure to HF and oxygen during both maintenance and start-up activities. SCC on the exterior of Alloy 400 components has been experienced after an HF leak to atmosphere. Therefore, it is of significant benefit for Alloy 400 materials of construction by both keeping oxygen out of the unit and HF-freeing Alloy 400 equipment during maintenance activities before exposure to air takes place.

Stress-relieved material cracking in service has resulted in confusion as the effectiveness of post-fabrication stress-relieving heat treatments has improved over time. Some of the first work on SCC of Ni-Cu alloys by HF is that by Dr. Harry Copson and his colleagues at the International Nickel Company Research Laboratory in the 1940s and 1950s. They showed that stress-relieving at 1000 °F to 1200 °F (538 °C to 649 °C) was effective in preventing SCC. The presence of oxygen and SO<sub>2</sub> can increase the tendency toward SCC of Ni-Cu alloys, so over the years the recommendation for stress relief has crept up to include 1300 °F (704 °C). If you are dealing with annealed Alloy 400, 1300 °F (704 °C) is an acceptable temperature for stress relief. However, if the material is cold-worked (e.g. cold drawn) to increase its strength, exposure to the higher stress-relieving temperature may recrystallize the cold-worked material, thus erasing its higher strength. In this case, the stress-relieving temperature is often limited to 1150 °F (621 °C).

To help reduce the potential for SCC, and in some cases localized weld attack, many refiners use heat treatment of Alloy 400. Temperatures ranging from 1175 °F (635 °C) to as high as 1325 °F (718 °C) are used, but no industry consensus has been developed as of yet. Unlike the research done by Dr. Copson, MTI MS-4 recommends thermal stress relief of Alloy 400 at 1250 °F to 1350 °F (677 °C to 732 °C). A failure report was shared at a NACE TEG 119X meeting that reported testing showed heat treating at a 1300 °F (704 °C) temperature was required to reduce internal residual stress and that lower temperatures did not provide a reduction in cracking resistance.

However, rather than eliminating the potential for SCC, pitting, and denickelification, heat treatment of Alloy 400 only lowers their potential. Thus, minimizing simultaneous exposure of Alloy 400 components to HF and oxygen is a key to controlling this degradation mechanism. To this end, complete HF removal and neutralization of Alloy 400 before exposure to air will minimize this potential. Another concern about using higher temperatures for heat-treating Alloy 400 welds is that it can lower the yield stress.

The HF regeneration system combines the potential for corrosion due to high temperatures with the potential for forms of degradation due to simultaneous exposure to HF and oxygen. In the overhead of the HF regeneration tower, preferential corrosion has been experienced on welded Alloy 400 piping. Weldments in this service can experience preferential corrosion. Heat treatment can reduce the potential within the HAZ, but it can increase the potential for preferential corrosion of the weld metal. Preferential corrosion of the HAZ has also been experienced on both circumferential and long weld seams in HF regeneration service. While these forms of degradation do not occur in all cases, knowledge of them is helpful for inspection planning purposes.

Variations in Alloy 400 composition can also affect its resistance to corrosion. For example, Grade M-35-1 is the preferred cast version of Alloy 400 because of its weldability and low niobium content. Owner-operators tend to avoid Grade M30C, as it contains niobium carbides, and they are preferentially corroded by HF. Also, it has been reported that weld electrodes higher in niobium and/or titanium may cause Alloy 400 welds to be preferentially attacked by HF in higher temperature services. The most common place where this has been experienced is in the overhead system of the HF regeneration tower.

#### **m) Magnetic Properties of Alloy 400**

The Curie point (the temperature below which a metal exhibits magnetic properties, also called Curie temperature) for Alloy 400 can change below 120 °F (49 °C) and can be affected by the exact Ni-Cu composition as well as by cold working. The values for the Curie point represent the range that can be expected from normal alloy manufacture. Therefore, some heats will be magnetic at room temperature and others not. Although the magnetic response is relatively weak, it can be significant in magnetically driven pumps and in instruments such as magnetic level gauges and rotameters. If there is a strong requirement for nonmagnetic characteristics, other alloys may be considered (e.g. Alloy C-276).

#### **n) Alloy K-500 Cracking Susceptibility**

Alloy K-500, a hardenable, heat treatable grade of Ni-Cu alloy, is also susceptible to SCC when simultaneously exposed to HF and oxygen. Limiting the hardness level for high-strength applications like relief valve springs, pump shafts, valve stems, and bellows to HRC 30 has been successful in managing the potential for cracking in Alloy K-500 components. Alloy K-500 has been used by many as the default Bourdon tube material in unit pressure gauges by most manufacturers. There have been many cases of HF SCC in Bourdon tubes in HF service. This is likely due to the material having been heavily cold-worked and then exposed to oxygen in HF service. Some refiners use a diaphragm and barrier fluid to maintain an oxygen-free environment at the Bourdon tube to avoid SCC.

#### **o) Alloy 400 and K-500 Internal Bolting Applications**

Alloy 400 and Alloy K-500 have been used in HF alkylation units for internal bolting (e.g. for distributors and trays). These bolts may contain residual stresses that resulted from either cold working or overtightening. Annealing of Alloy 400 and Alloy K-500 internal bolting has been performed to improve the resistance to cracking in HF service when exposed to oxygen. Installation procedures to prevent overtightening of internal bolting composed of these materials can help minimize residual stresses and thereby improve the resistance to cracking in HF service. One method that has been successfully used is to tighten the nuts finger-tight and then further tighten by a quarter turn.

#### **p) Effect of Mercury on Alloy 400 and K-500 Applications**

The presence of mercury is known to have caused SCC in Alloy 400 and is suspected to have caused SCC in Alloy K-500. SCC in the presence of mercury can even happen in the absence of HF. The source of mercury is typically mercury-containing crudes, but it can also be a contaminant in purchased or imported feedstocks. There has been reported experience of mercury from crude oil causing cracking in welded Alloy 400 components in HF alkylation units. It has also been reported that mercury may have caused failures of Bourdon tubes made from Alloy K-500 in unit pressure gauges. Mercury can also dissolve the gold plating on remote pressure instrument diaphragms. Mercury can be removed from unit feeds by the use of an appropriate bed of adsorbing material.

#### **q) Cu-Ni Alloys in HF Service**

Cu-Ni alloys (UNS C70600 and UNS C71500) have been successfully used as heat exchanger tubing in HF alkylation units because of their corrosion resistance to rich HF. For example, UNS 71500 (70/30 Cu-Ni) has been specified for cooling water heat exchanger bundle materials for both its cooling water corrosion resistance and its high corrosion resistance to rich HF, even in HF condensing services. Cu-Ni alloys have essentially the same degradation mechanisms as Alloy 400. When Cu-Ni alloys in HF service have been cold-worked (e.g. heat exchanger U-bends and PRD bellows), SCC and intergranular corrosion has been experienced as a result of denickelification after being simultaneously exposed to HF and oxygen. Cold-worked U-bends are typically stress-relief heat treated to help lower this risk. These alloys, therefore, also benefit from keeping oxygen out of the unit and HF-freeing equipment during maintenance activities before long-term exposure to air takes place.

#### **r) Pure Copper Materials in HF Service**

While pure copper has some resistance to HF, most refiners only use it for temporary drains and dispose of it after one use. The main reason it has not found more use in HF alkylation service is its susceptibility to both SCC and high corrosion rates upon simultaneous exposure to HF and oxygen. Another factor cited for not using copper is its softness and therefore its susceptibility to mechanical damage.

#### **s) Cu-Zn Alloys in HF Service**

Cu-Zn alloys, which are typically used in cooling water services in other refinery units, are not normally used in HF alkylation units. They suffer embrittlement and are sensitive to velocity-assisted corrosion.



## F.2.6 Corrosion of Spec Breaks Between Alloy 400 and Carbon Steel

In services where carbon steel is corroding at unacceptably high rates, Alloy 400 has been used as a local upgrade. Dilute HF in water services is one example. An upgrade in these services could set up a galvanic cell in DMWs and accelerate the corrosion rate of carbon steel adjacent to the weld. This has been experienced in acid neutralization scrubber systems. In these areas, an effective practice is to extend the Alloy 400 overlay to where HF is no longer normally present.

DMWs between carbon steel and Alloy 400 may produce very high hardness zones that are highly susceptible to corrosion and cracking, especially on the carbon steel side of the weld when in HF service. These damage mechanisms are caused by the dilution of iron into the alloy weld, which can cause areas of high hardness along the fusion line on the carbon steel side of the weld. Localized areas of free iron contamination of the weld surface can also exist. An effective practice is to apply a nickel filler (e.g. E/ERNi-1 butter layer) on the carbon steel before welding with Alloy 400 filler, which lowers the iron content at the alloy weld. In addition, this limiting of the iron content with the nickel weld layer is especially helpful. A key consideration is also to ensure the nickel weld layer extends past any Alloy 400 weld layers. An added benefit is that the nickel weld layer improves the weldability of Alloy 400 to carbon steel. Some owner-operators analyze the weld chemistry when qualifying dissimilar weld procedures to verify that the iron content does not exceed a set value. Limiting the iron content on the top  $1/16$  in. of the nickel weld layer to a maximum of 3 wt % Fe is especially helpful, because when above 3 wt % Fe, the corrosion resistance of the Alloy 400 drops significantly. Typical locations where carbon steel to Alloy 400 welds can be found include the settler return nozzle from the HF regeneration system and in the acid neutralization scrubber. See 6.3.2.5 and 6.3.2.7 for recommendations on DMWs and weld overlays.

Another common problem is the creation of a galvanic cell on the shell side when Alloy 400 or 70/30 Cu-Ni bundles are made with carbon steel tubesheets and may be lined or clad with Alloy 400 or Cu-Ni on the tube side. The crevice of the carbon steel tubesheet can be galvanically corroded by contact with the Alloy 400 or Cu-Ni tube. This creates an iron fluoride scale in the crevice that can swell and cause the tube to collapse inward, leading to flow restriction and potential water-side fouling. This often limits the life of this type of bundle, especially when installed in defluorinator systems. In addition, where either Alloy 400 or 70/30 Cu-Ni heat exchanger bundles made with alloy baffles contact carbon steel shells in phase change HF services, localized galvanic corrosion can occur on the shell.

Alloy 400 trays installed onto carbon steel tray rings in phase change HF services in fractionation towers can create a large galvanic cell (a large cathode with a locally small anode). The corroding carbon steel tray ring can experience enough iron fluoride buildup between the tray and ring to cause failure of the support bolts. In severe cases, the galvanic corrosion can progress into the carbon steel shell near the tray ring.

To avoid DMW corrosion and cracking as well as other issues associated with dissimilar welded piping connections, flanged connections are typically used where there needs to be a transition from one metallurgy to another. Thus far, there have not been any reported cases of galvanically accelerated corrosion of the carbon steel flange in this type of bolted joint. However, because there is a galvanic couple between metallurgies of the two flanges in this type of bolted joint, some users have reported that their flange face inspection program includes identification and close inspection of dissimilar metal bolted joints.

## F.2.7 Alloys C-276, C-2000, and C-22 HF Acid Corrosion

Alloys C-276 (UNS N10276), C-2000 (UNS N06200), and C-22 (UNS N06022) have been used for instrumentation, tubing, piping, valves, pump cases, and in locations where condensation of HF is an issue. These alloys are more resistant to corrosion than Alloy 400 when the system contains oxygen but have been reported to be less resistant to corrosion than Alloy 400 when oxygen is not present. They also show higher resistance to HF SCC than Alloy 400 in some circumstances but are can still susceptible to SCC. For example, failures have occurred due to SCC of these alloys in areas where the components were highly cold-worked or had been welded prior to simultaneous exposure to HF and oxygen. Because of these issues (reported at the NACE TEG 205X information exchange), some refiners require these materials to be solution annealed after welding.

**NOTE** In the broadest sense, solution annealing is the process of heating an alloy to an elevated temperature to promote a homogenous chemistry, equiaxed microstructure, and uniform mechanical properties to produce what is considered a stress free, or “soft” material. Thus, a solution annealing heat treatment may impact the tensile and hardness properties of the material. It has been reported that components undergoing a successful solution annealing have shown increased SCC resistance. However, solution annealing is not easy to accomplish with large components since the procedure requires both heating the entire component homogeneously (e.g. in a furnace), heat soaking it for a predetermined time, and then immediately quenching it.

While these alloys fall under the general classification of either Ni-Cr-Mo or Ni alloys, they, like Cu-Ni and Ni-Cu alloys, greatly benefit from keeping oxygen out of the unit and HF-freeing equipment during maintenance activities before long-term exposure to air takes place. Refiners that have these alloys in place tend to use the same operating temperature limits as with Alloy 400.

Based on the information presented during various NACE TEG 119X Hydrofluoric Acid: Materials for Receiving, Handling, and Storing meetings and in the *Materials and Corrosion* article “Corrosion behavior of nickel alloys in wet hydrofluoric acid,” Alloy C-2000 has better cracking and corrosion resistance than other alloys in this family. When compared to the environmental cracking resistance of Alloy 400, each of these alloys performed better than Alloy 400. It was noted in the article that the cracks in Alloy C-2000 were difficult to find, even with metallography. Based on this work and field experience, it has been theorized that the presence of tungsten (W) in Alloy C-276 and Alloy C-22 may increase their susceptibility to environmental cracking, where Alloy C-2000 contains only trace W. At this time, however, there is no industry consensus on the role of tungsten in nickel alloys. Regardless, some have recommended the use of Alloy C-2000 rather than the other two alloys in this family.

Similar to Alloy 400, potential liquid metal embrittlement after exposure to mercury is a potential concern for these alloys. NACE Paper 10294 suggests that Alloy C-276 does not exhibit SCC in the presence of mercury. However, this testing was not performed in the combined presence of mercury and HF, and there is no known commercial experience to confirm that Alloy C-276 resists SCC in the presence of mercury.

Similar to what has been experienced when Alloy 400 is connected to carbon steel, there have been reports of galvanic corrosion when these alloys are connected with carbon steel in that the carbon steel preferentially corrodes. Most of these reports have been in threaded connections where a component was upgraded, but some have been when the components were welded together. In most reports, a continuous phase of water with HF was present.

## F.2.8 Aluminum

**Aluminum is readily attacked by HF. Aluminum is also a very soft and easily damaged metal, making it especially susceptible to cross-threading when installing screwed fittings, which can lead to leaks. As such, aluminum and aluminum alloys are not considered HF resistant materials for design and specification including use in sample containers.**

## F.2.9 Castings

Carbon steel and Alloy 400 are commonly used for castings in HF services and some of the Ni alloys in G.2.7 are finding more use in HF service. Properly produced cast alloys have performed as well as their wrought equivalents in HF alkylation service. However, castings can contain flaws such as Si slag inclusions, porosity, chaplets, and shrinkage cracking that can allow HF to eventually leak through wall. Therefore, some users of cast equipment have imposed additional NDE (radiography and sensitive leak testing) on both new equipment and equipment that has been in service and repaired to reduce the probability of leaks when in HF service.

It has been noted that all of the Ni-Cu alloys, including Alloy 400, are more difficult to cast than carbon steel. It has also been reported that the use of the cast version of Alloy C-2000 and C-22 (CX2MW) is preferred by



some vendors for casting equipment such as pumps, because they believe casting with these alloys are more forgiving than the cast equivalents of Alloy 400 and C-276. See 6.2.3.5 for recommendations on castings QA/QC.

Helium testing of cast components using the water submersion version of the test and/or hydro testing with a liquid prior to helium testing can cause false-negative results. Some owner-operators are thus moving toward helium wand testing or vacuum box testing as their preferred method.

### F.2.10 Polymers

Fully fluorinated plastics (e.g. PTFE, FEP, and PFA) have been used in HF services, with PTFE being the material with the most experience. PTFE-lined piping has been used downstream of the HF regeneration system where the tower bottom stream is neutralized. HF can permeate through PTFE, which can result in corrosion in flanged connections and the carbons steel pipe. In addition, when a vacuum is pulled on a PTFE-lined pipe, the liner can collapse. See the discussion in NACE 5A171 for additional details.

Fluoropolymer rubbers (e.g. PTFCE-E-TFCE polymers, VF2-TFCE polymers, and propylene tetrafluoroethylene rubber) have been used successfully in HF alkylation services when elastomers are needed. When used, the most success has been experienced when they do not contain any fillers that are susceptible to attack by HF.

When specifying instances using plastic-lined pipe, flange joint integrity due to cold flow can be a challenge. Plastic lined piping installation considerations include: a retorque plan for flanges in plastic-lined HF service piping, cases and any potential for lining collapse due to exposure to vacuum conditions.

### F.2.11 Graphite

One additional material that finds extensive use in HF alkylation units is graphite. It is typically found in valve packing material and flange gaskets. Contamination of graphite with boron has been found to result in integrity issues when exposed to HF in the HF manufacturing industry. Therefore, nuclear-grade graphite is used to mitigate this concern. The refining industry has not experienced the same issues and thus does not specify nuclear-grade graphite. Either PTFE or flexible graphite is typically used as the nonmetallic material in gaskets in HF services.

There has been some discussion around the potential use of graphite/carbon for random packing in HF regeneration services. In a similar type of equipment in HCl service, significant galvanic corrosion was experienced between the carbon packing and the alloy C-276 pressure boundary, which resulted in the alloy component being replaced after a short period of time. While a similarly rapid degradation mechanism is possible in HF services, there is no reported experience to share as of this writing.

### F.2.12 Glass/Silica

Silicon and silica-based compounds are readily attacked by HF. Some of the reaction products (e.g. silicon tetrafluoride, fluorosilicic acid) are very corrosive as well. For this reason, all silica-based materials (e.g., glass, silica-containing catalyst support, silica, silicone, ceramics) perform poorly in HF services. As an example, failure to remove blasting grit from vessels during turnaround can result in the formation of silicon tetrafluoride and/or fluorosilicic acid and result in very aggressive corrosion on vessels and/or piping. Another example is that if silicone is used even as a temporary adhesive to hold gaskets in place, it will likely lead to flange leak problems. On the other hand, Alloy 400 typically contains 1 % to 2 % silicon and has not been an issue. This is due to the silicon being tied up within the metal. Further, silicon is needed for castability and nickel-silicides are needed for strength.

Glass, refractories, silica-containing catalyst support, silicone, and other silica-based materials are not recommended materials for HF services and normally non-HF services that could be exposed to HF if an upset were to occur. For glass, these restrictions apply even when used in conjunction with a protective shield made of HF-resistant material [e.g. polychlorotrifluoroethylene (CTFE)-coated gauge glasses].

Care and removal of silica containing materials used for turnarounds and maintenance, such as blasting grit, is a consideration for HF alkylation unit equipment and piping before returning the equipment or piping to service. Some materials that can contain silicone include barrier fluids used in instrumentation, lubricants, polytetrafluoroethylene (PTFE) paste, ceramic packing, and valve packing materials

Glass bottles used for sample containers for normally non-acid containing product streams such as alkylate product rundown is one acceptable use for glass.

Another location where silicone has been used in HF alkylation units has been in remote-seal type level instruments. Silicone has been used as the liquid fill material in the capillary line between the remote seal and the transmitter. Although the capillary lines are separated from the process fluid by a diaphragm, there is a possibility of the formation of fluorosilicic acid if there is a leak in the diaphragm. The use of a fill fluid that is not reactive with HF, such as chlorotrifluoroethylene polymer (CTFE) or another halocarbon, is preferred over silicone.

### F.2.13 Anti-seize Agents

Anti-seize agents that contain silica, magnesium, or lithium are readily attacked by HF. Nickel-based and molybdenum-disulfide-based anti-seize agents work well as long as they do not contain silica, magnesium, or lithium.

## F.3 HF Alkylation Corrosion Zones

### F.3.14 General

The terms fresh HF, rich HF, phase change HF, dilute HF in water, and fractionator HF are defined in Section 3 and further described in this annex. How these corrosion zones mechanisms can impact inspections and corrosion are introduced in 6.1 of this document. These terms describe the HF services of interest for corrosion monitoring and inspection purposes in HF alkylation units. See Figure G.1 for a generic view of where each corrosion zone applies during normal operation. Transient conditions may change the type of corrosion exposure within these corrosion zones, which may require supplementing the corrosion zone mechanical integrity practices to account for these transient exposures. Note that previous versions of this document used the terms “main acid,” “trace acid,” and “dilute acid” for corrosion monitoring and inspection purposes but are being replaced with corrosion zone terminology in the Fifth Edition of API 751.

The following approaches are typically used in combination to manage corrosion in HF alkylation units.

- a) Controlling process variables to minimize corrosion via IOWs. See G.5 for a list of example IOWs in HF alkylation units.
- b) Modifying the equipment to remove exposure to the corrosive environment (e.g. removing dead-legs, providing a dry purge in normally stagnant systems).
- c) Using materials that are resistant to the corrosion mechanisms present in the particular area of the unit.

### F.3.15 The Fresh HF Corrosion Zone

Fresh HF corrosion zone contains HF as delivered by the supplier. The acid receiving and storage system metallurgy is typically carbon steel. Fresh HF at ambient temperatures forms a tight protective iron fluoride scale on carbon steel and has a very low general corrosion rate, < 2 mpy. If the drum used to store fresh HF is used to store rich HF (see G.3.3), the acid receiving drum is then typically considered in rich HF corrosion zone service for inspection purposes.

**NOTE** Because of the properties associated with the MHF, loading lines and associated equipment where fresh acid is brought into the unit are defined differently (refer to 6.4.2.5 for additional discussion on MHF).

### F.3.16 The Rich HF Corrosion Zone

The rich HF corrosion zone contains HF acid with hydrocarbon and water. Two primary locations where this corrosion zone is found are reactor acid and boot acid. Both typically contain > 80 wt % HF, < 2 wt % water, and dissolved light hydrocarbons. Rich HF is created inside HF alkylation units due to the ability of HF to absorb water from unit feeds plus the ability to retain ionic polymers in the acid phase from the hydrocarbon reactions that occur. The polymers are otherwise known as acid soluble oils, or ASOs, and can be found in the reactor acid. Rich HF is sometimes referred to as circulating acid or circulating HF. Circulating HF also contains dissolved light hydrocarbons including ASO, but the amount is equilibrium-limited to about 3 wt %. Per NACE 5A171, water is the primary corrosive species in HF for the metallurgies discussed in NACE 5A171.

The rich HF corrosion zone includes areas where a predominantly hydrocarbon stream contains residual amounts of entrained acid. The specific example is the effluent piping from the settler to the first preheat exchanger before the fractionator/isostripper.

Like fresh HF, rich HF at ambient temperature produces a tight, adherent, protective iron fluoride scale that generally creates < 2 mpy corrosion rates in low-RE carbon steel components and generally < 5 mpy corrosion rates in high-RE carbon steel components. These corrosion rates increase with operating temperatures.

For rich HF services, preferential weld corrosion may be found after many years of service for higher RE and E6010/6011 welds at temperatures close to ambient. There have been reports of this being the case on acid cooler welds, acid storage drums, and settler outlet hydrocarbon stream welds upstream of tower preheat exchangers.

Most units operate with circulating acid water content less than approximately 1.5 wt % due to the implication water has on contributing to phase change HF corrosion (see G.3.4). Historically, some units have reported operating with rich HF water contents up to 2.5 wt % with manageable damage on the reactor/settler system within their planned maintenance intervals, meaning that rich HF water content has a relatively low effect on corrosion rates in lower temperature areas such as these. When operating at a higher acid water content, in addition to implications in phase change HF corrosion zones, significantly higher corrosion rates have been experienced in the acid draw from the overhead accumulator drum, which is in rich HF service. Depending on unit experience, capability, and turnaround interval, the damage caused by acid high water content may be considered acceptable by the owner-operator. However, as owner-operators continue extending turnaround intervals, limiting the acid water content becomes more and more important for achieving desired run length, primarily due to effects outside of rich HF corrosion zones, but not exclusively.

The intermittent exposure of HF deinventory facilities to rich HF is also considered relatively noncorrosive as long as appropriate dry and oxygen-free blanketing gas is provided for the equipment. Where blankets are used on acid or feed storage, considerations include both the oxygen content of the blanket as well as the solubility of the blanketing gas in the liquid phase. Where a dry blanketing gas is not used or the equipment is not purged with a dry blanketing gas after use, these HF deinventory facilities would be considered to be in the phase change HF corrosion zone.

When acid is stored in process equipment, there is a potential for rich HF to end up in areas that are not designed for HF service. As such, higher corrosion rates may be experienced in these locations after being exposed to rich HF.

### F.3.17 The Phase Change HF Corrosion Zone

Phase change HF corrosion zone occurs in areas where HF is either being condensed or vaporized and either by design or inadvertently, such as condensing in overhead lines. In addition, the phase being either condensed or vaporized is usually, but not always, rich HF. Because of the nature of the HF water equilibrium, a water-rich HF phase condenses, and that liquid phase can be 2 to 3 times more corrosive than the base corrosion rate on carbon steel and can be localized depending on operating conditions and where it condenses. See Figure 2 of NACE 5A171 for a specific example in an HF/water system.

Phase change HF corrosion zone also occurs where a rich HF phase is either being absorbed into a liquid hydrocarbon stream or is forming by desorption from a liquid hydrocarbon stream. While liquid-liquid phase equilibria data are not readily available for HF-water-light hydrocarbon systems, if HF is preferentially absorbed from rich HF when contacted by liquid hydrocarbon, the remaining rich HF phase will be richer in water and therefore increase corrosion rates. A similar water-enriched rich HF phase would also form upon cooling of a liquid hydrocarbon stream that is saturated with HF/water. An example of this is the fractionation section feed line through the feed preheat system where the process transitions from rich HF to phase change HF corrosion zones during heating and possible cooling in the line from the exchangers to the tower.

For units that carry out internal regeneration, it is important that the amount of reactor acid added to the main fractionator/isostripper feed does not exceed the solubility limit of rich HF in hydrocarbon at the operating temperature. This can result in the remaining HF phase becoming richer in water than the initially injected reactor HF, thus becoming more corrosive.

Other locations where phase change HF occurs include:

- a) upper trays and overhead system of the main fractionator/isostripper,
- b) upper trays and overhead systems of the depropanizer,
- c) upper section and overhead of the HF/propane stripper,
- d) iC4 vapor side draw from the main fractionator/isostripper and points downstream,
- e) HF regeneration system, including both overhead and bottom products,
- f) various unit dead-legs (see G.4.1 and G.4.3.7), and
- g) acid flare header.

The rich HF formed in many of the phase change HF corrosion zone locations listed above originates from dissolved HF and water in liquid hydrocarbon streams. As mentioned in G.3.3, some of these streams can contain entrained rich HF droplets as well. In addition, for the distillation towers listed above, phase change HF corrosion zone normally starts approximately 3 to 5 trays below the feed tray and continues into the tower overhead and condensing systems.

The corrosion that occurs at phase change HF corrosion zone locations is not necessarily uniform. Designs that minimize the area exposed to the initial HF/water phase formed will minimize the impact of the corrosion. For example, an exchanger that rapidly condenses the incoming vapor will minimize the tube area exposed to liquid with the highest water concentration. Phase change HF corrosion zone can also result in preferential weld corrosion. There have been reports of this being the case in the main fractionator/isostripper overhead line, as well as in the various fractionators such as the main fractionator/isostripper, debutanizer, HF regenerator, and HF/propane stripper.

Two-phase main fractionator/isostripper feed (e.g. after adding too much reactor acid during internal regeneration or having significant carryover from the settler) can result in higher levels of HF and water in the iC4 stream leaving the column. If enough is present, water-rich HF can condense out as a second liquid phase when the iC4 stream is condensed. This HF/water phase can approach the corrosive water-rich HF phase.

When a tower is operated at lower-than-normal pressure-compensated temperatures, HF and water will penetrate further down the tower than when operated at normal pressure-compensated temperatures. If the pressure-compensated temperature is low enough, HF and water can exit in either lower side draws or out the bottom. This can result in accelerated corrosion in lower side draws and tower bottom streams. Of particular concern are the treating sections downstream of the HF/propane stripper bottoms, iC4 draw, and the normal butane draw. If enough rich HF gets in these systems, the corrosion can accelerate significantly. For the HF/propane stripper bottoms and normal butane draw, an exotherm in downstream defluorinators and/or

caustic treater can result in vessel temperature rise beyond design and potentially vessel overpressure, either of which can cause vessel rupture. See 8.2 for additional information. Another issue with HF and water penetration down towers is in the tower bottom section dead-legs (see G.3.6 for more information).

Reducing the amount of water in rich HF will typically reduce corrosion activity in phase change HF corrosion locations. Plants typically set a 1.5 wt % limit on circulating acid water content for this reason, and plants that run internal regeneration typically set a 1.0 wt % limit on circulating acid water content. Both types of units may target lower acid water content than these to reduce corrosion rates in the phase change HF corrosion zone. In cases where water content exceeds the limits mentioned above, this will increase the corrosivity within the phase change corrosion zone.

Phase change HF corrosion zone locations are where most of the higher corrosion rates on welds and carbon steel with high RE are reported vs low-RE carbon steel. As with rich HF locations, corrosion rates in phase change HF locations also increase with operating temperatures. Thus, equipment such as tower feed lines downstream of preheat trains may have IOWs to limit corrosion rates or may have alloy equipment installed.

### F.3.18 The Dilute HF in Water Corrosion Zone

Dilute HF in water corrosion zone occurs where a water phase can form, which will contain a low concentration of HF. Any hydrocarbon present can be in the liquid phase, vapor phase, or both. In some cases, the water phase can be very corrosive. Locations of interest for dilute HF in water corrosion include:

- a) the defluorinators and downstream equipment all the way to the downstream caustic treaters,
- b) various unit dead-legs, and
- c) in the acid flare header.

The last two locations are also included on the list of phase change HF locations in G.3.4. The difference is the composition of the HF/water phase that forms. For both dead-legs and flare header locations, dilute HF can transition to rich HF if more HF is added. It is also possible for rich HF to transition to dilute HF if water is added. Dead-legs that are associated with the defluorinators and downstream points will be in the dilute HF in water corrosion zone.

Owner-operators typically use one or more means to mitigate corrosion in dilute HF in water corrosion zone downstream of defluorinators. One way is to keep the temperature at the outlet of the coolers upstream of the KOH treaters above the solubility limit of water in the hydrocarbon stream (see Table G.1). Note that water has a lower solubility in butane than in propane at the same temperature. As untreated butane can have significant organic fluorides, butane treating systems are typically more prone to corrosion damage by dilute HF in water than propane systems. If no dilute HF in water phase forms, significant corrosion is not very likely. Designing piping to prevent the accumulation of free water in carbon steel piping and equipment between the defluorinators and KOH treaters may help manage corrosion but may not eliminate problems depending on the amount of HF breakthrough and water present. Another option is to upgrade to HF-resistant alloy metallurgy between the last exchanger after the defluorinators to the inlet of the KOH treaters. Annex G.3 contains further information on dilute HF in water in dead-legs and acid flare systems away from the defluorinators.

Stagnant areas and dead-legs in alumina treating equipment are very susceptible to localized corrosion if dilute HF with water is present. This corrosion can be aggressive enough that upgrading from carbon steel to an HF-resistant alloy is the only prudent course of action. Some owner-operators have experienced similar issues in KOH treaters and downstream points. This was likely due to allowing the drum to be completely spent, thus allowing dilute HF with water to go through and exit the KOH treaters and into the rundown.

Dilute HF with water corrosion on PRV dead-legs from defluorinators has been aggressive enough in some cases that the materials of construction were upgraded. In one case, the piping was upgraded to Alloy C-276. Unfortunately, HF SCC occurred around the welds after only a short time in service. This was due to oxygen being left in the dead-legs during the bed change-out. A proper heat treatment after welding (see 6.3.2.4 for



recommendations and G.2.5.2 for information) lowers the susceptibility for SCC in this and other HF-resistant alloys upon simultaneous exposure to both HF and oxygen.

One owner-operator reported having to replace their alumina treaters due to hydrogen blistering caused by the formation of dilute HF with water on the vessel walls. This happened because insulation was removed during turnaround but was not replaced. Maintaining insulation on defluorinators is an important part of managing dilute HF with water corrosion in this service.

Corrosion rates in dilute HF in water services can range from moderate (typically 5 mpy to 20 mpy) to severe (greater than 50 mpy) due to increased HF breakthrough. The behavior of low-RE vs high-RE carbon steel is significantly different in dilute HF in water corrosion zone than in other corrosion zones (see G.2.2.3).

### F.3.19 The Fractionator HF Corrosion Zone

Organic fluorides are produced as intermediates during reactions between HF and unit feed olefins. Some of the organic fluorides stay in the reactor acid due to being more chemically similar to acid than to hydrocarbon, but not all. Thus, the hydrocarbon feed to the fractionation section contains some amount of organic fluorides. In fractionation towers, they separate by boiling point, just like the other hydrocarbons present. Some have a high enough boiling point to drop into reboilers. As the reactions that produce organic fluorides are exothermic, applying heat allows some of them to carry out reverse reactions and produce HF and olefins. Thus, the bottom of fractionation towers produces HF. Rich HF and water in the fractionation section feed normally penetrate a limited number of trays below the feed tray in fractionation towers before being stripped and going either out the tower overhead or out a side draw above this location. The fractionator HF corrosion zone is the section of towers between the bottom where HF is being produced by thermal defluorination and where the HF and water in tower feed have been stripped out.

Thermal defluorination is encouraged by unit design and operation. One benefit is to reduce organic fluorides in both alkylate and normal butane. Another is to reduce the load on alkylate and normal butane defluorinators. A third is to reduce unit HF consumption. Thermal defluorination of organic fluorides occurs more readily at higher temperatures. Some owner-operators set minimum temperatures on the main fractionator/isostripper tower bottom and furnace outlet to encourage it. The combination of carbon steel metallurgy, HF, and temperatures results in corrosion rates that are generally limited to < 5 mpy in this corrosion zone. Towers that operate at lower bottom and reboiler temperatures will have less thermal defluorination occur, so the corrosion effect will be less.

In Figure G.1, note that feed to the propane defluorinators is in the fractionator HF corrosion zone. The normal butane line between the main fractionator/isostripper and defluorinator is in this zone as well.

Even though only low concentrations of HF are produced by thermal defluorination, the HF can build up to significant levels in places such as high point stagnant areas and dead-legs in the bottom section of fractionation towers (e.g. pressure-relief system inlet lines). The combination of high temperature and HF accumulated in these lines can result in significant corrosion. The presence of water significantly increases the corrosivity and fouling. Corrosion is typically accelerated where the dewpoint occurs (HF or HF and water). Many owner-operators have either implemented a purge/flush on these tower dead-legs or upgraded to flanged Alloy 400 spool pieces to manage the corrosion.

Another aspect of the dead-leg issue in fractionation towers is unit start-ups, shutdowns, and upsets. Any of these three conditions can allow HF and water to penetrate far enough down the tower to reach a dead-leg and for it to consequently become wet.

Finally, some owner-operators store unit acid in fractionation towers at times. This is another way in which dead-legs that are normally in HF service can become wet.

## F.4 Specific Applications of HF Alkylation Unit Corrosion Zones



## F.4.20 Stagnant Zones and High Point Dead-legs

Stagnant zones and high point dead-legs in all HF corrosion zones are known to have potential localized corrosion issues. But, corrosion rates and corrosion types differ depending on location and process effects. For dead-legs in the rich HF, phase change HF, and dilute HF in water corrosion zones, the iron fluoride scale formed from corrosion can hydrate and grow in volume, potentially as much as 10-fold. Any volume of iron fluoride scale can result in a partially restricted relief path, and larger volumes can completely plug piping systems and relief paths. Potential areas where this can occur include relief valve inlet lines, bypasses, and dead-legs off of vapor lines. Locations seeing the most significant volumes of corrosion and iron fluoride formation are often where high-RE carbon steel is present.

Per G.3.6, some dead-legs in HF service are normally dry, such as tower PRV inlet lines. However, if and when water gets into the lines by any means, unexpected corrosion (high rates) and fouling can occur. To manage corrosion in stagnant zones and high point dead-legs and where dead-leg removal is not an option, some owner-operators have either implemented a purge/flush on the line or upgraded to materials that are more HF-resistant or manage by comprehensive inspection (e.g. 100 % coverage with radiography or UT inspection).

Because of this type of behavior, vapor dead-legs on HF service piping are typically handled as part of the phase change HF corrosion zone.

## F.4.21 Fractionation Tower Vent Systems

Phase change HF corrosion has been experienced off fractionation tower overhead systems, specifically in lines that vent non-condensable molecules to the acid neutralization scrubber. This is most likely to be an issue when the non-condensable venting rate is high and can be aggravated by issues with the exchanger not cooling the non-condensables to a low enough temperature to condense most of the rich HF.

The most common cause of a high non-condensables rate is a significant level of light ends in the feed, which concentrate in the overhead system. Another cause of this type of corrosion damage that has been reported is the use of pressurized nitrogen in hydrocarbon storage tanks to increase head for pump operations. This has resulted in sufficient dissolved nitrogen in the unit feed to increase the accumulation rate of non-condensable molecules in the unit. Both the phase change HF and dilute HF corrosion zone type behavior can cause aggressive corrosion to develop in the vent line to the acid neutralization scrubber due to condensation.

## F.4.22 HF Regeneration System Corrosion

### t) General

A slipstream of rich HF from the reactor/settler acid loop is sent to the HF regeneration system for removal of built-up levels of water and ASOs/polymer. This is done by sending the stream to the tower and then stripping it in the tower typically with hot iC4 vapor. The tower overhead consists primarily of iC4 and HF, with relatively minor amounts of water and other light hydrocarbons. The tower bottom consists of an HF/water phase that can be near the azeotrope composition and an ASO/polymer phase. As acid feed to the tower can be up to 90 % vaporized, the HF regeneration system is almost entirely a phase change HF corrosion zone. The exception to this is the caustic wash point, which is in the dilute HF in water corrosion zone. Unlike other locations in the phase change HF corrosion zone, operating temperatures and compositions in much of the system typically require the use of a material that is more resistant than carbon steel, such as Alloy 400. In general, corrosion rates on Alloy 400 may be higher than those seen in other portions of the unit but can be managed with proper controls. Welds and weld overlays may be more problematic in the HF regeneration section of the unit. This is primarily due to system operating temperatures. See 6.2.3.3 for guidance on temperature. The HF regeneration system is divided into subsystems below.

#### **u) HF Regeneration Preheat**

Both acid feed and stripping iC4 to the HF regeneration system are normally heated in one or more preheat exchangers. Depending on unit design, the acid feed is either heated and not boiled or heated and boiled to a target vaporization of about 80 %. Stripping iC4 is superheated and then injected into the column bottom. When temperatures for these two feed streams are above those given in G.2.1 for carbon steel, Alloy 400 is called for in the lines leading into the tower. For units that partially vaporize the acid feed, Alloy 400 is typically used in the last preheat exchanger bundle. Bundle life of 2 to 3 years is not uncommon. Carbon steel bundles have also been used in the last preheat exchanger for units that partially vaporize acid feed. Bundle life for this metallurgy can be as low as 2 to 4 months.

#### **v) HF Regeneration Tower**

In the HF regeneration tower where boiling and condensing are actively occurring, Alloy 400 may have corrosion issues for thinner components such as tower trays and other mass/heat transfer media. Both PTFE and PTFE-lined carbon steel have been used for Raschig rings and random packing when Alloy 400 had corrosion issues. Some have considered the use of graphite/carbon for random packing in this service. See 6.2.4.2 and 6.2.4.3 for requirements on the use of PTFE and graphite/carbon materials and G.2.9 and G.2.10 for further information on both PTFE and graphite/carbon.

Alloy 400 corrosion can increase significantly if the hot iC4 stripping vapor is introduced directly into the tower, as this increases local temperatures. Corrosion on Alloy 400 may be reduced by introducing the stripping vapor into the liquid level at the base of the tower.

#### **w) HF Regeneration Bottoms**

Components in the HF regeneration bottom system include the bottoms piping, mixer, and downstream drum. This requires designing and operating the system to prevent backflow of caustic to upstream of the mixer, operating caustic recycle flow at both consistent and sufficient flow rates, and not allowing caustic strength to be too low. More typical is to either replace components as needed based on inspection results or upgrade metallurgy to Alloy 400. Some owner-operators have used Alloy C-276 in valves for better corrosion/erosion performance. Alloys 400 and C-276 have also been used on the downstream separator drum where neutralizing the tower bottom stream or backflow of caustic has been an issue. However, there is at least one report that the use of Alloy C-276 for the ASO mixer did not provide a significant improvement in service life over Alloy 400. See G.2.5 for further information on HF-resistant alloys. Some owner-operators have trialed PTFE-lined piping for the tower bottom stream between the tower and the caustic mixer. The most significant issue was cold flow of the PTFE at flanged connections, and so was not highly successful.

#### **x) HF Regeneration Overhead Vapor Piping**

Regeneration tower overhead vapors are typically sent to either the fractionation section or to the settler where the vapors are condensed. However, in some cases, a separate water-cooled exchanger is used to condense the stream. Figure 3 from NACE 5A171 indicates lower corrosivity for vapor-only streams than liquid streams for carbon steel in AHF at the same temperature. Experience in refining applications has found this relationship to generally hold true for HF service. The same is likely true for HF-resistant alloys. However, industry experience has been inconsistent regarding corrosion in Alloy 400 overhead piping in HF regeneration service. Where regeneration tower overhead vapors are injected directly into acid settlers, there have been cases reported of localized corrosion and dissimilar weld cracking of the vapor injection nozzle where it enters the settler.

In HF regeneration systems, over 90 % of the water in the acid feed goes overhead in most cases. Of the water that goes out the bottom of the tower, it is always accompanied by HF at greater than or equal to the amount required by the HF/water azeotrope. Thus, the HF-to-water ratio in the overhead stream is only marginally higher than that in the acid feed. Consequently, a corrosive water-enriched HF phase initially forms when condensation occurs in the tower overhead. HF regeneration overhead lines that experience condensation are therefore at a higher corrosion risk. Erosion-corrosion and preferential weld corrosion have been noted as

issues in this system. The damage mechanisms and rates depend on the specific operating conditions, contaminants, and the design of the system.

#### **y) HF Regeneration Overhead Condenser and Cold Piping**

When HF regeneration system overhead vapor is condensed in a fractionation tower overhead condenser, corrosion issues may be significantly less. One theory is that once actual condensation begins, the water-enriched HF phase initially formed is rapidly diluted by condensing HF, thus giving only limited condenser surface area with high water content in the acid phase. A rapid change in temperature of the process stream may play a role as well. Another theory is that condensing zones in fractionation towers are already in phase change HF corrosion zone, so adding another stream that contains both HF and water where the composition of that stream is not significantly different than the HF/water composition in the tower overhead makes little difference regarding corrosion rates. Regardless, carbon steel is often adequate for both the condenser and acid boot rundown piping to the reactor/settler section.

Corrosion in the overhead line from the top of the tower can be high on Alloy 400 and Alloy 400 welds (see G.4.3.7).

#### **z) HF Regeneration System Dead-legs**

Dead-legs in HF regeneration systems have caused issues in both the tower and overhead piping, especially where the dead-leg was not insulated or insulation in poor condition. As tower vapor enters uninsulated dead-legs, some of the vapor condenses. The HF liquid phase formed will have a considerably higher water content than the vapor stream (see G.3.4 and G.4.3.5). When the water-enriched liquid runs into the tower or overhead piping, it heats up, preferentially driving off HF, making the remaining liquid richer in water. The combination of a high-water content liquid phase and normal operating temperatures results in pitting and metal loss of Alloy 400 and carbon steel. LOPC events have happened as a result of this phenomenon in Alloy 400 equipment. These dead-legs are considered to be in the phase change HF corrosion zone.

NOTE This type of damage has been noted to occur at locations not typically considered to be dead-legs (e.g. thermowells and blinded nozzles).

### **F.4.23 Acid Flare/Relief Header and Acid Neutralization Scrubber Corrosion**

Acid flare/relief headers and acid neutralization scrubbers are prone to both phase change HF and dilute HF in water corrosion. All HF in the unit (with the exception of fresh HF) contain water and any partial phase change from vapor to liquid in the header will produce a more corrosive liquid phase (phase change HF corrosion zone). Water ingress into the header upstream of the acid neutralization scrubber by any means can make corrosion more aggressive (dilute HF in water corrosion zone).

When there is liquid in the flare header, the corrosion on the pipe wall can be more aggressive where the vapor-liquid interface occurs.

If HF is not sufficiently neutralized in the acid neutralization scrubber, there have been reports that Alloy 400 piping was not sufficient to provide a reasonable service life in the downstream header. Some have noted significant corrosion in the acid neutralization scrubber when the acid gas is not well mixed with the neutralizing solution, resulting in the drop out of an acidic aqueous phase. This has allowed both carbon steel clad with Alloy 400 and solid Alloy 400 to corrode through wall. This environment can result in what is termed "elephant skin" type corrosion on Alloy 400. These corrosion effects are irrespective of the neutralizing solution used.

The acid neutralization scrubber can also experience very high temperatures when a stream containing a high concentration of HF going through it. Typically, the upper section of the acid neutralization scrubber is constructed with Alloy 400 (cladding or solid) to tolerate corrosion where the HF is being neutralized and pH transitions between basic and acidic. In addition to corrosion, other degradation mechanisms have also been experienced in the acid neutralization scrubber and associated piping, including galvanic corrosion between Alloy 400 and carbon steel, Alloy 400 SCC (see G.2), and caustic SCC of non-PWHT carbon steel.

#### F.4.24 Corrosion in Product Rundown

Corrosion in product rundown systems including alkylate is typically not an issue unless there are issues with tower operations and/or unit upsets. Examples that have been noted include the following.

- a) On the bottom of the HF/propane stripper, a low point chemical cleaning connection without a drain failed due to HF corrosion. The corrosion occurred due to the tower being shut down for an extended period during a weather event and HF settling out of the hydrocarbon and ending up in the low point chemical cleaning nozzle. Once the unit started up, the composition of the trapped HF changed, resulting in phase change type corrosion rates.
- b) Another incident occurred in the butane product line. Inspection of the welds in the line revealed that they had been preferentially corroded. This was caused by the defluorinator/KOH treater system operating poorly for a long period of time and the HF preferentially attacking the welds that were high RE.

#### F.4.25 Sources of Water and HF Alkylation Corrosion

##### aa) General

Four potential scenarios where local corrosion rates can be high due to local HF-water composition are discussed below.

##### bb) Cooling Water Ingress

One scenario is when HF leaks into cooling water. A relatively minor amount of HF in cooling water will dramatically increase local corrosion rates per NACE 5A171, Figure 2. If not identified quickly enough, significant corrosion is most likely to occur on the tubesheet and channel and to a lesser extent on the piping associated with the leaking exchanger, and in a worst-case scenario the entire cooling water system. During extended excursions, localized corrosion at the HAZ of the weld has been seen in carbon steel piping. IOWs for the monitoring of HF in cooling water can be effective in preventing long-term damage to the cooling water system. The use of welded tube-to-tubesheet joints or double tubesheets are methods refiners have used to decrease the leak potential in exchangers.

In a non-dedicated cooling water system, HF ingress can create corrosion problems throughout the system, including other units.

The pressures on the HF alkylation unit are typically high enough on the process side that the HF goes into the cooling water; however, during transient operations or conditions when process pressures are lower than cooling water pressure, the reverse can occur.

##### cc) Steam Condensate Ingress

Another scenario is when either steam/steam condensate leaks into the process or HF leaks into steam condensate. HF leaking into steam condensate can occur where the process pressure is higher than the steam pressure in reboilers when a tube or tubesheet joint leaks. A relatively minor amount of HF will dramatically increase local corrosion rates due to the HF/water composition at the operating temperatures involved. Steam condensate leaking into the process can occur where steam pressure is higher than process pressure in reboilers when a tube or tubesheet joint leaks. If the stream being heated contains any HF, it will be very corrosive locally. Also, the water can condense in dead-legs and/or in tower overhead systems and increase corrosion rates regardless of whether the stream being heated contains HF. Because of these concerns, special design considerations are used to reduce the frequency of HF ingress into water or water ingress into the process, such as triple rolling, seal or strength welding of tubes to tubesheet joints, use of double tubesheets, the use of U-bend vs floating head heat exchangers, and the use of seamless tubes. IOWs for the monitoring of HF in the steam condensate can be effective in preventing long-term damage to the steam system.

In a non-dedicated condensate system, HF ingress can create corrosion problems throughout the system, including other process units.

Special considerations need to be taken in transient operating conditions where the pressure difference changes or reverses.

#### **dd) Turnaround Water**

It is typical to experience a 1 % to 2 wt % increase in HF water content when HF is re-introduced into the unit after a turnaround. The primary sources of this increase are:

- a) inadequate dry-out of dead-legs and low points during start-up, especially if loose scale or solids/sludges from pre-turnaround unit cleaning are left inside the unit,
- b) water created from the reaction of HF with iron oxides that were made when the unit was open,
- c) water dissolved in hydrocarbons, and
- d) water remaining in the system from hydro testing (see 6.6.5).

Re-introduction of HF can result in local pockets of high concentrations of water until it either absorbs into or is pushed downstream by the process stream. Figure 2 of NACE 5A171 directly applies to the absorption case when HF is present. Carbon steel will experience increasing corrosion rates until the HF in water concentration reaches about 30 wt % water and then decreases as HF concentration further increases.

A number of means can be utilized to decrease the effects of turnaround water:

- a) reintroduce acid to the unit as quickly as possible during start-up,
- b) dry down unit hydrocarbon until very little free water accumulates in distillation tower acid boots,
- c) check and purge all low point bleeders before and after introducing hydrocarbon back into the unit during start-up,
- d) flush through distillation tower acid boots after acid is reintroduced to the unit,
- e) use a liquid other than water for pressure testing unit equipment,
- f) remove solids and sludges from unit equipment during a turnaround, and/or
- g) remove dead-legs that are known to accumulate water and are not needed for operations.

#### **ee) Wet Unit Feeds**

Wet unit feeds or filling towers/equipment without a subsequent dry-out can be another significant source of water (see 5.3.2.2.3).

When water-containing streams (e.g. wet iC4 seal flush or wet saturated butanes to fractionation section feed) are directly fed into HF-containing unit streams, corrosion rates can increase, especially in the mixing zone between the streams. This is due to the HF being at higher water content in the mixing zone and thus being more corrosive. Because of this, significant corrosion can occur at the mix points.

Once the streams are fully mixed and at the bulk composition, the corrosion rate decreases. Managing feed water content is thus important for managing local corrosion rates. Methods used to manage feed water typically include setting feed and reactor acid loop water content limits and operating the HF regeneration



system to a target water content in the reactor acid loop. IOWs for the monitoring of water content in the feed streams can be effective in preventing damage.

**ff) Low Point Dead-legs**

When the unit is starting up or has been down for a period of time, HF and/or water can settle into low points, including dead-legs. Dead-legs that cannot be drained once the unit is online can be problematic. See 6.5.4.2. On example of this is a chemical cleaning nozzle at the bottom of a fractionation section tower that was blind-flanged and did not have a drain.

If water is in the dead-leg, the metallurgy is carbon steel, and HF is present during operations, HF will preferentially absorb into the water phase and result in accelerated corrosion rates as discussed in G.4.3.7. Then if the dead-leg contains both HF and water, HF may preferentially dissolve in the hydrocarbon phase or may preferentially dissolve in the HF/water phase, depending on the liquid-liquid phase equilibria. However, in a liquid system, a very wide HF/water composition range is possible with much of it very corrosive to carbon steel.

A similar issue is mentioned in Section 6 of this document where concentric orifices in horizontal lines have the potential to trap liquid and not allow a line to be drained fully. Issues with trapped liquid can also occur when plug valves are installed in a line that is not designed to drain from both sides of the valve. Unlike gate valves, when plug valves are open, the liquid in the line can become trapped on one side of the valve if there is no drain present in that area. This type of trapped water can result in the inability to liquid-free lines prior to opening and/or following closing of the system.

## **F.5 Implementation of IOWs on HF Alkylation Units**

This section provides guidance on the implementation of IOWs on HF alkylation units and uses terminology that is consistent with API 584. Keeping IOW parameters within established limits is a key goal for managing HF alkylation unit degradation mechanisms, as noted in G.3 and 6.1.5. While the parameters identified in this section are the typical parameters to be considered as part of an IOW program, they do not represent all the parameters potentially, which need to have IOWs established, as the complete set for a given unit depends on unit configuration, equipment design and condition, materials of construction, operating history, and experience.

Table G.1 (below) provides high-level guidance for each parameter typical for an HF alkylation unit IOW program. The implementation details for each parameter (e.g. monitoring techniques, frequency of monitoring, parameter limits, specific equipment impacts, operations response to exceedances, inspection response to exceedances) are typically defined when IOWs are defined and implemented for any given unit. The first three columns in the table are self-explanatory. The API 584 level in the last column uses C for Critical, S for Standard, and I for Informational as defined in that document. IOW and operating envelope terminology (5.3.3) regarding critical parameters may not be the same in every case. Many parameters considered critical for HF alkylation units are given and presented in the main section of this document. Some IOWs may have more than one limit associated with them. (e.g. C, S, and/or I).

Information limits may be typically based on historic operating conditions and known corrosion history for these operating conditions for the impacted system. The duration and magnitude of operation outside the historic limits can be defined to flag potential changed damage exposure potential and the need to modify the inspection plan for the impacted equipment.



**Table G.1—Typical IOW Parameters for HF Alkylation Units**

	<b>Operating Parameter Description</b>	<b>Damage/Mechanical Integrity Impact</b> (Reference)	<b>Equipment/System(s) Affected</b>	<b>Suggested IOW Category</b> C = Critical S = Standard I = Informational
1	Maximum arsenic content in fresh HF shipments	Arsenic promotes hydrogen damage to carbon steel in all corrosion zones.  (Annex I. 4)	Unit carbon steel plate in HF service	I (troubleshoot with supplier)  or  S (max level for acceptance)
2	Maximum Mercury in refinery crude feed/alkylation unit feed	Promotes SCC of Ni-Cu and Ni alloys. Applies only to units that run or potentially run mercury-containing feeds.  (6.2.3.3, Annex G, G.2.5.6)	Most locations with HF-resistant alloys, especially in the propane section of the unit	I (troubleshoot source)
3	Maximum Feed moisture (includes all olefin and butane feeds into the unit)	Increased feed moisture will directly increase water in acid content leading to:  Increased water in entrained RHF in effluent increasing phase change corrosion in fractionation.  Increased corrosion potential with recycle iC4 mixing zone.	Phase change corrosion zone  -Fractionation heating and cooling exposure  -Fresh feed/recycle mixing zone.  -Regeneration system	I (operating at sustained higher water impact on water in acid)

		Increasing regeneration to reject water increasing regeneration system corrosion.  (Annex G, G.3.4, G.4.6.5)		or  S (max target impact on drier operation)
4	Maximum Combined feed sulfur	Feed sulfur makes low-density ASO and reduces acid strength impacting:  Poorer acid settling and increased RHF entrainment in effluent increasing phase change corrosion in fractionation.  Increasing regeneration to reject light ASO increasing regeneration system corrosion.  (Annex A, Table A.1, Low Acid Strength)	Phase change corrosion zone  -Fractionation heating and cooling exposure  -Regeneration system	I (operating at sustained higher S impact on strength)  S (max target impact on upstream S removal adjustment)
5	Minimum acid strength	Low acid strength impacts:  Poorer acid settling and increased RHF entrainment in effluent increasing phase change corrosion in fractionation.  Increased organic fluoride make impacting fractionation deadlegs (thermal defluorination). Runaway Potential.  Increased organic fluoride product treating dilute HF corrosion due to increased water make.  Increasing regeneration to maintain strength increasing regeneration system corrosion.  (Annex G, G.3.4, Annex A Table A1, Low Acid Strength)	Phase change corrosion zone  -Fractionation heating and cooling exposure  -Regeneration system  -Fractionation Deadlegs  Dilute HF in Water Corrosion Zone  -Defluorination Dilute HF	I or S (operating at sustained lower historical strength)  C (minimum to avoid runaway)

6	Maximum circulating HF water content	<p>High water in HF content impacts:</p> <p>Increased water with entrained RHF in effluent increasing phase change corrosion in fractionation.</p> <p>Increasing regeneration to maintain remove water increasing CBM and regeneration system corrosion</p> <p>(Annex G, G.3.4)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation heating and cooling exposure</p> <p>- Regeneration system</p>	<p>I (sustained increase above historical)</p> <p>S (Maximum target for increasing regeneration)</p> <p>C (very high water direct action )</p>
7	Maximum reactor/acid cooler temperature	<p>Increased temperatures will:</p> <p>increase circulating rich HF corrosion and,</p> <p>increase the potential for hydrogen charging related damage in the reactor/acid cooler/settler system.</p> <p>(Annex G, G.3.3)</p>	<p>Rich HF Corrosion Zone</p> <p>-Settler</p> <p>-Reactor</p> <p>-Acid cooler</p>	<p>I (tracking sustained increase temperatures contributing to corrosion)</p> <p>S (controls/limits implemented)</p>
8	Maximum total hydrocarbon flow-through settler (alternatives are maximum vertical velocity and minimum residence time)	<p>Increased flow rate/velocity or decreased residence time can increase entrainment of rich HF into the fractionation section, increasing phase change corrosion.</p> <p>(Annex G, G.3.4, Annex A, Table A.1, Corrosion)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation heating and cooling exposure</p>	<p>I (tracking sustained increase throughput contributing to corrosion).</p> <p>S (controls / limits)</p>

				implemented)
9	Maximum settler acid level	<p>Decreased hydrocarbon residence time can increase entrainment of rich HF into the fractionation section, increasing phase change corrosion.</p> <p>(Annex G, G.3.4)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation heating and cooling exposure</p>	S (controls / limits implemented)
10	Minimum settler acid level	<p>A low acid level can lead to hydrocarbon carry under and emulsion formation and increases organic fluoride make leading to:</p> <p>Increased thermal defluorination impacting fractionation deadlegs.</p> <p>Increased product defluorination water make impacting dilute HF corrosion exposure.</p> <p>Carry under can also lead to increased difficulty in emulsion separation in the settler, leading to increased rich HF entrainment into the fractionation section, increasing phase change corrosion.</p> <p>(Annex G, G.3.4)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation heating and cooling exposure</p> <p>-Fractionation Deadlegs</p> <p>Dilute HF in Water Corrosion Zone</p> <p>-Defluorination Dilute HF</p>	S (controls / limits implemented)
11	Minimum I/O Ratio	<p>Lower I/O ratio decreases hydrocarbon/acid density difference which can increase entrainment of rich HF into the fractionation section, increasing phase change corrosion.</p>	<p>Phase change corrosion zone</p> <p>-Fractionation heating and cooling exposure</p>	I (tracking sustained decrease contributing to corrosion)

		(Annex G, G.3.4)		S (controls / limits implemented)
12	Maximum tower feed temperature	<p>A maximum temperature may be defined that can flag a change in the historical phase change corrosion exposure within the feed piping and tower inlet and feed zone.</p> <p>(Annex G, G.3.4)</p> <p>Maximum temperature to avoid hot HF corrosion of CS.</p> <p>(Annex G, G.2.1.1)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation feed systems and tower inlet nozzle and feed zone.</p>	<p>I (tracking sustained increase contribution to corrosion)</p> <p>S (controls / limits implemented)</p>
13	Minimum tower feed pre-heat temperature	<p>For towers with pre-heat exchangers, a minimum temperature may be defined that can flag a change in the historical phase change corrosion exposure within the feed piping and tower. Low feed temperature in the tower can cause accelerated corrosion of the feed distributor / feed tray and tower shell.</p> <p>(Annex G, G.3.4)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation feed systems and tower inlet nozzle and feed zone.</p>	<p>I (tracking sustained decrease contribution to corrosion).</p> <p>S (controls / limits implemented)</p>
14	Maximum fractionation overhead temperature	<p>Maximum temperature to avoid hot HF corrosion of CS.</p> <p>(Annex G, G.2.1.1)</p>	<p>Phase change corrosion zone</p> <p>-Fractionation top and overhead</p>	<p>I (tracking sustained increase contribution to</p>

			piping.	corrosion) or S (controls / limits implemented)
15	<b>Minimum fractionation overhead temperature</b>	A minimum temperature may be defined that can flag a change in the historical phase change corrosion exposure within tower top and overhead piping.  (Annex G, G.3.4)	Phase change corrosion zone  -Fractionation top and overhead piping.	I (tracking sustained decrease contribution to corrosion).
16	<b>Maximum total hydrocarbon flow-through separator drum (alternative minimum residence time)</b>	Increased flow rate/velocity or decreased residence time can increase entrainment of rich HF (boot acid) from the separator drum i.e. recontactor, overhead accumulator, separator, into the downstream fractionation (depropanizer, HF/propane Stripper) increasing phase change corrosion.  (Annex G, G.3.4)	Phase change corrosion zone  -Fractionator feed preheat and tower feed zone downstream of separator.  - Fractionator tower top, reflux zone and overhead piping.  -HF/propane Stripper Top.	I (tracking sustained increase contribution to corrosion).
17	Maximum fractionator overhead receiver acid boot level	Free boot acid carryover into HF/propane stripper feed can:  Increase phase change corrosion in HF/propane stripper top and overhead  Increase potential phase change corrosion lower into	Phase change corrosion zone  -HF/propane stripper Top and overhead piping.  -HF/propane stripper bottom including low point deadlegs.	S (controls/limits implemented)  C (proactive shutoff to



		<p>HF/propane stripper bottom including deadlegs</p> <p>(Annex G, G.3.4)</p> <p>Increase HF carry under into the downstream defluorinator, which increases the potential for excessive temperatures and creep/stress rupture.</p> <p>(4.7 f), Annex J, J.1.3 a)</p>	<p>Dilute HF in Water Corrosion Zone</p> <p>-Propane defluorinator system through KOH treater</p> <p>-Defluorinators</p> <p>Fractionator HF Corrosion Zone</p>	avoid exotherm)
18	Minimum HF/propane stripper overhead vapor to feed ratio	<p>Insufficient stripping results in HF in the tower bottom leading to:</p> <p>Increase potential phase change corrosion lower into HF/propane stripper bottom including deadlegs</p> <p>(Annex G, G.3.4)</p> <p>Increase dilute HF corrosion potential downstream of the defluorinators due to higher water production and fluoride breakthrough due to alumina consumption.</p> <p>(Annex G, G.3.5)</p> <p>Increase HF carry under into the downstream defluorinator, which increases the potential for excessive temperatures and creep/stress rupture.</p> <p>(4.7 d), 8.2.4 a), Annex J, J.1.3 d)</p>	<p>Phase change corrosion zone</p> <p>-HF/propane stripper bottom including low point deadlegs.</p> <p>Dilute HF in Water Corrosion Zone</p> <p>-Propane defluorinator system through KOH treater</p> <p>-Defluorinators</p>	S (controls/limits implemented)
19	Maximum fluorides at	<p>High inlet fluorides will increase defluorinator water production and increase the water dewpoint temperature of the outlet stream. The higher fluorides can also increase the potential for having increased free HF in the outlet stream. Any water that condenses will absorb any HF present and causes dilute HF in water corrosion on</p>	<p>Dilute HF in Water Corrosion Zone</p> <p>-Defluorinator outlet</p> <p>-Product condenser</p>	I (tracking sustained increase contribution)

	inlet to defluorinator	carbon steel.  (Annex G, G.3.5)	-KOH treater/aqueous caustic treater inlet	S (controls/limits implemented)
20	Maximum defluorinator bed temperature or delta temperature	Possible exotherm due to HF breakthrough could lead to exceeding vessel design temperatures  (4.7 d), Annex J, J.1.6 a)	Defluorinator system	C (for temperature or delta temperature that approaches design temperature limit)
21	Maximum defluorinator outlet free HF or total fluoride content	A breakthrough will lead to:  dilute HF corrosion of defluorinator outlet equipment and excessive caustic consumption and  (Annex G, G.3.5)  possible exotherm from the reaction between HF and caustic in KOH treater/aqueous caustic treater.  (4.7 d), Annex J, J.1.6 c)	Dilute HF in Water Corrosion Zone  -Defluorinator outlet  -Product condenser  -KOH treater/aqueous caustic treater inlet  -KOH treater/aqueous caustic treater	S (controls/limits implemented)
22	Increase in arsenic in spent propane defluorinator alumina	Arsenic promotes hydrogen damage to carbon steel in all corrosion zones  (6.2.2.3, G.2.1.3)	Unit carbon steel plate in HF service	I (tracking for potential increase in charging potential)

23	Minimum KOH treater inlet temperature	<p>Low inlet temperatures to the KOH treater can result in condensation of water, which will absorb any HF present (regardless of cause) and cause dilute HF in water corrosion on the carbon steel. The higher fluorides can also increase the potential for having increased free HF in the outlet stream. This can be aggravated if the dewpoint of the process stream is increased due to increased fluorides in the feed.</p> <p>(Annex G, G.3.5)</p>	<p>Dilute HF in Water Corrosion Zone</p> <p>-Condenser and outlet piping</p> <p>-KOH treater inlet</p>	<p>I (tracking sustained decrease)</p> <p>or</p> <p>S (controls/limits implemented)</p>
24	Minimum Liquid Treater KOH or NaOH Treater Strength	<p>Product treatment by liquid KOH or NaOH requires a minimum strength to ensure no acidic breakthrough.</p> <p>(8.2.1)</p>	<p>Liquid KOH or NaOH treater and downstream piping and equipment</p>	<p>S (controls/limits implemented)</p>
25	Maximum KOH treater bed temperature or delta temperature	<p>Higher temperatures can indicate:</p> <p>Possible exotherm due to HF breakthrough could lead to exceeding vessel design temperatures.</p> <p>(Annex J, J.1.6.d)</p> <p>High temperature increases the potential for caustic-induced cracking in non-PWHT vessels.</p> <p>(No reference)</p>	<p>KOH treater</p>	<p>S (for caustic cracking risk).</p> <p>C (for temperature or delta temperature that approaches design temperature limit).</p>

26	<p>Minimum KOH treater brine pH</p> <p>NOTE In lieu of brine pH, treater effluent copper strip testing, freeze testing, or amount and frequency of brine drain can be used.</p>	<p>Low pH indicates that KOH is either spent or ineffective, allowing corrosive dilute HF in the drum bottom and potentially into the product rundown stream.</p> <p>(6.5.12.4, Annex G, G.3.5)</p> <p>(8.2.4 d).</p>	KOH treater and downstream piping and equipment	S (controls/limits implemented)
27	Maximum tube metal temperatures in fired heater	<p>Increased potential for creep/stress rupture</p> <p>(Annex A, Table A.1 Furnace Tube Failure)</p>	Fired heater	<p>S (controls/limits implemented) and/or</p> <p>C (shutdown)</p>
	Minimum fired heater pass flow	<p>Low flow to fired heater pass leading to creep/stress rupture</p> <p>(Annex A, Table A.1 Furnace Tube Failure)</p>	Fired heater	<p>S (controls/limits implemented) and/or</p> <p>C (shutdown)</p>
	Minimum fractionation	For excessively low temperatures, there is an increased potential for creep/stress rupture in downstream defluorinators. Low or excessively low bottom temperature is most likely only during start-up/shutdown	Defluorinators	

28	bottoms temperature	<p>and malfunctions.</p> <p>(Annex J, J.1.3)</p> <p>A minimum temperature is needed to keep HF and associated water from penetrating down the tower and causing phase change corrosion lower than normal in the tower and associated dead-legs.</p> <p>(Annex G, G.3.4, G.3.6)</p>	<p>Fractionator HF Corrosion Zone</p> <p>-Fractionation bottoms and downstream systems including debutanizer.</p>	S (controls/limits implemented)
29	Maximum fluorides in debutanizer feed	<p>Increased corrosion in the top of the debutanizer tower and overhead system, due to HF formation caused by thermal defluorination.</p> <p>(No reference)</p>	<p>Phase change corrosion zone</p> <p>-Debutanizer tower top and overhead system</p>	<p>I (tracking for potential increase in corrosion).</p> <p>or</p> <p>S (controls/limits implemented)</p>
30	Alkylate storage tank bottoms water pH	<p>Low pH can lead to increased tank corrosion. A caustic heel is generally kept in the tank and pH monitoring ensures adequate caustic strength for corrosion protection. Salt formation can confound the ability of pH to manage corrosion. (6.5.12.3, 8.2.3, Annex A, Table A.1 Corrosion)</p>	Alkylate storage tank	S (controls/limits implemented)
31	Maximum acid vaporizer heat medium inlet temperature	<p>High heating medium temperature increases corrosion of Alloy 400 and carbon steel present in the HF regenerator system preheat section.</p> <p>(6.2.3.3, Annex G G.2.5.1, G.4.3.2)</p>	<p>Phase change corrosion zone</p> <p>-Acid vaporizer/superheater</p>	S (controls/limits implemented)

32	Maximum HF regenerator system tower acid feed temperature	High process temperatures increase corrosion of Alloy 400 and carbon steel present in the HF regeneration system preheat section and locations downstream  (6.2.3.3, Annex G G.2.5.1,G.4.3.2)	Phase change corrosion zone  -HF regeneration system preheat and into the tower	S (controls/limits implemented)
33	Maximum iC4 stripping vapor temperature to HF regenerator/rerun	High temperatures increase corrosion of Alloy 400 in HF Regenerator.  (6.2.3.3, Annex G G.2.5.1,G.4.3.2)	Phase change corrosion zone  -HF regeneration system	S (controls/limits implemented)
	Maximum HF regeneration tower feed rate	Maintain tube and piping velocity below licensors recommendation. This is to reduce erosion/corrosion of Alloy 400 tubes in the vaporizer and piping.  (ref XX)	Phase change corrosion zone  -Acid vaporizer/piping	S (controls/limits implemented)
34	Maximum HF regeneration overhead piping velocity (for Alloy-400 piping)	This is to reduce erosion/corrosion of Alloy 400 overhead piping and condenser to maintain velocity at licensors recommendation,  (Annex G G.2.5.1,G.4.3.5)	Phase change corrosion zone  -HF regeneration system overhead and condensing section	S (controls/limits implemented)
35	Maximum HF regenerator overhead vapor temperature	Higher average temperatures could increase:  corrosion rates of Alloy 400 and/or carbon steel in the system and  can move the location where phase change corrosion can occur as acid/water condenses. Applies only to units with refluxed HF regeneration systems.  (Annex G G.2.5.1,G.4.3.6)	Phase change corrosion zone  -HF regeneration system overhead	I (tracking for potential increase in corrosion)  and/or



				S (controls/limits implemented)
36	Maximum HF regeneration system overhead condenser outlet temperature	Higher temperatures can lead to higher corrosion rates in carbon steel. Applies only to units where an exchanger condenses the HF regeneration system tower overheads.  (Annex G G.4.3.6)	Phase change corrosion zone  -HF regeneration system overhead condenser	I (tracking for potential increase in corrosion)
37	Maximum HF regeneration system tower bottoms temperature	Increased temperature leads to increased corrosion on Alloy 400.  (6.2.3.3, Annex G G.4.3.4)	Phase change corrosion zone  -HF regeneration system tower bottom and bottoms piping circuit	I (tracking for potential increase in corrosion)  and  S (controls/limits implemented)
38	Minimum HF regeneration system bottoms liquid level	In units with a submerged sparger, minimum liquid level required to ensure that the hot stripping iC4 is submerged in the liquid to control hot corrosion of Alloy 400 and a minimum amount of HF leaves the tower with the ASO.  In units without a submerged sparger, minimum liquid level required to ensure hot stripping iC4 is not sent out of the bottom piping which could increase Alloy 400 piping corrosivity and fatigue potential at the caustic mix point.  Applicability depends on the tower bottom design.	Phase change corrosion zone  -HF regenerator tower	S (controls/limits implemented)

		(Annex G G.4.3.3)		
39	Maximum ASO caustic mix point temperature	<p>High temperatures can:</p> <p>increase corrosion in this system and</p> <p>increase the potential for caustic-induced cracking in non-PWHT vessels</p> <p><b>(No reference)</b></p>	<p>Dilute HF in Water Corrosion Zone</p> <p>-Caustic mix point and downstream separation drum</p>	I (tracking for potential increase in corrosion and possible cracking potential)
40	Minimum ASO neutralizer caustic circulating strength	<p>Low caustic strength can result in ASO not being neutralized, which results in corrosion of the caustic mixer, ASO neutralizer, and downstream piping and equipment. pH is not an acceptable substitute monitoring parameter.</p> <p><b>(No Reference)</b></p>	<p>Dilute HF in Water Corrosion Zone</p> <p>-Caustic mixer, inlet line to ASO neutralizer, ASO neutralizer, ASO rundown, and surge drum vent line</p>	S (controls/limits implemented)
41	Minimum ASO neutralizer caustic circulating rate	<p>A low caustic circulation rate can result in ASO not being neutralized, which results in corrosion of the caustic mixer, ASO neutralizer, and downstream piping and equipment.</p> <p><b>(No Reference)</b></p>	<p>Dilute HF in Water Corrosion Zone</p> <p>Caustic mixer, inlet line to ASO neutralizer, ASO neutralizer, ASO rundown, and surge drum vent line</p>	S (controls/limits implemented)
42	Maximum ASO neutralizer caustic circulating temperature	<p>Impact of maximum temperature to ASO neutralizer equipment and piping:</p> <p>accelerated corrosion</p> <p>or cracking of non-PWHT equipment and piping</p>	<p>Dilute HF in Water Corrosion Zone</p> <p>Caustic mixer, circulating caustic piping, inlet line to ASO neutralizer, and ASO neutralizer</p>	S (controls/limits implemented)

		(No Reference)		
43	Minimum acid relief main header purge velocity	This is to reduce moisture from the acid neutralization scrubber backing into the header, leading to fouling and corrosion.  (8.1.2)	Phase change corrosion zone  -Acid relief header	S (controls/limits implemented)
44	Maximum Acid neutralization scrubber maximum flare system liquid knock out drum level	May result in high rates of HF to the acid neutralization scrubber (ARN/RGS) causing increased exotherm temperatures, which could increase the potential for caustic induced cracking in non-PWHT equipment/piping.  (Annex A, Table A.1 ARN)	Dilute HF in Water Corrosion Zone  Acid neutralization scrubber	S (control/ limits for caustic cracking)
45	Maximum acid neutralization scrubber circulating base (caustic) solution temperature	Impact of maximum temperature of ARN/RGS equipment and piping:  detect excess HF and exotherm potential  accelerated corrosion  or cracking of a non-PWHT  (8.1.1)	Dilute HF in Water Corrosion Zone  Acid neutralization scrubber circulation loop	S (controls/limits implemented)
46	Minimum acid neutralization scrubber circulating base (caustic) solution	Detect autorefrigeration of large LPG release that could trigger freezing/plugging (overpressure) or brittle fracture potential.	Dilute HF in Water Corrosion Zone	C (shutdown)

	temperature	(4.7 e))	Acid neutralizer scrubber	procedure)
47	Minimum acid neutralization scrubber caustic circulating strength	Low caustic strength can result in acid gases not being neutralized, which results in corrosion of the acid neutralization scrubber bottom and overhead downstream flare piping and equipment. pH is not an acceptable substitute monitoring parameter.  (8.1.1)	Dilute HF in Water Corrosion Zone  Acid neutralization scrubber liquid system,  Overhead downstream flare piping and equipment	S (controls/limits implemented)
48	Minimum acid neutralization scrubber/caustic circulating rates	Low caustic circulation can result in acid gases not being neutralized, which results in corrosion of the acid neutralization scrubber bottom and overhead downstream flare piping and equipment.  (8.1.1)	Dilute HF in Water Corrosion Zone  Acid neutralization system,  Overhead downstream flare piping and equipment	S (controls/limits implemented)
49	Maximum oxygen in unit blanketing or purge gas (including nitrogen)	Promotes SCC of many HF-resistant alloys.  (8.3.5, Annex G G.2.5.2)	All locations with HF-resistant alloys that are normally in HF service	S (controls/limits implemented)
50	Maximum fluorides in cooling water	HF in cooling water will cause rapid corrosion damage at the leak point and increase cooling water system corrosion rates.  Tracking of fluorides is performed over pH due to buffering in the cooling water can delay detection if using pH.  (8.3.2, Annex G G.4.6.2)	Cooling water system	S (controls/limits implemented)

51	Maximum fluorides or conductivity in condensate or minimum pH in condensate	HF in steam condensate will cause rapid corrosion damage at the leak point and increase condensate system corrosion rates.  (8.3.4,Annex G G.4.6.3)	Steam condensate system	S (for either fluorides or conductivity or low pH/C for either high fluorides or very low pH)
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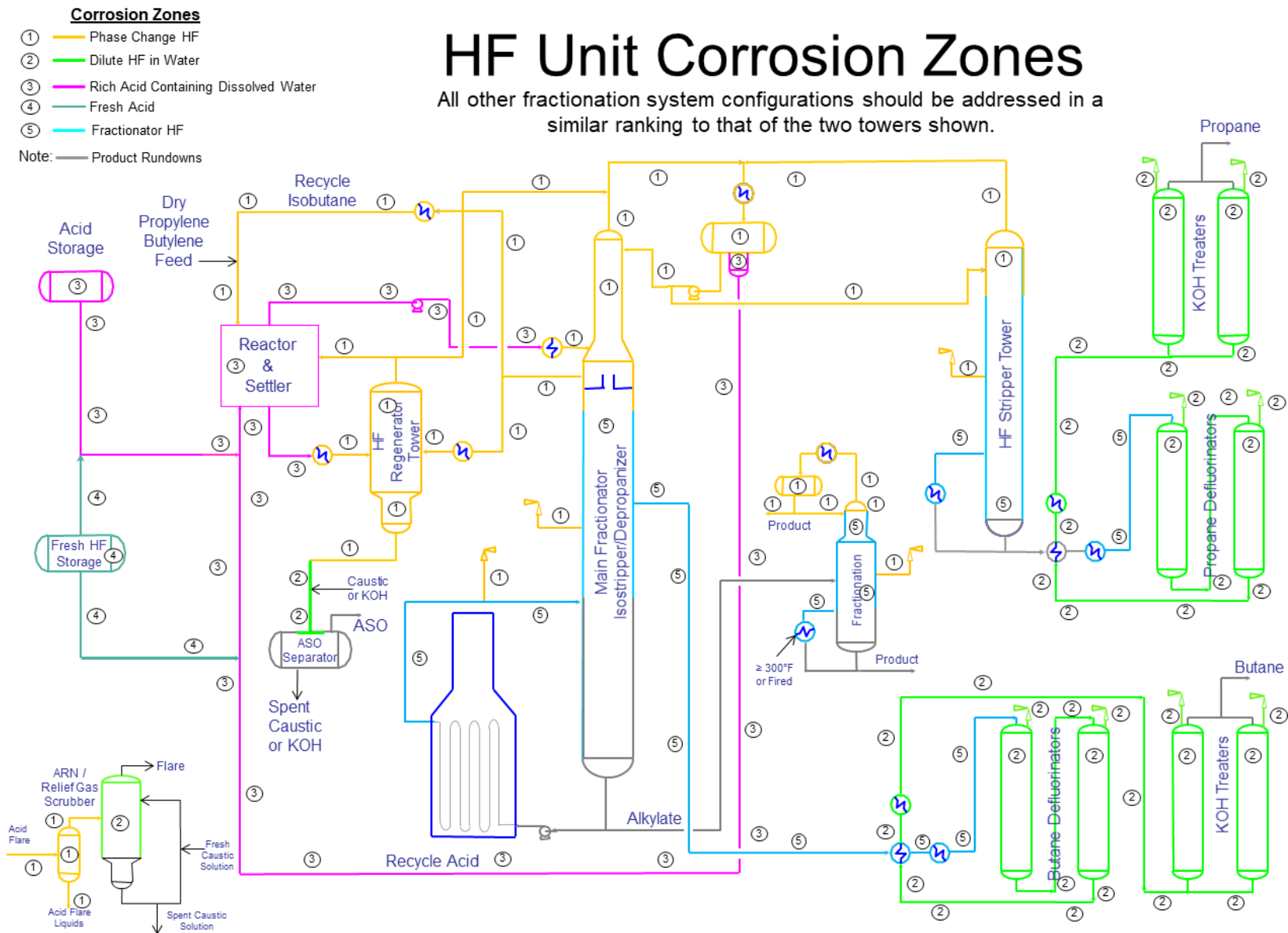


Figure G.1—Corrosion Zone Diagram

## **Annex G** (informative)

### **Inspection Considerations Specific to HF Alkylation**

#### **G.1 General**

This annex presents key considerations for inspection specific to HF service. The information is primarily based on user experience and published information. The information may be useful in developing the site's inspection program.

#### **G.2 Material Verification Program (MVP)—Instruments**

##### **G.2.26 General**

Use of instrumentation for PMI is one option for verifying material. Understanding the use, limitations, and differences in the available technology to verify materials of construction with these instrument types and techniques is critical when performing material analysis. Each MVP will have different requirements when it comes to identifying the material to be analyzed. Each alloy or material will have various elemental requirements and restrictions. Understanding each technique will help determine which technology to use to verify the material. Additional information on materials verification can be found in API 578.

##### **G.2.27 X-ray Fluorescence (XRF)**

XRF is the most commonly used nondestructive test (NDT) method offering the user a portable handheld analyzer that delivers fast, accurate results. Handheld XRF analyzers use an X-ray tube to emit an X-ray beam into a sample, exciting the electrons and displacing them from the inner shell. The vacancy from the inner shell then gets replaced with an electron from an outer shell. As this electron fills the vacancy of the inner shell, it releases energy in the form of a secondary X-ray. This release of secondary energy is known as fluorescence. Each element present will emit unique energy characteristics of itself. By measuring the unique characteristic of released energy emitted from the sample, it is possible to determine which elements are present. This is called qualitative analysis. Then, by measuring the intensities of the unique energy and applying correction factors, it is then possible to measure how much of each element is present in the sample.

Some XRF analyzers are capable of measuring light elements in low concentrations such as silicon, phosphorus, sulfur, aluminum, and magnesium. XRF has limitations on the elements that can be measured. Elements lighter than magnesium cannot be measured using XRF. This limitation of XRF makes it impossible to grade materials such as low carbon stainless steels, carbon steel, and low alloy materials because carbon cannot be measured utilizing XRF analyzers. For example, XRF can measure the elements required to identify carbon steel and can detect element levels of Cu, Ni, and Cr to delineate high-RE material from low-RE material; however, XRF cannot be used to determine carbon content for the calculation of CE or use of the less restrictive RE limits (see Section 3 for the definition).

##### **G.2.28 Optical Emission Spectroscopy (OES)**

OES is an optical method that can be used to detect almost all types of elements, including carbon and light elements in a variety of different matrixes. In the OES technique, atoms are also excited; however, the excitation energy comes from a spark formed between the sample and instrument electrode. Unlike XRF that utilizes an X-ray tube to irradiate the sample, OES uses the energy of a spark that causes the electrons in the sample to emit light, which is converted into a spectral pattern. Each element produces a unique color of optical light. By measuring the intensity of the peaks in this optical light of the spectrum, the OES analyzer can produce qualitative and quantitative analyses of the material composition. Even though OES is considered a nondestructive testing method, the sample needs to be prepared with a mechanical sanding device and the



spark does leave a small burn on the sample surface that would need to be removed after the analysis is complete.

The OES technique is used to grade material by measuring the element carbon to identify alloys such as low carbon or high carbon stainless steels, low alloy carbon steels (e.g. 41xx series, 86xx series), and 10xx series carbon steels, to name a few. Therefore, OES can be used to analyze for both RE and CE in carbon steel.

OES instruments vary in weight and size depending on the manufacturer but can weigh 50 lb or more and require an argon tank that, depending on the size of tank utilized, would also weigh about 20 lb. Because of the weight and size of this field mobile OES, working in elevated work areas could require mechanical assistance to lift an OES instrument to higher elevation platforms.

Also, when performing an analysis with OES, each sample to be analyzed will require sample preparation utilizing a grinder that uses a zirconium aluminum oxide or ceramic sanding disc to prepare the surface. Sample preparation is a critical step in any OES analysis and a sample that is not properly prepared will yield undesirable and inaccurate results.

### G.2.29 Laser-induced Breakdown Spectroscopy (LIBS)

The LIBS technique utilizes a pulsed laser to ablate the surface of the sample creating a plasma. As the plasma cools, the electrons from the cooling plasma are excited, causing the plasma to emit light. Each element of the periodic table produces a LIBS spectral peak unique to itself. By using a detector to measure the unique characteristics of light emitted, it is possible to detect what elements are present within the sample. By measuring the peaks of light and their intensities in the sample, the chemical composition can be rapidly determined and quantified in weight percent concentrations (%), or parts per million (ppm).

<http://bit.ly/2Kj4NuR> LIBS has been around for many years and is a technique used primarily in laboratory equipment. With recent advances in technology, the technique has now been developed into a portable handheld analyzer capable of measuring carbon in the field for material identification and grading of materials. Like OES, argon is still needed to analyze carbon in a LIBS handheld analyzer. Instead of an external argon tank, regulator, and hose connection to the OES unit, the handheld version of the LIBS analyzer uses a consumable argon cartridge integrated into the instrument. With the analyzer's battery, the instrument weighs less than 6.5 lb.

Sample preparation is still required for analysis, but the handheld size of the instrument, the grinder, and zirconium aluminum oxide or ceramic sanding discs can all be contained in a small case and transported to elevated working platforms and hard to access areas with minimal effort, giving the user true field portability in a handheld carbon analyzer. Proper sample preparation is a critical step in the analysis of the sample. Poor sample preparation will yield undesirable results. With proper sample preparations, the user can achieve fast, reliable, and accurate results. The LIBS analyzer can be used to measure light elements in low concentrations such as carbon, silicon, and aluminum. The capability of the LIBS analyzer gives the user the ability to easily grade "L" and "H" grade stainless steels, low alloys, and carbon steels. The instrument can also perform CE or RE calculations programmed by the user in an easy-to-use and intuitive interface.

## G.3 Critical Check Valves

Critical check valves are defined in API 570. Owner-operators define critical check valves based on risk, system configuration, and other factors.

Potential critical check valves include the following.

- a) Critical check valves identified by a layers of protection analysis.
- b) Utilities that have a permanent connection to the process, such as nitrogen to acid unloading and steam to reboilers.

- c) Air reservoirs for remotely activated valves.
- d) Feed lines from unit dryers.
- e) Fired heater outlet check valves.
- f) Fresh acid pump discharge, especially if there is no remote block valve (RBV) present.
- g) Feed pump discharge check valves, especially if there is no RBV present.
- h) Reboiler pump discharge check valves.
- i) Feed pump discharge where the flow splits to two different destinations where reverse flow could result in overpressuring equipment.
- j) Emergency mitigation systems air pot check valves.
- k) Lines that could send acid to the defluorinators.
- l) Lines that could allow acid to exit the unit boundaries/into areas where HF is not present.
- m) Check valves on the outlet of pumps in all corrosion zones, where RBVs have been installed only on the inlet.
- n) Check valves for which a higher reliability factor than a typical check valve was used in the quantitative risk assessment or other risk assessment methodology.

#### H.4 Plug Valves

Because of their design, plug valves can trap liquid on one or both sides of the valve when installed in horizontal lines. Unlike gate valves, plug valves when fully open still have part of the plug that extends above the ID of the pipe. The potential to trap liquid around the plug valves, especially if retrofitted in place of gate valves, may pose a corrosion risk. Some owner/operators monitor with inspection plans and/or mitigate with low point drains or procedural modifications (e.g. for line clearing, water removal).

## Annex H (informative)

### Procedures for Unloading HF Acid Tank Trailers

Various hazard reviews of HF alkylation units have identified HF unloading as having a need to use rigorous methods to ensure that the unloading is completed safely for the entire process. Because of this, it is helpful for HF unloading to follow a carefully written procedure. Nitrogen-pressured unloading is the most commonly used procedure, but other procedures, such as pumped unloading, are also used.

The following is one possible example of a procedure for nitrogen-pressured HF unloading from tank trailers. The details may vary from unit to unit. This procedure is written to accommodate the type of unloading station described in Section 7 and is adaptable to other types of transport containers such as rail tank cars or portable ISO tanks.

NOTE The “should” and “shall” statements below are part of the example and not intended to generate additional requirements. See Section 7 for recommendations and requirements for acid unloading.

#### Example Procedure

- o) Traditional Class C (OSHA “Level B”) protective clothing shall be available to refinery personnel and truck drivers. Class C (OSHA “Level B”) PPE shall be worn by all personnel involved in making and breaking connections, leak testing, and transferring HF. Typically, hose connection, transferring acid, and hose disconnection is completed by the truck driver. Some facilities may require these tasks completed by the operators or maintenance team.
- p) At least two people should be available full-time for HF unloading. At least one qualified person from the refinery HF alkylation unit shall participate. The driver performing the unloading should remain in Class C (OSHA “Level B”) protective clothing for the duration of the acid transfer. All other persons observing the unloading should do so from a distance while wearing the minimum required PPE for the alkylation unit.
- q) Before HF is delivered, the refinery owner-operator shall verify that the HF storage vessel level indication, process valves, and the nitrogen pressure controller are properly configured and operable. The level in the HF storage vessel should be checked to ensure that there is room for the volume of fresh HF to be received.
- r) The refinery owner-operator shall review the HF material certification documentation to see that it is AHF and that the QC limits are met. As arsenic is known to promote blistering and cracking of carbon steel, the arsenic content of fresh HF should be minimized and limited to not more than 25 ppm by weight.
- s) The safety shower and eyewash station in the transport unloading area shall be tested.
- t) The water mitigation system shall be tested and put in the predetermined setting prior to positioning the tank trailer. The area cameras shall be positioned to provide coverage from the control room or satellite building. If cameras are not used, other remote visual surveillance shall be put in place.
- u) HF transport containers shall be unloaded with sufficient lighting and staff available for emergency response.
- v) The refinery owner-operator shall ensure that adequate neutralization capability for unloading is available in the neutralization section before beginning the unload. Testing the strength of the caustic solution is suggested.

- w) The refinery owner-operator shall ensure that the transport brakes are set, the wheels are chocked, the bonding system is in place, warning signs are posted, and access to the unloading facility is restricted during transport siting.
- x) For truck deliveries, the keys shall be removed from the ignition and kept in a safe location mutually agreed upon by the refiner owner-operator and the truck driver.
- y) The refinery owner-operator shall verify that the pressure of the HF storage vessel is below the transport vessel operating pressure.
- z) The operability of both the transport container's remotely activated valves and the unit's remotely activated valves shall be tested prior to unloading.
- aa) Check the nitrogen supply relief valve setting, which should be at least 20 % less than the transport container product relief valve setting.
- bb) The refinery owner-operator should confirm that the nitrogen meets the minimum criteria for oxygen content as specified in 8.3.5 and is water-free.
- cc) The refinery owner-operator and the truck driver shall verify that the HF and nitrogen piping are depressurized prior to removing blind flanges. Then the blind flanges on the HF unloading line and the nitrogen pressure inlet line shall be carefully removed. Flange connections shall be visually inspected. The HF unloading and nitrogen lines (usually high-integrity chemical transfer hoses having flanged connections) should be connected to their respective openings using new, solid, 1/8-in.-thick PTFE or PTFE encapsulated steel gaskets. B7 or B7M studs should be used. If the bolts show evidence of corrosion or have been exposed to HF, they should be replaced with new bolts. Bolts should be tightened to the required torque spec.
- dd) The refinery owner-operator shall confirm that the lines are purged with nitrogen prior to use. The refinery owner-operator in conjunction with the truck driver shall pressure test with nitrogen both the nitrogen and HF unloading lines by using a crossover between the nitrogen line and the HF unloading line. The refinery owner shall verify the nitrogen regulator pressure setting during the pressure test. The refinery owner-operator in conjunction with the truck driver shall test all connections with a liquid leak detector, such as soapy water. After the leak test, the system shall be depressurized and secured.
- ee) The refinery owner-operator shall ensure proper lineup to the HF storage vessel. The valve at the end of the unloading line at the unit's unloading manifold shall remain closed at this time.
- ff) The dome on the transport container should be opened slowly in case the valve stems are leaking HF into the dome. Once the dome has been opened, it should be secured to the railing to prevent accidental closure.
- gg) The refinery owner-operator in conjunction with the truck driver shall pressurize the transport container with nitrogen to a pressure higher than that of the HF storage vessel plus any liquid head before the liquid discharge valve is opened. This will prevent the backflow of liquid or gas into the transport container from the HF storage vessel.
- hh) The refinery owner-operator shall open the unit's manifold HF valve slowly. The refinery owner-operator in conjunction with the truck driver operator shall visually inspect the hoses and connections for HF leaks. If no leaks are present, the transport's HF valve shall be opened slowly to permit HF to flow into the HF storage vessel.
- ii) In the event of a leak, immediately close the transport and the unit's unloading line valves. Depending upon the nature of the leak, it may be necessary to bleed off pressure from the unloading operation. Any spilled HF should be neutralized per the unit's response procedure.
- jj) The truck driver shall periodically check the nitrogen pressure of the transport container during the unloading operation. The refinery owner-operator shall periodically check the pressure and HF level in

the HF storage vessel to ensure that HF is being received. When the transport container is empty, the storage vessel's pressure will equalize with the container's pressure. The transport container's gauge pressure will fall quickly, and the hose may move around when the container is empty.

- kk) When the HF transfer is completed, the refinery owner-operator shall close the unloading line valve at the HF storage vessel. The HF level in the HF storage vessel should be checked to ensure that the amount unloaded is equal to the amount delivered.
- ll) The truck driver shall close the nitrogen valve on the transport container. The pressure in the transport container should be vented to the neutralization section using the unloading line and the appropriate vent line. The pressure shall be reduced to less than 20 psig to meet transportation regulatory requirements.

NOTE Transportation regulations preclude shipment of emptied containers as placarded at a pressure greater than 41 psia.

- mm) The truck driver shall close the transport container's HF unloading valve. Using the crossover line, the unloading hose and line should be purged with nitrogen for a period sufficient to remove liquid and vapor to the maximum extent practicable. The truck driver shall close the transport container's air-to-open remotely activated valve(s). Subsequently, the operator shall close the vent line to the HF relief header and the valves at the end of the nitrogen line at the unit manifold. The refinery owner-operator shall verify that the unloading hose and lines are depressurized by opening the appropriate drains or vents. The refinery owner/operator shall close the HF unloading valve at the manifold and the truck driver shall close the transport vessel hose block valve.
- nn) The truck driver shall disconnect the hose fittings from the transport container, decontaminate as necessary, and stow. The truck driver shall reinstall the blind flanges on the transport hoses. The truck driver shall close and secure the transport container dome for transport.
- oo) Blind flanges shall be reinstalled on the unloading manifold using a new site approved gaskets. B7 or B7M studs should be used. If the bolts show evidence of corrosion or have been exposed to HF, they should be replaced with new bolts.
- pp) Tools, equipment, and PPE used in unloading shall be decontaminated before being removed from the unit.

## **Annex I**

### **(informative)**

## **LPG Treater Systems—Safety Interlocks**

### **I.1 LPG Treater Systems—Safety Interlocks**

#### **I.1.30 General**

This annex provides supplemental considerations for the design of a safety instrumented system for automatic protection of defluorinator and KOH treater and aqueous caustic treater vessels in HF service.

Refer to 8.2.4 regarding safety instrumented systems being installed to prevent or lessen the probability of sending an unexpected, excessive HF intrusion into these treaters.

This annex is purely informative and is not intended to be included within the scope of API 751 audits.

#### **I.1.31 Propane/IC4 (Overhead) Scenario Identification and Mitigation**

The availability requirement of each system will depend on the initiating frequency and consequence of potential scenarios involving HF intrusion into these vessels. In general, LPG treating systems downstream of an overhead drum with an acid-collecting boot (typically propane treater system) have the highest potential for liquid HF intrusion and, therefore, require the most robust protection. Defluorinator and/or KOH treating systems for butane or alkylate products may require simpler systems for adequate protection.

#### **I.1.32 Overfill of HF Acid Boot into HF Stripper Feed**

The most common scenario for an excessive exothermic reaction in this system is sending a concentrated HF stream to the HF stripper by overfilling the HF acid boot of the HF stripper feed drum or depropanizer feed drum directly upstream. When liquid HF begins to enter the HF stripper tower, tray temperatures will decrease due to tray compositions becoming more HF-rich. If not immediately corrected, high concentrations of liquid HF will be allowed to exit the bottom of the HF stripper tower and into the defluorinators.

Proactive initiators can be used to indicate this developing problem prior to allowing HF acid into the downstream treaters. Typically, a combination of several instruments is needed to provide adequate protection through redundancy, each independently able to initiate a shutdown of the treater circuit. Options for instrumentation to provide proactive protection include the following.

- a) High-High Acid Boot Level Switch—Often a nuclear instrument.
- b) High-High Acid Boot Level Indication—Often used in combination with high-high acid boot level switch for redundancy.
- c) HF Stripper Delta Temperature—This provides an indication of liquid HF acid in the HF stripper tower feed. DTs across the stripper can be measured in different ways. If the delta T is measured between the top and the middle of the column or between the top and bottom of the column, low delta T is an indication that HF has slipped down to the lower temperature indicator (TI) point in the delta T measurement. If the delta T is measured across the bottom 10 to 15 trays of the column (between the middle of the column and the bottom), high delta T is an indication that HF has reached the upper TI point in the delta T measurement. Shutdown triggers are typically set ~5 °F beyond the normal operating tower delta temperature values.
- d) HF Stripper Feed/Overhead Flows—Indicates liquid HF acid in HF stripper tower feed when tower overhead flow decreases and bottoms flow increases, typically 25 % to 30 % of tower feed is the flow overhead in normal operation.

- e) Low HF Stripper Bottoms Temperature—Indicates potential for liquid HF acid in HF stripper tower feed.

### I.1.33 Reverse Flow of HF into Pump Seal Flush System

At some sites, the HF stripper bottoms is the source of seal flush for pumps in HF service. During transient operations, such as loss of HF stripper reboiler heat source, the seal flush header supply pressure can be lower than the stuffing box pressure of the pump and allow reverse flow from the process stream into the flush header. Although the flush system often has check valves to minimize backflow, they can and do fail. This can allow an HF-rich stream to flow directly into the HF defluorinators or KOH treater. If the process stream is a high concentration HF stream (i.e. acid boot return pump, HF regeneration system feed pump), the resulting exothermic reaction will be severe. High defluorinator temperatures from a reverse flow of a seal flush system supplied by the HF stripper bottoms stream have been reported in the industry.

- a) The instrumentation on the overhead HF acid boot and HF stripper will not directly indicate a reverse flow scenario. Temperature indications in the downstream treater beds can be used to initiate a system shutdown. Options for instrumentation to provide a reactive indication of these conditions include High-High bed temperature in defluorinator.
- b) High-High delta temperature across defluorinator.

The RBVs for treater isolation or diversion can be strategically placed between treaters and the piping that supplies pump flush systems to ensure a potential backflow can be stopped to the treaters once detected.

### I.1.34 Acid Purity Runaway

During an acid purity runaway, a significantly greater quantity of organic fluorides than normal can be generated. Some of these organic fluorides will thermally decompose in the bottom of the fractionator towers, generating significantly greater amounts of HF than is normally present in the bottom section of these towers. In addition, a larger amount of acid can be carried over from the reaction section to the fractionator, increasing the partial pressure of HF in the fractionator, and thus potentially causing HF to drop further down the tower than normal. This can lead to a significant amount of HF in the fractionator bottoms and side-draw streams where it is typically not present. In some cases, free HF has been reported in the alkylate run-down stream and in the n-butane upstream of the treaters following an acid purity runaway.

Because of these factors, large exotherms in the butane treater systems have been reported in industry during an acid purity runaway event, with the potential to cause a loss of containment and fire. Temperature indications in the downstream treater beds can be used to initiate a system shutdown.

Options for instrumentation to provide a reactive indication of these conditions in the treater include:



- gg) High-high bed temperature in defluorinator
- hh) High-high delta temperature across defluorinator
- ii) High-high bed temperature in KOH treater
- jj) High-high delta temperature across KOH treater

### **I.1.35 Inadvertent Bypass of Defluorinators on Start-up**

Refer to 8.2.4 regarding including potential for inadvertent bypassing of the defluorinators or similar valve misalignment when assessing the instrumentation needs of KOH treater protection systems. This type of scenario has been reported in industry, resulting in loss of containment and fire. Although prior incidents occurred on unit start-up, other transient operations may also be a consideration for where this may occur.

Reactive initiators on the KOH bed can be used to indicate a valve misalignment or inadvertent bypassing of the defluorinators:

- a) high-high bed temperature in KOH treater,
- b) high-high delta temperature across KOH treater.

### **I.1.36 Dead-leg Associated HF Slug**

During transients that cause a loss of heat to a fractionation tower, HF can migrate to the bottom of the tower or into the piping for side draw streams where it does not typically exist in significant quantities (i.e. n-butane side draw or HF stripper bottoms). If the tower bottoms or side draw streams are stagnant for a period of time, free HF can phase separate from the hydrocarbon in the dead/stagnant leg. When the flow is re-introduced to the treater (either defluorinator or KOH treater), a slug of concentrated HF liquid can create a significant temperature excursion. Similar scenarios have been reported in the industry, resulting in loss of containment and fire.

Temperature indications in the downstream treater beds can be used to initiate a system shutdown. Options for instrumentation to provide a reactive indication of these conditions include:

- a) high-high bed temperature in defluorinator,
- b) high-high delta temperature across defluorinator,
- c) high-high bed temperature in KOH treater,
- d) high-high delta temperature across KOH treater.

The location of RBVs used to isolate these circuits during transients can also be optimized to minimize or eliminate the potential for dead-legs when isolated. For example, some sites with a butane side draw isolate the draw when the draw tray temperature reaches a specified low temperature. If the flow control valve is used, which is typically located at grade, the piping from the Isostripper tower to the butane flow control valve can fill with HF-rich hydrocarbon and subsequently be routed to the downstream treaters. If an RBV located at the tower outlet nozzle is used, the potential for an HF-filled dead-leg is eliminated.

### **I.1.37 Reverse Flow of HF into Olefin Feed Dryers**

During a unit shutdown or other scenarios in which both olefin feed flow and iso-recycle flow is lost, HF can migrate from the reaction section into feed dryers. The exothermic reaction with the activated alumina or mole sieve catalyst can be as severe as in LPG product treaters.

To address this scenario, some sites have given check valves that prevent backflow from the reaction section into the feed dryers a “safety critical” status or installed RBVs to isolate the reaction section from the feed dryers.

If a unit has a separate dryer system for make-up iC<sub>4</sub>, an examination of a reverse flow scenario to this system is also advised.

#### **I.1.38 Additional Possible Scenarios**

Other credible ways to get an HF stream into the LPG treaters or feed driers may need to be considered by the site, including temporary connections and start-up lineups.

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## **Annex J**

### **(informative)**

## **Design Considerations for Assessment and Mitigation Options**

### **J.1 Overview**

This annex is provided as a supplement to Section 9 of the recommended practice and is intended to give additional information and guidance on the various topics of Section 9. The additional information and guidance are provided to clarify the intent of Section 9 and to promote a consistent approach to mitigation. The information provided is for illustrative purposes and does not constitute an endorsement or a recommendation for implementation, as site-specific considerations need to be factored into any such analysis.

### **J.2 Assessment Approach Considerations**

#### **J.2.39 General**

This section of the annex provides guidance to satisfy the required quantitative assessment (see 9.3). The owner-operators have a choice of conducting either a risk-based or consequence-based approach to satisfy the requirement of conducting a quantitative approach. Whichever assessment approach is chosen, dispersion models are used. The following are examples of dispersion models that have been validated with experimental data that are in wide use for these analyses at the time of publication of this document.

Public domain:

- a) HEGADAS (steady-state and transient),
- b) SLAB,
- c) DEGADIS,
- d) ALOHA®.

Commercially available:

- e) PHAST™ and PHAST™ derivatives,
- f) SafeSite®.

This list does not preclude the use of other dispersion models verified to be validated with experimental data.

#### **J.2.40 Consequence-based Approach**

In a consequence-based approach, the analyst is required to identify and evaluate an MCE. See 3.1.51 for MCE definition. The hazard endpoint is either a concentration-based endpoint or a dosage-based endpoint based on a referenced probit equation (see Annex D). The owner-operator selects the endpoint criteria that they will use as well as the receptors of concern (e.g. fence line, off-site residential, etc.) to determine the extent of the hazard zone. It may be valuable to select a dispersion model and software package that can generate both concentration and dosage-based profiles.

Often it is not apparent which event of the many possible scenarios is the most appropriate to evaluate. Therefore, it is usually necessary to evaluate a variety of possible events to determine which is/are to be used in the analysis. The owner-operator selects scenarios based on the potential for toxic exposure from a

hypothetical HF release, using release sizes that have a reasonable probability of occurrence, considering the concentration of HF in the process equipment, HF inventory, operating conditions, equipment and piping design, industry incident history, and other factors. The analysis includes the time needed to activate mitigation systems to determine the extent of the hazard zone both before and after deployment. Several release scenarios are typically required to be modeled to identify the scenario that generates the greatest downwind distance. Some historical industry incidents involved effective hole sizes between  $\frac{3}{4}$  in. and 2 in. and were long duration events; therefore, a pump seal failure scenario may not be considered a credible MCE as it is too small and may be too short of duration with typical isolation.

#### J.2.41 Risk-based Approach

There are three general methods by which risk can be assessed by an owner-operator: qualitative, semi-quantitative, and quantitative. While the qualitative and semi-quantitative approaches provide valuable insight and are appropriate for some risk management applications, only the quantitative methods provide sufficient analytical capability and objectivity to address the complex interactions between the HF alkylation process and the associated mitigation systems. Furthermore, the quantitative methods provide the capability to calculate scenario risk exposure, aggregate risk exposure, and individual and societal risk results needed to make informed decisions.

The three general risk methods are described as follows.

- a) *Qualitative methods* rely primarily upon the judgment and experience of multidisciplinary teams, and minimal quantification and evaluation resources are required. Examples of qualitative methods include, but are not limited to, PHAs, preliminary hazard reviews, root cause failure analyses, and aspect identifications.
- b) *Semi-quantitative methods* use numerical/qualitative techniques and conservative estimates regarding the frequency of initiating events and the effectiveness of the existing safeguards. Examples of semi-quantitative methods include, but are not limited to, layers of protection analyses and safety integrity level analyses.
- c) *Quantitative methods* are the most detailed and use a standard set of equipment failure rate data, discharge modeling, dispersion modeling, and probabilities (e.g. weather, ignition, vulnerability) to provide a numerical understanding of overall risk. As such, quantitative methods provide the greatest level of understanding of the risk associated with processes or systems and provide an objective basis for comparison of risk exposures for the various equipment/mitigation configurations that may exist. The results of quantitative methods are numerical estimates of risk that can be compared to established risk criteria. *Guidelines for Chemical Process Quantitative Risk Analysis* published by the AIChE Center for Chemical Process Safety provide a reference for conducting quantitative risk studies.

### J.3 Design Considerations for HF Detection and Mitigation Systems

#### J.3.42 General

Several factors are taken into account when designing HF mitigation systems. The design will be highly dependent on both individual site details and the results of the assessment approach used. The degree of mitigation desired will depend on the refinery's setting, local topography, proximity to the public, and the risk tolerance of the owner-operator. It is important to consider the mechanisms that may result in a loss of containment when designing mitigation systems. If a release of HF occurs because of corrosion or other simple mechanical degradation, the detection and mitigation systems will likely be unimpeded to function as designed. If the loss of containment is the result of a fire or explosion (either on the HF alkylation unit or an adjacent unit), these systems may fail to function as intended unless there are significant redundancies for these systems and/or the utilities serving these systems included in the design.

The following subsections provide additional information and design considerations to help the owner-operator design the chosen HF detection and mitigation systems. Consideration may be given to activating mitigation systems automatically on HF releases of consequence rather than requiring operators to manually activate them.

### J.3.43 HF Detection

#### kk) General

An effective HF detection system provides early, and reliable, indication of an HF release such that appropriate mitigative actions can be taken. Although the local concentration of an accidental HF release may substantially exceed the range of the instrument, the objective is early detection and notification of a release rather than the determination of exact concentrations.

It is highly desirable for detectors to have good stability. Significant zero or span drift over time requires frequent calibration to minimize inaccurate readings and spurious alarms.

#### ll) Performance Characteristics of HF Sensors

The intent of the technologies is for the detection of elevated HF in the sample space and is not intended as an accurate representation of total HF emissions. All HF measurements will be attenuated at higher concentrations and high humidity or atmospheric contaminants due to HF reacting or combining to forms that are not well detected by the technologies. These effects are generally less significant at the low concentrations used for safety monitoring alarm levels.

Key design considerations for the selection of components and the design of the detection system include the following when selecting detector types:

- a) detector type;
- b) detection range;
- c) detection setpoints;
- d) selectivity;
- e) response time;
- f) stability;
- g) reliability, in terms of maintainability, compatibility with the refinery environment, and experience in similar applications;
- h) elevated releases.

Table K-1 has been provided to assist in comparing some of these considerations for all known HF sensor types in use at the time of publication of this document. While Fourier transform near-infrared technology (FTNIR) spectroscopy can be used for HF detection similar to tunable diode lasers (TDLs), it is typically slower and more expensive than laser technology and is not currently in wide use.

**Table K.1—Considerations for HF Sensors in Wide Use as of This Publication**

Characteristics	Point Sensor Technologies			Perimeter Detection Technology
	Chemical Cell	Silicon Wafer	Short Path Spectroscopy	Open Path Spectroscopy
Detectability	Parts per million (ppm) at the sample point	HF detectable at the sample point (trip)	Parts per million (ppm) in the sample path	Parts per million-meters (ppm-m) path integrated concentration along a line-of-sight path between a transmitting device and a retroreflector or receiver
Detection range (typical)	0.1 ppm to 20 ppm	>10 ppm	0.02 ppm to 200 ppm	0.2 ppm-m to 1000 ppm-m
Response time (typical)	10 sec to 120 sec May vary with temperature.	>10 sec	0.25 sec to 20 sec	Provides the fastest response to HF presence
Selectivity	Selective for free HF gas. May also respond to a number of ionizing gases such as HCl, SO <sub>2</sub> . May also be affected by environmental changes, especially temperature and humidity.	Selective to airborne acid fluorides. May respond to environmental changes such as condensing moisture or fine airborne particles or aerosols.	Highly specific for free HF gas.	Highly specific for free HF gas
<b>Ambient Condition Considerations</b>				
Temperature	May slow or fail to respond in low temperatures, especially at the low end of the detection range	May slow or fail to respond in low temperatures, especially at the low end of the detection range	No effect	No effect
Humidity and free moisture, including fog/steam clouds	May cause baseline drift and potentially false positive alarms. May require increased maintenance frequency. May increase response time by several seconds, particularly at the lower end of the detection range.	May cause baseline drift and potentially false positive alarms. May require increased maintenance frequency. May increase response time by several seconds, particularly at the lower end of the detection range.	Very high fog density may cause temporary operation loss in short open paths	High fog density or heavy precipitation may cause temporary operation loss
Placement	Mount at serviceable height or location. Higher sensor density can improve detection reliability.	Mount at serviceable height or location. Higher sensor density can improve detection reliability.	Mount at serviceable height or location. Short path transmitter units to be on a suitably rigid mounting structure. Some distance from potential sources of high concentration HF can improve reliability in severe conditions.	The rigidity of mounting posts used to install the components increases in importance with an increasing line-of-sight distance, to ensure the detector stays aligned with the source. Consider pathways that minimize beam interference by maintenance equipment, steam clouds, or direct sunlight. Some distance from potential sources of high concentration HF can improve reliability in severe conditions.

Detection technologies are as follows.

- a) Electrochemical Cell—change in electrochemical potential of a gel electrolyte caused by the diffusion of HF through a sample port membrane.
- b) Silicon Wafer—Irreversible change of window opacity due to etching of silicon by HF exposure.
- c) Short Path Laser Spectroscopy—Absorption of characteristic infra-red light energies by HF gas in a sample path that is confined or limited in length to be representative of average local concentration, typically 0.5 m to 5 m.
- d) Open Path Laser Spectroscopy—Absorption of characteristic infra-red light energies by HF gas in a sample path through open air to indicate area HF density, typically 5 m to 200 m.

#### **mm) HF Sensor Reliability**

It is important to consider the reliability of a detector in terms of maintainability, compatibility with the local environment, and operation during abnormal conditions. If a detector is not properly calibrated and maintained, it may fail to respond in the event of a release. Detector elements may deteriorate or be consumed over time or may become poisoned by other gases so that the response to a release is impaired. Since the detector will most likely be installed outdoors, local weather and environmental conditions for the location are considered. Electrical classifications for the location and material selection for components that may come in contact with HF are also considered.

#### **nn) HF Sensor Deployment**

The placement of HF sensors may be affected by refinery and unit geometry, potential leak sources and release rates, maintenance requirements and access needs, mitigation system characteristics, and other features relevant to the site. In some cases, a single detector type deployment may not provide all the desired characteristics; therefore, implementing an integrated system of multiple detector types may be considered. When multiple detector types are used, the relative features and capabilities of the different types are reflected in the system layout, and the features complement each other. In general, a detection system using more than one technology type will be found to be more reliable, provided no common failure modes exist for the types employed.

#### **oo) Remote Surveillance**

Video cameras can be useful tools for alerting operators to vapor clouds and other emergency situations. When used in conjunction with the detection systems described above, video cameras can significantly improve the operator's ability to assess a potential emergency and determine its exact location and scope. Cameras are also valuable for directing and observing the effects of mitigation measures. Elevated locations typically work well and give an overview of the unit. The reliability of video cameras may be affected by glare from the sun, heat exposure, moisture, and long-term low-level HF background exposure.

#### **pp) Hydrocarbon Detectors**

Hydrocarbon detectors can be used to supplement an HF detection system since most unit streams are mainly composed of LPG with soluble levels of HF.

### **J.3.44 Water Mitigation**

#### **qq) Associated Studies**

Amoco, Allied-Signal, Du Pont, and Lawrence Livermore National Laboratory voluntarily conducted a series of six experiments involving atmospheric releases of HF in an attempt to characterize its behavior. These large-scale HF release field tests were performed in 1986 at the Department of Energy test facilities located in



Nevada. This HF test program, known as the Goldfish series, illustrated the potential hazard of an HF spill as well as showing that water had the potential to mitigate an HF release.

The HF molecule is highly hygroscopic and is attracted to the water molecule. Similar to how iron is attracted to a magnet, HF and water molecules form strong electrochemical bonds. Based upon these intermolecular interactions from polarity and hydrogen bonding, researchers associated with the Goldfish tests anticipated that water sprays would be effective in absorbing HF vapors from the air. To test this hypothesis, three of the Goldfish tests were conducted with a water spray curtain. These specific experiments clearly showed that water mitigates an HF release by mixing and absorbing the released HF and thus significantly reduced the measured downwind HF concentration in these studies.

Following the Goldfish tests, 20 companies formed a joint research program called the Industry Cooperative Hydrogen Fluoride Mitigation Assessment Program (ICHMAP) to evaluate various mitigation options including the use of water sprays to mitigate an HF release. One of the primary goals of the program was to understand the factors that would influence the effectiveness of a water mitigation system and provide information that can be used in designing effective water mitigation. In addition to the 87 field tests conducted in the summer of 1988, the program also included laboratory testing of water spray curtains at BETE Fog Nozzle Inc. facilities and then additional field tests in November 1990 with firewater monitors (cannons/turrets).

Schatz and Koopman presented the test results from the program at the Control of Accidental Releases of Hazardous Gases, American Institute of Chemical Engineers (AIChE) Meeting in Philadelphia, PA in August 1989 and subsequently published a paper<sup>2</sup> about the research program test results and findings. Diener with Exxon also published a paper<sup>3</sup> on mitigation of HF releases and in the paper described both water mitigation and vapor barrier mitigation systems. Vasilis M. Fthenakis, in his book *Prevention and Control of Accidental Releases of Hazardous Gases*,<sup>4</sup> includes a chapter on water mitigation written by Dr. Schatz that also describes the ICHMAP program and the test results and findings from the ICHMAP<sup>5</sup> program.

These authors all concluded that water spray mitigation systems (spray curtains, water cannons, or a combination of both) when properly designed are effective at significantly mitigating HF releases. Furthermore, these authors agreed that the primary parameter affecting the removal (scrubbing) efficiency of an HF release is the volumetric ratio of water to HF. The authors collectively concluded that scrubbing efficiencies of 25 % to 90+ % are achieved for water-to-HF liquid volumetric ratios from 6/1 to 40/1 and higher.

In 1993, Congress required the EPA to carry out a review of HF to identify potential hazards to public health and the environment considering a range of events and to make recommendations for reducing the hazards, if appropriate. EPA performed a literature search that included many of the above-mentioned publications and shared its findings as part of a report. The conclusions of the EPA report mirrored that of the industry researchers. According to the EPA, "These studies [Goldfish and ICHMAP] of water spray mitigation showed that water to HF ratios of 40:1 could result in 90 percent reduction in the amount of airborne HF."<sup>6</sup>

The conclusions from Diener, ICHMAP, and the EPA are currently considered when designing a water mitigation system, seeking to maximize the effectiveness of the available water to mitigate a potential HF release, while also taking into consideration the specific equipment layout of the HF alkylation unit. The primary objective of a water mitigation system is to maximize the contact between the deployed water and a potential HF release to ensure the maximum HF removal efficiency to protect workers and the public. The realization of this objective is not achieved through a one-size-fits-all approach but is dependent on individual alkylation unit conditions.

<sup>2</sup> K.W. Schatz and R.P. Koopman, "Water spray mitigation of hydrofluoric acid releases," *Journal of Loss Prevention Process Industries*, Volume 3, April 1990.

<sup>3</sup> R. Diener "Mitigation of HF releases," *Journal of Loss Prevention Process Industries*, Volume 4 January 1991.

<sup>4</sup> Fthenakis V.M., *Prevention and Control of Accidental Releases of Hazardous Gases*, Van Nostrand Reinhold, 1993.

<sup>5</sup> *Id.*, Chapter 11.

<sup>6</sup> EPA Report to Congress, "Hydrogen Fluoride Study Final Report," 1993, pg. 130.

## rr) HF Release Water Mitigation Design Considerations

### J.3.44.rr.1 General

Accordingly, water mitigation systems for potential HF releases can be designed using two fundamental concepts:

- allow the HF release to disperse into a water spray and allow the cloud and water to interact with each other,
- direct the water spray at the HF release.

These options offer different approaches to applying mitigation water, depending on alkylation-unit-specific design constraints such as a structure or elevation. Both approaches can be effective in their ability to deliver water to the release, and in some cases, a hybrid of the two concepts can be applied. The mitigation effectiveness of the water spray system is achieved as long as the requisite volumetric ratio of water contacting the HF is met. One of the HF scrubbing/removal efficiency curves from the ICHMAP test program is shown in Figure K.1. More curves can be found in the documents listed in the references.

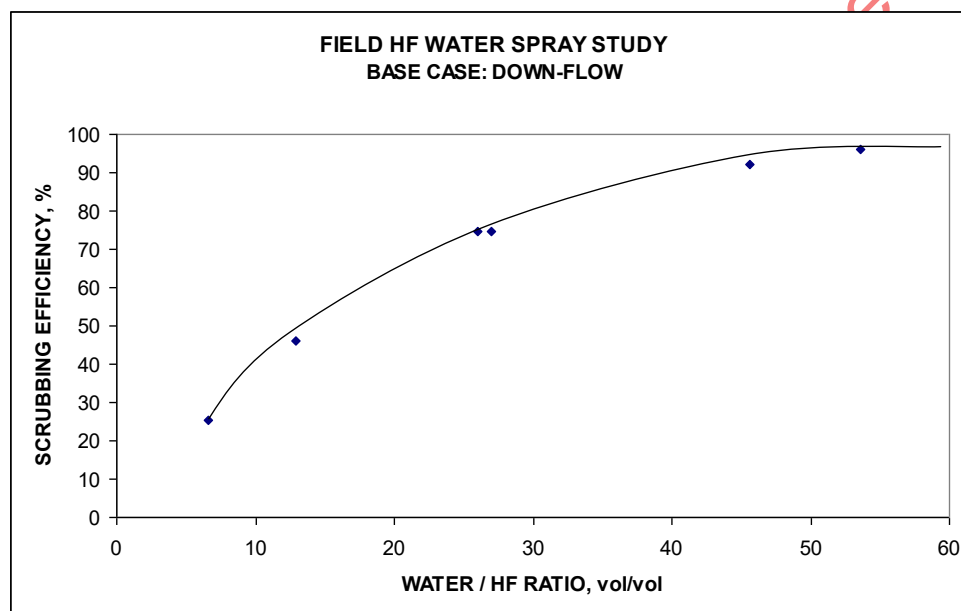


Figure K.1—Field HF Water Spray Study Base Case Downflow <sup>7</sup>

The following regression was developed <sup>8</sup>:

$$Y = a + bX + cX^{0.5} + d * \ln X$$

where

$$a = -50.1041;$$

$$b = -3.6554;$$

$$c = 67.9256;$$

$$d = -39.0460;$$

$$X = \text{volumetric ratio of water/HF};$$

<sup>7</sup> Fthenakis V.M., *Prevention and Control of Accidental Releases of Hazardous Gases*, Van Nostrand Reinhold, 1993.

<sup>8</sup> *Id.*, Chapter 11.

$Y$  = scrubbing efficiency (%).

For example, if the most probable scenario in a site's risk assessment from the strong acid section of an HF alkylation unit is a 1000 lb/min release of 90 wt % HF (thus, 900 lb/min of HF), a water mitigation design that provides a 40:1 water-to-HF ratio [36,000 lb/min or roughly 4,350 gallons per minute (GPM) contacting the release] will achieve roughly 90 % removal efficiency.

The subsequent section discusses design considerations for each of the two concepts. A site may choose to use either concept or a combination of both for individual release scenarios. For sites that also employ a RATS, the design deinventory time may also have an impact on the design of the water mitigation system.

### **J.3.44.rr.2 Concept #1: Allow an HF Release to Come to the Water**

#### **K.3.3.2.2.1 General**

For this concept, the objective is to create a continuous barrier of water using either water spray nozzles (water curtain) or water cannons (water wall), which will absorb an HF release and induce HF scrubbing/removal. Dispersion modeling to indicate the HF concentration at the plane where the HF cloud interacts with the water barrier may be used to assist in the calculation of scrubbing efficiency.

The water spray wall barrier can be created by using water spray nozzles, water cannons, or a combination of both.

Barrier design is based on allowing the release to travel to the water barrier and come in contact at a distance from the release source to permit the cloud to expand and lose its momentum. HF scrubbing/removal efficiency will be reduced if the HF is traveling at high velocity when it interacts with the water wall/curtain due to release momentum. The initial jet velocity of an HF release dissipates by the resistance of air as well as by interference with equipment within the path of the cloud. However, in some cases, there may not be enough room for momentum dissipation and to reduce the velocity of the release. For the HF cloud to lose momentum, become diluted with air, and spread out, a jet release may either:

- a) travel downwind an unobstructed distance of 45 ft or more for release momentum to drop sufficiently <sup>9</sup>,
- b) encounter equipment interference (vessels, pipe rack, etc.),
- c) be targeted by momentum-breaking water cannons, which have an unobstructed path to the HF release point,
- d) in certain releases, such as jet releases closer to the water barrier or in high-wind-speed conditions, deferring to Concept #2 (direct water spray to the HF release) may be required to achieve the desired scrubbing efficiency.

#### **K.3.3.2.2.2 Water Curtain**

Figure K.2 shows what a water curtain may look like. Water curtain spray nozzles can produce a mist of water with a droplet size < 300 microns. The droplet size is large enough to ensure that the water curtain remains stable under various wind conditions. The nozzles used for water curtain sprays are typically different than those used for deluge systems as described in Concept #2.

The height of the water curtain may either be such that elevated releases will not go over the top of the curtain and bypass the water, or else alternate mitigation (such as those referenced in Concept #2) may be used for

<sup>9</sup> S. Mukherjee, S. Dharmavaram, and S. Jaskolka, "Effectiveness of water sprays in mitigating toxic releases," *Process Safety Progress*, Published online 4 December 2017, <https://doi.org/10.1002/prs.11948>.

elevated releases. Lastly, the design of the appropriate height of the curtain considers the force created by the sprays to prevent the cloud from going over the curtain.



**Figure K.2—Example Water Curtain**

#### **K.3.3.2.2.3 Water Wall**

Figure K.3 shows what a water wall might look like. HF-specific water cannons utilize pressure-balanced nozzles in a wide ( $110^{\circ}$  to  $135^{\circ}$ ) cone. These cannons produce a finer droplet size (500 microns to 600 microns) than the traditional fire monitors (cannons) tested in the ICHMAP program, which produced a larger droplet size (800+ microns). These nozzles are designed to be placed at a distance and create a stable high-density wall of water as seen in the picture. The placement of the cannons ensures the water sprays overlap to create a wall of water that the release cannot go through. Pressure-balanced cannons can produce the appropriate spray patterns at a range of water flow rates from 800 GPM to 2000 GPM. Furthermore, the spray patterns of these cannons can be remotely adjusted to target a potential release, thus providing operational flexibility to use the most appropriate water spray mode in the event of a release.



**Figure K.3—Example Water Wall**

Where possible, the water wall may be designed to form a cloud trap by arranging the extended line of nozzles in a curved pattern or by trapping the cloud within a “U” or “V” shaped pocket. The minimum number of nozzles required to form the trap is based on site-specific considerations.

For example, under certain conditions, a wide-cone balanced pressure nozzle set at a  $110^{\circ}$  to  $135^{\circ}$  cone angle can deliver at least a 50 ft to 90 ft diameter cone in calm wind conditions.

The height of the cannons is typically at 25 ft above grade; however, in large alkylation units where inventory may be at much higher elevations, (e.g. in some designs), cannon height may be increased to provide coverage to where the reactor risers enter the settler. In units where HF inventory is significantly higher than 50 ft above grade, the cannons may be located at a higher elevation to capture releases and to prevent them from traveling over the water wall.

The line of cannons is typically aligned and far enough back from the process area that there is no gap in the continuity of the water wall resulting from interference of the spray cone pattern by process equipment or piping. If a gap in the water wall cannot be avoided, additional small cannons or spray curtain, supplied with additional water, may be provided to maintain continuity of the water wall. A solid wall partition as well as large process equipment (e.g. heaters and towers have effectively been used as partitions) may also be considered as a physical barrier to augment the water spray. Curtains consisting of two or more parallel manifolds vertically apart could be considered equivalent to a single wide cone nozzle if the curtain manifold is close enough to the wide cone nozzles to maintain the required overlap.

The water wall mitigation system can be partitioned into zones (e.g. each side of the perimeter is a single zone if size allows) in order to allow selecting the mitigation components that are preferred to be placed in



operation (one or two sides of the water wall perimeter instead of the entire water wall) based on release size, location, and wind speed and direction.

### **J.3.44.rr.3 Concept #2—Direct Water to the HF Release**

#### **J.3.44.rr.3.1 Aim-and-Shoot Water Mitigation System**

Figure K.4 shows what an aim-and-shoot water mitigation system may look like. Directing water to the HF release is primarily accomplished by using water mitigation cannons in a narrow-angle mode and consists of a sufficient number of nozzles to utilize the total required water flow rate. These cannons can be used in combination with a water wall, water curtain, or independently to provide mitigation of HF releases. These are typically elevated cannons located within the alkylation unit, normally spaced about 50 ft from potential release sources, and are remotely operated for aiming control. The cannons are typically sized for 1500 GPM to 2000 GPM fixed water flow with a normal flow pattern (30° cone angle) for optimal scrubbing efficiency. Using a narrower cone angle less than 30° reduces HF scrubbing/removal efficiencies and may impact some equipment. Multiple water cannons may be aimed at the potential release location. Cannons are typically designed to apply the water from an elevated position (typically 25 ft to 50 ft above grade), which improves the coverage of the equipment. The cannons may be located on existing structures or standalone towers.



**Figure K.4—Example Aim-and-Shoot Water Mitigation System**

The fresh acid unloading area is usually outside and away from the perimeter of the process area water barrier. These areas can be protected by providing a separate aim-and-shoot or water barrier system or extending the process area water barrier. If remotely activated aim-and-shoot technology is employed, the cannons may be pre-positioned by operations onto the unloading end of the truck and the HF piping in the unloading area prior to starting the unloading.

### J.3.44.rr.3.2 Equipment Deluge Systems

Figure K.5 shows what an equipment deluge system may look like. For some areas in or around the alkylation unit, water coverage from cannons is obstructed by other equipment, or it is impractical to design a wall or curtain for the equipment height. For these situations, a deluge spray directly aimed at equipment such as pumps and vessel boots beneath a large horizontal vessel can be used. Often these spray systems are further augmented by water from a remotely controlled cannon. These deluge systems typically use the same water nozzles used for firefighting, which are less efficient at HF capture than nozzles designed for water curtains; however, the same nozzles used for water curtains can be used for these deluge systems. A localized water spray deluge focused on each pump seal has been used to provide incipient vapor containment in the event of a seal leak.



Figure K.5—Example Equipment Deluge System



## **ss) Activation**

### **J.3.44.ss.4 General**

Water mitigation systems can be activated by operators (manual activation) or by computerized logic (detector-initiated activation).

### **J.3.44.ss.5 Manual Activation**

Operator (manually) activated systems rely on human intervention to initiate the water mitigation system.

### **J.3.44.ss.6 Detector-initiated Activation**

Pre-programming can reduce the time between release detection and effective water mitigation. Any automation of the water mitigation system may use a specified voting logic (e.g. 2oo2 or 2oo3) per detection of HF from all of the technologies used for the site's HF sensors. The sequence and type of detector that is alarming may be used to determine release location and direction of release travel so that appropriate mitigation system equipment is activated in the path of the release. As a secondary indicator, the use of a local weather station can provide wind direction and wind speed information, which can be used for refinement and targeting of the water mitigation equipment.

A high-integrity microprocessor can be pre-programmed to automatically select which cannons or spray curtain segments to activate in a water wall or curtain system. A high-integrity microprocessor can also be pre-programmed to automatically select and target the aim-and-shoot water cannons and momentum-breaking water cannons to spray to specific release locations. Refer to 9.5 regarding the length of time the activated cannons and curtains are to be kept operating so the operator can determine which water mitigation components will provide the most direct and effective mitigation.

## **tt) Other Considerations**

- a) Evaluate the water supply, as the requirement of an HF mitigation system may be the largest consumer of water on site. The existing water supply system may need to be augmented.
- b) Review drainage, storage, and treatment capabilities due to the potential for a large quantity of water being sprayed in response to an HF release.
- c) Evaluate specific cold weather conditions for the location.
- d) Consider the egress of personnel who may be working in the alkylation unit (especially at heights) from the unit once the water mitigation system is activated.

### **J.3.45 Remotely Activated HF Block Valves**

The goal for installing remotely activated block valves is to be able to isolate sources of HF or pressure from the point of release. Examples of locations to consider for installing remotely activated block valves include:

- a) reactor hydrocarbon feed lines, including isorecycle and olefin feed lines;
- b) fractionator overhead accumulator/depropanizer feed settler HF boot return lines, both at the individual boots and at the return point to the reactor/settler system;
- c) HF circulation pump suction and discharge (pump circulated units);
- d) the HF regeneration system HF feed line (pump circulated units);
- e) HF cooler HF draw lines to HF regeneration system (gravity circulated units);

- f) HF regeneration system HF feed pump suction;
- g) the HF regeneration system overhead line (gravity circulated units);
- h) the stripping iC4 line to HF regeneration system;
- i) the HF unloading station;
- j) HF acid sample/online analyzer supply/return lines.

### **J.3.46 Rapid Acid Transfer Systems (RATS)**

#### **uu) General**

The general factors listed below are provided for consideration in the design of a RATS.

#### **vv) Deinventory Time**

As discussed in the main body 9.6.3, for an automated transfer system to be considered “rapid,” the total duration of the release from occurrence through isolation in the receiving vessel is typically 15 minutes or less.

#### **ww) Amount of HF Transferred**

The amount of HF to transfer is established early in the design process. It may be sufficient to move most of the HF that could be involved in a release rather than trying to move all of it.

#### **xx) Motive Force**

HF movement may require a motive force that will be available during a release. The options available include gravity, existing pumps manifolded into appropriate low points, dedicated pumps installed for purpose, hydrocarbon pressure, and nitrogen pressure. When choosing the motive force, consideration is given to whether the motive force may result in a more extensive release.

#### **yy) Receiving Vessels**

A key design consideration is where the HF and entrained hydrocarbons will go. The options, depending on the volume to be moved and the sizes of the receiving vessels, include the HF-storage drum(s) or a dedicated receiving vessel inside the unit battery limits or elsewhere in the refinery.

#### **zz) Venting**

A design decision is whether or not to vent the receiving vessel(s) and neutralize the vapors generated during the movement of the HF.

#### **aaa) Control System**

The control system for the RATS can be simple or complex. It may be part of an overall unit safety system. The RATS may also include an overall unit shutdown logic. The initiation may be by a simple push-button or may be automatically triggered from a voting-logic HF detector system. Most RATS include numerous remotely activated valves controlled in a high-integrity microprocessor. The system may include timers, relays, and feedback such as valve position, vessel level indications, and fluid density. The transfer logic used to end the dump and isolate the acid in the safe location can use time, receiving vessel level, or fluid density. Most transfer logics include a maximum time after which the receiving vessel is isolated, in order to isolate whatever acid has been transferred in the case when the transfer stalls because the motive force is lost in the case of a large leak.

### J.3.47 Unit Standby System

One strategy that can be taken is to have a safety system that automates operational control moves to place the unit in an idle, standby, or shutdown status in the event of an emergency or incident. Industry experience has shown that in a severe release event, it may be too difficult for the control person to determine where the incident originates from.

The idling, standby, or shutdown safety system can also be capable of being manually initiated by a qualified control board person. Instead of one person trying to execute many moves in the correct order during a highly stressful time, this safety system could be configured to be activated by a single move, and the control system would sequence the steps in a manner developed by experienced and knowledgeable personnel.

A Process Hazard Analysis on this safety system's control steps and sequencing is appropriate when developing the control logic or modifying the process.

This idle, standby or shutdown safety system can consist of, but is not limited to:

- k) Rapid Acid Transfer Systems (RATS, RADS or AES). Acid is contained, secured and isolated from the main process unit.
- l) Feeds diverted from the unit. (some RATS, AES may already do that)
- m) Recycle streams diverted from the main acid systems. (some RATS, AES may already do that)
- n) Energy sources isolated from the unit.
- o) Unit equipment pressures reduced.
- p) Systematic shutdown and isolation of equipment that could be the source of the incident.
- q) Unit relief gas scrubbers remain in operation

## J.4 Passive Mitigation Systems

### J.4.48 Barriers

Barriers are a potential mitigation tool that can be used on an HF unit. The principle of the technology is to provide an obstruction to a potential release point that will dissipate the jet release energy and provide a coalescing surface. Barriers are most effective when used in combination with either water mitigation (see 9.5) or vapor suppression additives (see 9.7). Barriers can be used to ensure that a potential release is directed into the mitigating water, thus improving the contact between HF and water and producing more efficient scrubbing of HF from the cloud. Barriers can reduce the airborne amount of a potential HF release. Barriers can be installed near pressurized volumes of HF and on concentrated HF piping connections (Klaus W. Schatz, "Containment of an Aerosolable Liquid Jet." U.S. Patent 5286456, issued February 15, 1994).

Catch pans are an extension of barrier technology and can be placed primarily under or near HF-containing vessels to capture HF and/or direct the liquids to a special containment area.

### J.4.49 Inventory Control

Another means of passive mitigation that can be applied to a unit is to reduce the amount of HF that can be released. HF process vessels can be segmented to minimize the amount of HF that could be released if one side of the vessel is compromised. HF vessel and exchanger designs may consider techniques that minimize HF volume requirements.

Some of the existing gravity circulation units can be retrofitted with an internal baffle in the settler that can help reduce the available inventory for release in the HF-acid cooler standpipes and reactor risers.

#### **J.4.50 Vapor Suppression Catalyst Additives**

The use of vapor suppression catalyst additives is another option that can be used to further reduce the overall risk of the HF unit. Catalyst additives can help by limiting the amount of HF that could become airborne if a leak develops. The percentage of HF released that remains airborne decreases with increasing release sizes, decreasing pressure, and decreasing distance to impingement.

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