



# **CODE OF PRACTICE COMPRESSED FLUORINE AND MIXTURES WITH INERT GASES**

**Doc 140/18**

Revision of Doc 140/11

***EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL***



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# CODE OF PRACTICE COMPRESSED FLUORINE AND MIXTURES WITH INERT GASES

As part of a programme of harmonization of industry standards, the European Industrial Gases Association (EIGA) publication, EIGA Doc 140, “*Code of practice: Compressed fluorine and fluorine mixtures with inert gases*”, has been used as the basis of an internationally harmonized gas association’s publication on this subject.

This publication is intended as an international harmonized publication for the worldwide use and application by all members of Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association, (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Regional editions have the same technical content as the EIGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Regional regulatory requirements are those that apply to Europe.

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**Amendments from 140/11**

| <b>Section</b> | <b>Change</b>                                  |
|----------------|--|
|                | Editorial to align style with IHC associations |
|                | Revision to reflect current philosophies       |

Note: Technical changes from the previous edition are underlined

## 1 Introduction

Fluorine is a highly toxic and oxidizing gas that presents health risks such as poisoning by inhalation and safety risks such as combustion.

Fluorine and fluorine mixtures can be safely handled if equipment is properly designed and maintained, handling precautions are taken, and employees are trained. As a minimum, all personnel shall have access to the safety data sheet (SDS) and be trained in the use of the SDS and other reference material.

## 2 Scope and purpose

This publication is for suppliers, distributors, and users of gaseous fluorine and mixtures of fluorine with inert gases and handling equipment. This publication is intended for fluorine and mixtures where the resulting fluorine concentrations greater than or equal to 0.5% fluorine are considered to present a risk of reaction due to the oxidizing potential.

This publication provides a good understanding of the potential hazards involved in storage, use, and transportation of compressed fluorine and its mixtures with inert gases and approaches to be taken to minimise the risk of incidents.

The manufacture, purification, liquefaction, and analysis of fluorine or its mixtures with inert gases are beyond the scope of this publication, although the general guidance given is also relevant to these processes.

An audit checklist is located in Appendix A of this publication.

## 3 Definitions

For the purpose of this publication, the following definitions apply.

### 3.1 Publication terminology

#### 3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

#### 3.1.2 Should

Indicates that a procedure is recommended.

#### 3.1.3 May

Indicates that the procedure is optional.

#### 3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

#### 3.1.5 Can

Indicates a possibility or ability.

### 3.2 Technical definitions

#### 3.2.1 Auto-ignition temperature

Temperature at which a substance will spontaneously ignite in a specified oxidant at a given pressure.

### 3.2.2 **Bundle (of cylinders)**

Assembly of cylinders that are fastened together and interconnected by a manifold and carried as a unit.

### 3.2.3 **Cylinder**

Transportable pressure receptacle having a water capacity that does not exceed 150 L and can be filled with gas under pressure.

### 3.2.4 **Cylinder recovery vessel**

Pressure receptacle with a water capacity not exceeding 3000 L into which damaged, defective, leaking or non-conforming pressure receptacle(s) are placed for the purpose of transport (for example, for recovery or disposal).

NOTE 1 A cylinder recovery vessel is often fitted with a gauge to indicate internal pressure and with valves to enable purging. Referred to in the *UN Recommendations on the Transport of Dangerous Goods – Model Regulations (UN Model Regulations)* as a salvage pressure receptacle and also known as a salvage cylinder [1]<sup>1</sup>.

NOTE 2 –Due to the strong oxidizing potential of fluorine, the use of a cylinder recovery vessel for pure fluorine or high concentrations of mixtures may not be appropriate. Refer to Section 12 for details.

### 3.2.5 **Gas cabinet**

Locally ventilated enclosure designed to contain a gas supply cylinder and, where appropriate, an associated purge gas supply cylinder. The gas cabinet also encloses the gas supply handling equipment such as purge manifolds, process gas pressure reducing regulators, and control systems. The gas cabinet can be quite complex in design, often being equipped with automatic microprocessor control.

### 3.2.6 **Immediately Dangerous to Life or Health (IDLH)**

Concentration value from which one could escape without loss of life or immediate or delayed irreversible health effects (30 minutes is considered the maximum time for escape so as to provide a margin of safety) [2].

### 3.2.7 **Impingement site**

Impingement occurs when the flow stream changes direction abruptly, or when the presence of eddies leads to the impact of particles with the system walls [3].

### 3.2.8 **Lethal concentration 50 (LC<sub>50</sub>)**

Concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50% of the entire defined experimental animal population. Usually measured in ppm or mg/m<sup>3</sup>.

### 3.2.9 **Occupational exposure limit (OEL)**

Values set by competent national authorities or other relevant national institutions as limits for concentrations of hazardous compounds in workplace air.

### 3.2.10 **Monel<sup>®</sup>**

U.S. registered trademark for an alloy of copper and nickel, UNS N04400.

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<sup>1</sup> References are shown by bracketed numbers and are listed in order of appearance in the reference section.

### 3.2.11 Oxidizing potential

Oxidizing power of a gas compared to that of oxygen, given as a dimensionless number, where oxygen = 1 [4].

### 3.2.12 Passivation

Pre-treatment method to allow the formation of a self-limiting protective fluoride film on the surface of the material in a controlled manner, which limits any additional fluorine reaction.

### 3.2.13 Permissible Exposure Limit (PEL)

Eight (8) hour time-weighted average occupational exposure limit set by the U.S. Occupational Safety and Health Administration (OSHA).

### 3.2.14 Pressure

Bar shall indicate gauge pressure unless otherwise noted (bara for absolute pressure).

### 3.2.15 Risk assessment

Documented assessment of the risks of a specific operation to personnel and the environment. This process usually takes into account safety controls inherent in equipment, operating procedures, and the personal protective equipment (PPE) provided. Sometimes, it may be deemed appropriate to improve operational safety controls after undertaking a risk assessment.

### 3.2.16 Short-Term Exposure Limit (STEL)

Time-weighted average concentration, usually averaged over 15 minutes, aimed at avoiding acute effects.

### 3.2.17 Threshold Limit Value–Time-Weighted Average (TLV<sup>®</sup>-TWA)

Time-weighted average concentration for a normal 8-hour work day or 40 hour work week to which nearly all workers may be exposed, day after day, without adverse effect [5].

### 3.2.18 Tube

Transportable pressure receptacle of seamless or composite construction having a water capacity exceeding 150 litres but not more than 3 000 litres.

NOTE Tubes are often connected together in a manner similar to that for bundles and mounted on a vehicle trailer for transport, storage, and use. In Europe, these are defined as battery vehicles or multiple element gas containers (MEGCs).

NOTE Also known as tube trailers, ISO tube modules, or ISO containers.

## 4 Properties of fluorine

Fluorine is a gas at normal pressure and temperature with a very pungent odour. It is heavier than air and is highly oxidizing and highly toxic. When exposed to moisture, it can become corrosive to materials. See Tables 1,2 and 3.

In Europe, fluorine is classified as Comp.Gas, H280; Ox. Gas 1, H270; Acute Tox.1, H330; Skin Corr.1A, H314; Eye Dam.1, H318; EUH071, see EIGA Doc 169 *Classification, and Labelling Guide in accordance with EC Regulation 1272/2008 (CLP Regulation)* [6]. For classification of fluorine in the United States, refer to CGA C-7, *Guide to Classification and Labelling of Compressed Gases* [7]. In Japan, fluorine is classified as Oxidizing gases 1, H270; Gases under pressure, Compressed gas, H280; Serious eye damage/eye irritation 2A, H319; Acute toxicity, inhalation 1, H330; Reproductive toxicity 2, H361; Specified target organ toxicity, single exposure 1, H370; Specified target organ toxicity, repeated exposure 1, H372.

#### 4.1 Fluorine identification

|                   |                |
|-------------------|----------------|
| Chemical formula: | F <sub>2</sub> |
| CAS No.           | 7782-41-4      |
| EC No             | 231-954-8      |
| UN No             | <u>UN 1045</u> |

#### 4.2 Physical properties of pure fluorine

**Table 1 Physical properties of pure fluorine**

| Property   | SI Units   | U.S. Units   |
|--|--|--|
| Chemical formula   | F <sub>2</sub>   | <u>F<sub>2</sub></u>                                   |
| Molar mass   | 37.977 g/mol   | <u>0.0418 lb/mol</u>                                   |
| Melting point  | -219.6 °C  | <u>-363.3 °F</u>                                       |
| Boiling point  | -188.1 °C  | <u>-306.6 °F</u>                                       |
| Latent heat of fusion at melting point   | 13.4 kJ/kg   | <u>5.8 Btu/lb</u>                                      |
| Gas density at 0 °C (32 °F), 1.01 bara   | 1.696 kg/m <sup>3</sup>  | <u>0.106 lb/ft<sup>3</sup></u>                         |
| Gas density at 15 °C, 1.01 bara  | 1.608 kg/m <sup>3</sup>  | <u>.100 lb/ft<sup>3</sup></u>                          |
| <u>Gas density at 21.1 °C (70 °F), 1 atm</u>   | <u>1.57 kg/m<sup>3</sup></u>                                     | <u>0.098 lb/ft<sup>3</sup></u>                         |
| Relative gas density (air = 1)   | 1.312  | <u>1.312</u>   |
| <u>Density of the liquid at -306.8 °F (-188.2 °C)</u>  | <u>1509 kg/m</u>   | <u>94.21 lb/ft<sup>3</sup></u>                         |
| <u>Density of the liquid at -320.4 °F (-195.8 °C)</u>  | <u>1568 kg/m</u>   | <u>97.91 lb/ft<sup>3</sup></u>                         |
| Latent heat of vaporization at boiling point   | 173 kJ/kg  | <u>74.8 Btu/lb</u>                                     |
| Critical temperature   | -129.0 °C  | <u>-200.2 °F</u>                                       |
| Critical pressure  | 52.2 bara (757.1 psia)   | <u>5220 kPa, abs</u>                                   |
| Critical density   | 570 kg/m <sup>3</sup>  | <u>35.6 lb/ft<sup>3</sup></u>                          |
| Heat capacity at 25 °C (77 °F)   | 0.82 J/g*K   | <u>0.1966 Btu/(lb<sub>m</sub>*°R)</u>                  |
| Entropy at 25 °C (77 °F), 1.01 bara  | 3.65J/(g*K)  | <u>0.7322 Btu/(lb<sub>m</sub>*°R)</u>                  |
| <u>Specific volume of the gas at 21.1 °C (70 °F), 1 atm</u>  | <u>0.635 l/g</u>   | <u>10.17 ft<sup>3</sup>/lb</u>                         |
| <u>Triple point</u>  | <u>-219.7 °C at 0.223 kPa, abs</u>                               | <u>-363.4 °F at 0.324 psia</u>                         |
| <u>Weight of liquid per gallon at</u><br><u>-306.8 °F (-188.2 °C)</u><br><u>-320.4 °F (-195.8 °C)</u>  | <u>1509.8 kg/m<sup>3</sup></u><br><u>1569.7 kg/m<sup>3</sup></u> | <u>12.6 lb/gal</u><br><u>13.1 lb/gal</u>               |
| <u>Heat capacity of the gas (C<sub>p</sub>)</u><br><u>at 32 °F (0 °C)</u><br><u>at 70 °F (21.1 °C)</u> | <u>0.828 kJ/(kg)(°C)</u><br><u>0.825 kJ/(kg)(°C)</u>             | <u>0.198 Btu/(lb)(°F)</u><br><u>0.197 Btu/(lb)(°F)</u> |
| <u>Heat capacity of the gas (C<sub>v</sub>) at 70 °F (21.1 °C)</u>                                     | <u>0.610 kJ/(kg)(°C)</u>   | <u>0.146 Btu/(lb)(°F)</u>                              |
| <u>Ratio of specific heats, C<sub>p</sub>/C<sub>v</sub>, at 70 °F (21.1 °C)</u>                        | <u>1.353</u>   | <u>1.353</u>   |

**Table 2 Physical properties of fluorine/nitrogen mixtures (10/90 mol %) - ideal mixture**

| Property                       | SI Units                | U.S. Units                      |
|--------------------------------|-------------------------|---------------------------------|
| Molar mass (mean value)        | 29.012 g/mol            | <u>0.0319 lb/mol</u>            |
| Gas density @ 0 °C, 1.01 bara  | 1.295 kg/m <sup>3</sup> | <u>0.0818 lb/ft<sup>3</sup></u> |
| Relative gas density (air = 1) | 1.002                   | <u>1.002</u>                    |

**Table 3 Physical properties of fluorine/nitrogen mixtures (20/80 mol %) - ideal mixture**

| Property                       | SI Units                | U.S. Units                      |
|--------------------------------|-------------------------|---------------------------------|
| Molar mass                     | 30.010 g/mol            | <u>0.0330 lb/mol</u>            |
| Gas density @ 0 °C, 1.01 bara  | 1.340 kg/m <sup>3</sup> | <u>0.0836 lb/ft<sup>3</sup></u> |
| Relative gas density (air = 1) | 1.036                   | <u>1.036</u>                    |



### 4.3 Chemical reactivity

As one of the most reactive of all the elements and one of the most powerful known oxidizing agents, fluorine is able to react with almost all elements and compounds depending on pressure and temperature, with the exception of lighter noble gases (for example, helium, argon), inorganic fluorides of the highest valence, and perfluorinated organic compounds.

Fluorine reacts with many organic substances even at room temperatures and is often accompanied by combustion and possible explosion.

The reactivity of fluorine is dependent on the pressure and temperature of the system. Dilution with inert gas has shown to reduce the oxidizing potential.

#### 4.3.1 Reaction with flammable gases

Fluorine will react with all flammable gases. As an example, fluorine and hydrogen react with extreme violence, thus producing a highly exothermic reaction [ $\Delta H_{f(g)} (25\text{ }^\circ\text{C}) = -271.7\text{ kJ/mol}$ ]. Even at very low temperatures (solid fluorine, liquid hydrogen), a violent reaction is produced.

#### 4.3.2 Reaction with water

Fluorine reacts with water to form oxygen, oxygen difluoride, and hydrogen fluoride. Small quantities of ozone and hydrogen peroxide can also be formed. Oxygen difluoride is much more toxic than fluorine.

#### 4.3.3 Reaction with halogens

If fluorine is combined with any of the other elements in Group VII/17 of the periodic table, it produces a highly exothermic reaction, from which a series of interhalogen compounds are formed (such as chlorine trifluoride, chlorine pentafluoride, bromine trifluoride, and iodine pentafluoride). Halogen fluorides are also widely used as fluorinating agents.

#### 4.3.4 Reaction with carbon

Carbon can react differently with fluorine depending on the carbon structure and surface configuration. Activated carbon can ignite at room temperature in presence of fluorine but it may also absorb fluorine until it is saturated and then detonate.

#### 4.3.5 Reaction with other non-metals

Boron, silicon, phosphorus, sulfur, selenium, and tellurium all react with fluorine to cause combustion and the formation of fluorides of the highest valence. Under normal conditions, oxygen and nitrogen do not react with fluorine, but reactions can occur under special conditions. Of the noble gases, radon and xenon react readily with fluorine while krypton reacts only under special conditions.

#### 4.3.6 Reaction with hydrocarbons and other organic compounds

All organic compounds, including hydrocarbons, react with fluorine. Ignition usually occurs and under certain circumstances the reaction can be explosive. The end product of the reaction is invariably carbon tetrafluoride. Under suitable reaction conditions, organic compounds can be partially or completely fluorinated with elemental fluorine, without causing destruction of the molecule.

With the exception of carbon tetrafluoride, all fully halogenated carbon compounds also react with fluorine. In many cases, however, this reaction proceeds so slowly that some of these materials such as polytetrafluoroethylene (PTFE), can be used as construction materials or sealants, provided reaction conditions (purity of the materials, pressure/temperature, and concentration of fluorine) are controlled.

#### 4.3.7 Reaction with metals

Fluorine reacts with many metals and alloys at room temperature, but it shall be understood that any metal can ignite in fluorine under specific conditions. Passivation of metals is used to protect them from additional fluorine attack.

#### 4.4 Toxicity

Pure fluorine is a highly toxic gas. Established levels of exposure for fluorine vary between countries and agencies. Refer to the governing agency in the country where the fluorine is being used. See Table 4 for examples of established maximum limits of fluorine exposure to personnel used in the industrial gas industry and Table 5 for established LC<sub>50</sub> values.

For more information, refer to the most recent SDS of the fluorine supplier.

**Table 4 Regulatory exposure limits for fluorine**

|  | <u>Value</u>   | <u>Value</u>                | <u>Reference</u> |
|--|----------------|-----------------------------|------------------|
| <u>OSHA PEL TLV-TWA</u>  | <u>0.1 ppm</u> | <u>0.2 mg/m<sup>3</sup></u> | <u>[8]</u>       |
| <u>American Conference of Governmental Industrial Hygienists (ACGIH) TLV-TWA</u>   | <u>1 ppm</u>   | <u>1.6 mg/m<sup>3</sup></u> | <u>[5]</u>       |
| <u>ACGIH TLV-STEL</u>  | <u>2 ppm</u>   | <u>3.1 mg/m<sup>3</sup></u> | <u>[5]</u>       |
| <u>National Institute for Occupational Safety and Health (NIOSH) IDLH</u>  | <u>25 ppm</u>  |                             | <u>[2]</u>       |
| <u>Acute Exposure Guideline Levels (AEGs)</u>  |                |                             |                  |
| <u>AEGL-1 (30 minutes)</u>   | <u>1.7 ppm</u> | <u>2.6 mg/m<sup>3</sup></u> | <u>[9]</u>       |
| <u>AEGL-2 (30 minutes)</u>   | <u>11 ppm</u>  | <u>17 mg/m<sup>3</sup></u>  |                  |
| <u>AEGL-3 (30 minutes)</u>   | <u>19 ppm</u>  | <u>29 mg/m<sup>3</sup></u>  |                  |
| <u>NOTES</u>   |                |                             |                  |
| <u>1 OSHA limits are the legal exposure limits allowed by U.S. law and are enforceable.</u>  |                |                             |                  |
| <u>2 ACGIH limits are recommended values and are not enforceable by law.</u>   |                |                             |                  |
| <u>3 NIOSH limits are recommended values and are not enforceable by law.</u>   |                |                             |                  |
| <u>4 AEGL-1 is the airborne concentration (expressed as ppm or milligrams per cubic metre [mg/m<sup>3</sup>]) of a substance above which it is predicted that the general population, including susceptible individual, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.</u> |                |                             |                  |
| <u>5 AEGL-2 is the airborne concentration (expressed as ppm or mg/m<sup>3</sup>) of a substance above which it is predicted that the general population, including susceptible individual, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.</u>   |                |                             |                  |
| <u>6 AEGL-3 is the airborne concentration (expressed as ppm or mg/m<sup>3</sup>) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life threatening health effects or death.</u>   |                |                             |                  |
| <u>7 In Europe, the SDS of the supplier shall be consulted to find the applicable regulatory exposure limits where determined in the different countries.</u>  |                |                             |                  |

**Table 5 Established LC<sub>50</sub> values**

|  | <u>Value</u>    | <u>Reference</u>           |
|--|-----------------|----------------------------|
| <u>LC<sub>50</sub> (1h rat) (pure fluorine)</u>                | <u>185 ppm</u>  | <u>[10]</u>                |
| <u>LC<sub>50</sub> (1h rat) (for 20% fluorine in nitrogen)</u> | <u>925 ppm</u>  | <u>calculated per [10]</u> |
| <u>LC<sub>50</sub> (1h rat) (for 10% fluorine in nitrogen)</u> | <u>1850 ppm</u> | <u>calculated per [10]</u> |

#### 4.5 Routes of exposure

There are two main routes of exposure for fluorine:

- inhalation; and
- eye and skin contact.

Exposure to fluorine shall be treated as an exposure to hydrofluoric acid. Hydrofluoric acid is one of the most hazardous chemicals used in industry. It is unlike other acids because it cannot be rapidly neutralized and can continue to destroy tissue for several days after exposure to skin. The fluoride ion readily penetrates the skin, causing destruction of deep tissue layers including bone.

One of the most serious consequences of severe exposure to hydrogen fluoride by any route is the marked lowering of serum calcium (hypocalcemia) and other metabolic changes, which can result in a fatal outcome if not recognized and treated. Hypocalcemia should be considered a potential risk in all instances of inhalation and whenever skin exposure exceeds 25 in<sup>2</sup> (160 cm<sup>2</sup>) [11].

#### **4.5.1 Inhalation**

Fluorine has a pungent, irritating odour. Harmful concentrations of this gas in the air can be reached very quickly on loss of containment. Inhalation produces hydrogen fluoride as the fluorine reacts with moisture in the lungs and respiratory tract. The principal effect of exposure to fluorine is pulmonary irritation, which can begin at concentrations as low as 2 ppm up to severe pulmonary oedema, which can lead to death. Some subacute exposure at 0.5 ppm can result in no significant pathology, but there is some retention of fluorine, primarily in the bones and teeth.

Other symptoms include:

- irritation of the nose and/or throat;
- coughing;
- choking;
- swelling of the throat;
- chest tightness;
- chills;
- fever;
- cyanosis; and
- severe pulmonary oedema [11].

#### **4.5.2 Eye and skin contact**

Fluorine is extremely corrosive to the eyes and skin. However, the effects may be delayed.

Skin burns are of two types:

- caused by hydrogen fluoride formed by fluorine in moist conditions; and
- caused by fluorine in dry conditions (similar to a second degree thermal burn).

Exposure to fluorine shall be treated as an exposure to hydrofluoric acid, which can cause serious, painful burns of the skin, eyes, and mucous membranes. Hydrofluoric acid burns can be more severe and are slower to heal than fluorine burns.

Symptoms can include:

- redness of the skin;
- severe, burning, or throbbing pain;

- whitish discoloration of the skin;
- blisters; and
- oedema.

Contact between the skin and high concentrations of fluorine gas under pressure will produce burns comparable to thermal burns along with chemical burn effects. Contact with lower concentrations results in a chemical type of burn resembling those caused by acid [11].

#### 4.6 Environmental issues

Fluorine is not categorized as a Class I or Class II ozone depleting substance and it does not have properties that contribute to global warming. However, fluorine is highly toxic and reactive on environmental release. Because of its toxic properties, fluorine and/or fluorine mixtures shall not be vented directly to the atmosphere and shall be treated through a designed abatement system.

Contact with water will form hydrofluoric acid, which creates aquatic toxicity concerns at very low concentrations (for example, 50 ppm to 60 ppm).

### 5 Oxidizing/reactivity hazards

The information presented in this section is for components in direct flow path of the fluorine. Components used for static seals, gaskets, etc., are chosen based on compatibility relative to the fluorine concentration and pressure.

#### 5.1 Introduction to fire and explosion hazards

Figure 1 illustrates that combustion requires the simultaneous occurrence of the following elements:

- the presence of an oxidizer (fluorine);
- a combustible material in contact with the oxidizer (fluorine handling equipment); and
- a source of ignition energy.

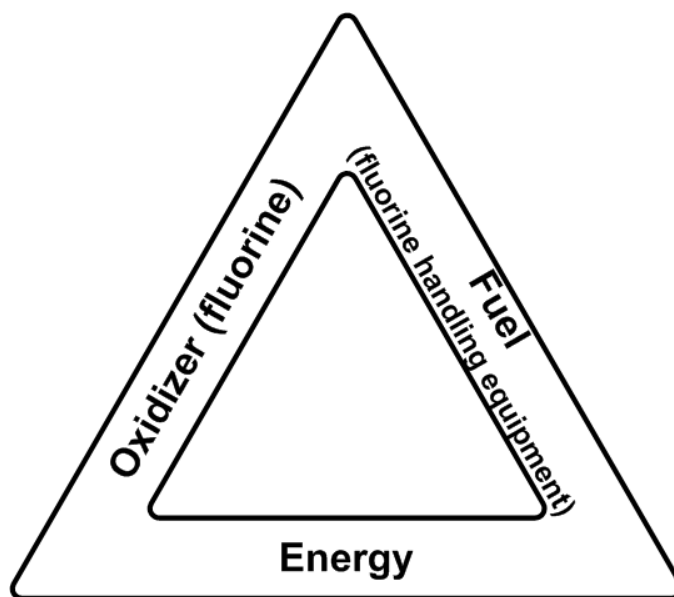


Figure 1 Fire triangle

Because of its very high oxidizing ability, the fluorine molecule can spontaneously react with most combustible substances, without any external ignition source. This behaviour is different from the properties of air/combustible or oxygen/combustible systems and therefore mixtures of fluorine and combustible substances can be regarded as self-ignitable or hypergolic. Several factors influencing the combustion are considered in the following paragraphs.

## 5.2 Factors influencing reaction, ignition, and combustion

Fluorine reactions are influenced by numerous factors. The majority of reported fluorine ignitions have been attributed to improper cleaning or use of a less resistant material in the system.

Reactivity of materials in fluorine systems is somewhat peculiar in that ignitions have occurred after years of service with no apparent change in operating conditions. Even under controlled test conditions, the ignition of some materials is not able to be repeated to a high degree of confidence. Therefore, the possibility of an ignition/fire shall be considered by the system designer when locating equipment especially in close proximity to personnel. Refer to Section 7 for additional details.

The primary factors that influence ignition in fluorine systems are:

- resistance of the material to fluorine (see 5.2.1);
- size and configuration of equipment (see 5.2.2);
- cleanliness of equipment and passivation with fluorine (see 5.2.3);
- fluorine pressure (see 5.2.4);
- concentration of fluorine in inert gas (see 5.2.5);
- gas temperature (see 5.2.6); and
- dynamic exposure of materials to fluorine (see 5.2.7).

### 5.2.1 Resistance of the material to fluorine

Most metals offer far better resistance to fluorine ignition than non-metals or polymeric materials. Metal composition, mass, and heat conductivity (ability to dissipate heat) are some factors that influence the potential for ignition. The use of polymeric materials in a fluorine system significantly increases the risk of fluorine ignition and their use is limited to specific applications. Ignition of even the most resistant metals with fluorine can occur if a less resistant material (for example, polymers, lubricants) ignites in the system. This mechanism of ignition is commonly known as the kindling effect.

#### 5.2.1.1 Auto-ignition temperature

The auto-ignition temperature is an important factor that needs to be considered when choosing materials to resist combustion in fluorine. The risk of combustion is higher when the auto ignition temperature is low since the energy required to reach this temperature is lower.

Unlike oxygen, where standardized tests exist to determine the auto ignition temperatures of materials such as described in ISO 11114-3, *Gas cylinders—Compatibility of cylinder and valve materials with gas contents—Part 3: Autogenous ignition test for non-metallic materials in oxygen atmosphere*, the testing for fluorine ignition and combustion is not standardized and in many cases is based on testing performed many years ago [12]. It is clearly recognized that the relative auto ignition temperatures in fluorine are much lower than for ignition in oxygen systems [13].

The auto-ignition temperature in fluorine service is affected by pressure, the fluorine concentration, and the system operating temperature.

### 5.2.1.1.1 Auto-ignition temperature of metals

Any metal can ignite in fluorine under specific conditions.

Temperature effects on common metals used for fluorine systems are shown in Table 6.

**Table 6 Temperature effects on common metals used for fluorine service**

| Metal               | Recommended temperature limits for 100% fluorine service based on industry practice (°C) <sup>1)</sup> | Test data from published literature             |   |  |  |
|---------------------|--|---|---|--|--|
|                     |  | Average ignition temperature (°C) <sup>2)</sup> | Threshold temperature for low probability of failure (°C) <sup>3)</sup> | Threshold temperature for high probability of failure (°C) <sup>4)</sup> | Temperature where metal-fluoride film can vaporize causing accelerated corrosion (°C) [14] |
| Copper              | 150  | 692   | 588   | 863  | No data  |
| Carbon steel        | 150  | 672 (iron)                                      | No data   | No data  | No data  |
| Stainless steel     | 150 (300 series)   | 681 (302 grade)                                 | 696 (304L grade)  | 1054 (304L grade)  | <sup>5)</sup>  |
| Monel               | 400 (UNS N04400)   | <sup>6)</sup>                                   | 924 (UNS N05500)  | 1041 (UNS N05500)  | 648  |
| Nickel (UNS N02200) | 600  | 1162  | >957<br>At sonic velocity   | >957<br>At sonic velocity  | 648  |

NOTES

<sup>1)</sup> Temperatures approaching the listed temperature can result in rapid corrosion to the metal even with only short term exposure. It is imperative that the user fully analyse (possible corrosion testing) the operating conditions (temperature, pressure, flow) and consequences of failure from corrosion prior to using a fluorine system at or higher than the listed temperatures.

<sup>2)</sup> Tests were with thin wire (0.25 mm to 0.50 mm [0.010 in to 0.020 in] diameter) in static fluorine at atmospheric pressure [14].

<sup>3)</sup> Tests were with 100 psia (6.9 bara) fluorine in static condition. Failure is defined as the temperature at which the onset of a discernible but relatively minor material response was observed in a few seconds [15].

<sup>4)</sup> Tests were with fluorine in static condition. Temperature at which the onset of a major material response was observed in a period of a few seconds or less [15].

<sup>5)</sup> Chromium in the stainless steel can form four types of fluorides. Below 150 °C, a protective chromium fluoride scale forms but this can be converted to a more volatile form above 150 °C, which can compromise the protective ability of the film.

<sup>6)</sup> The published ignition temperature for Monel from the reference paper is listed as 396 °C but accuracy of the measurement has been questioned in additional papers possibly because of temperature measurement technique [14]. Additionally, the ignition temperature could have been affected by the possible presence of detrimental minor alloying elements [15]. Industry experience suggests Monel (UNS N04400) auto-ignition temperature is greater than that of stainless steel, but precise measurements are not available.

### 5.2.1.1.2 Auto-ignition temperature of non-metals

Ignition tests on polymeric materials and lubricants in static and dynamic conditions have shown that the ignition risk increases with pressure and temperature. Most polymeric materials will spontaneously react upon exposure to fluorine. While some historical test results indicate little or no reaction under a given condition, there is a high degree of uncertainty of fluorine ignition/reaction especially with non-metals. Small amounts of contaminants or a slight change in operating conditions (velocity, pressure) can be enough to initiate ignition even after an extended time in fluorine service.

Highly fluorinated polymers such as polychlorotrifluoroethylene (PCTFE), PTFE, Perfluoro (alkoxy alkane) (PFA), including metal-filled (for example, bronze) types, exhibit the best resistance to ignition

in fluorine systems, but even their use shall be carefully reviewed and exposure minimized. Refer to 7.2.2 for additional details of non-metal use in fluorine service.

#### 5.2.1.2 Propagation of metal fires

The propagation of metal fires ignited in fluorine is also an important factor that needs to be considered when selecting metal equipment components, in particular if there are components with low auto-ignition temperatures (for example, polymeric materials). The consequences of the auto ignition of sensitive materials (polymeric materials) are aggravated when a metal propagates from ignition under fluorine pressure. The degree of propagation of a fluorine-metal fire is a function of the fluorine pressure and material. Nickel, copper, and Monel are the best metals for limiting the propagation if ignited.

#### 5.2.1.3 Heat capacity of materials

Metals have a significantly higher heat capacity because of a higher density than non-metals and therefore absorb significantly more heat with a lower temperature increase. Hence, metals are the preferred materials for use with fluorine.

#### 5.2.1.4 Thermal conductivity of materials

The higher the thermal conductivity of a material, the greater the rate of heat dissipation and the better the resistance to fluorine ignition.

As metals have a higher thermal conductivity than non-metals, metal systems are preferred.

Following the logic of heat dissipation, it is clear that the thinner the material, the more at risk the material is of ignition with fluorine.

Nickel, copper, and its alloys, for example, Monel, have better thermal conductivity than stainless steel and therefore are preferred, in particular for critical components.

#### 5.2.1.5 Heat of combustion of materials

This is the energy produced by the combustion of a material in contact with fluorine. Heat of combustion has also been considered a factor in the potential for a material fire to propagate once ignited. The burn ratio is the ratio of a metal's heat of combustion divided by the heat necessary to melt or vaporize the metal. Relative to oxygen burn ratio, fluorine burn ratios are significantly higher.

Therefore, materials with a low specific heat of combustion should be chosen wherever practicable.

For common metals, the heat of formation of the metal fluorides indicates that the heats of combustion in fluorine are greater than that in oxygen.

Aluminium and its alloys have a very high heat of combustion and a lower melting point than most other common metals. Therefore, they are typically not used for systems handling pure fluorine.

NOTE In the semiconductor industry, it is an accepted practice to use aluminum alloys in low fluorine concentrations at low pressure.

### 5.2.2 Size and configuration of equipment

#### 5.2.2.1 Material surface area

Fine mesh screen, sintered metal, etc., can have surface reactions with minimum heat sink effect, creating temperatures that can lead to ignition.

For a given mass of material, the risk of ignition increases with the surface area exposed to fluorine. Therefore, very careful material selection is necessary for equipment components with a low mass

and a high surface area that may be exposed to an ignition in contact with fluorine (for example, filters).

### 5.2.2.2 Minimization of less compatible materials

Less compatible materials are those that are easy to ignite with high specific heat of combustion (for example, non-metallic materials such as polymers) that can initiate the combustion of other materials including metals.

Non-metallic materials are not recommended for pipe or tubing in any fluorine applications or in flow paths (valve seats) for high pressure fluorine systems. Even in low fluorine pressure applications any non-metallic parts (for example, valve seats) are to be used in a manner that limits the mass of the less compatible material. The non-metallic material should be in close contact with a metal support. The metal support should contain sufficient mass to dissipate any heat that can be generated by the ignition of the non-metallic material.

### 5.2.2.3 Shape

Rapid changes in direction of flow (such as sharp bends in pipes or obstacles in the flow path) will result in a localised energy increase due to impingement of flowing particles on the surface. These factors should be taken into account when designing fluorine handling equipment.

## 5.2.3 Cleanliness of equipment and passivation with fluorine

These are key factors to minimize fluorine reaction, ignition, and combustion.

### 5.2.3.1 Cleaning and drying

Of critical importance in preventing fluorine reactions is system cleanliness, including strict control in the fabrication/assembly process. Contaminants, incompatible lubricants or materials, or residual cleaning agents within the handling equipment will ignite in contact with fluorine (for example, particles, dirt, grease, water).

All components shall be thoroughly cleaned and free from oils, grease, moisture, dirt, and particles. Contaminants shall be minimized by purchasing components cleaned to meet oxygen clean standards and ensuring strict control of the fabrication process [16, 17].

Drying of the system to reach target dew point level prior to introduction of fluorine is done to minimize corrosion (due to hydrogen fluoride formation) and ignition potential.

### 5.2.3.2 Passivation with fluorine

After cleaning, verification of cleanliness, and drying, the fluorine system is passivated, thus allowing the metal fluoride film to develop on the metal surface and thus preventing any further fluorine reaction.

The passivation is done in stages by increasing concentrations and pressure of fluorine to limit any reaction potential.

The passivation process can also result in removal of minor amounts of contaminants, but should never be used as a substitute for cleaning of the system.

## 5.2.4 Fluorine pressure

Gas pressure is an important parameter and directly influences the rate of reaction and ignition likelihood. Typically, handling of pure fluorine has three threshold pressure limits: 1 bar, 4 bar, and 30 bar. The 1 bar and 4 bar limits are used as a threshold pressure where different design criteria are used (materials of construction, shielding, etc.).

The 30 bar limit is in the UN Model Regulations and its harmonized transport regulations (European Agreement concerning the International Carriage of Dangerous Goods by Road and Rail [ADR/RID].



International Maritime Dangerous Goods [IMDG], U.S. Department of Transportation [DOT], etc.) [1]. According to these regulations, it is prohibited to ship gas cylinders with higher filling pressures of pure fluorine.

### **5.2.5 Concentration of fluorine in inert gas**

Mixtures of fluorine decrease in reactivity potential as the concentration of fluorine decreases in the mixture.

Mixtures of fluorine with a volume concentration of less than or equal to 0.5% are considered not to be oxidizers according to the UN classification regulations (ISO 10156, Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets) [18].

NOTE ISO 10156 specifies a test and a calculation method to be used to determine whether or not a gas or a gas mixture is more oxidizing than air for the purpose of classification and labelling of gases or gas mixtures according to the carriage of dangerous goods regulations by road in Europe (ADR).

The gas/mixture is assigned a coefficient ( $C_i$ ) based on the test results. The  $C_i$  coefficient relates the gas mixture to the oxidizing potential of air. Based on this ISO standard for non-tested oxidizing gases, the  $C_i$  coefficients are fixed conservatively at 40. This was done for the case of pure fluorine.

For fluorine-nitrogen mixtures the limiting concentration for classification is 0.5% of fluorine.

Typical mixtures are approximately 1% in rare gases, and 10% and 20% fluorine in nitrogen. In addition to the toxicity, these mixtures are classified according to regulations for the transport of dangerous goods as oxidizing and have to be handled carefully.

Mixtures of less than 35% fluorine are less reactive than pure fluorine at a pressure that corresponds to the fluorine partial pressure in the mixtures. Because of the decreased reactivity potential, a concentration of 35% is used as a threshold concentration below which different design criteria are used (materials of construction, shielding, etc.).

Mixtures of greater than 35% fluorine in inert gas shall be handled in systems designed for 100% fluorine.

### **5.2.6 Gas temperature**

As the gas temperature increases so does the ability of fluorine to destroy the protective fluoride layers, leading to a higher potential of ignition and accelerated corrosion of metals.

### **5.2.7 Dynamic exposure of materials to fluorine**

If particles are present in the fluorine system, higher velocity leads to higher kinetic energy of the particle and therefore higher temperature upon particle impingement, which can result in ignition of metal surfaces. Areas with tortuous passages and/or small crevices and abrupt changes in flow direction (impingement areas) are at increasing risk of particle impingement as the velocity increases.

There is potential for particle ignition with fluorine (as with all oxidizers) due to the high surface to mass ratio of a particle. The risk of ignition due to particle impact increases with the fluorine pressure.

Refer to 7.3.3 for additional details on velocity considerations.

## **6 Control of toxicity hazards**

As fluorine is a highly toxic gas every effort shall be made to avoid contact with personnel and environmental releases.

A risk assessment/hazard review shall be performed on all systems.

Because fluorine reacts with moisture, any release will form hydrogen fluoride and this shall be taken into account in the control measures adopted.

Special consideration shall be given to the following areas when designing systems to handle fluorine. Listed below are general considerations. Specific details are included in Sections 8 through 11.

- equipment design and site considerations (See Section 7);
- gas detection;
- ventilation;
- abatement systems; and
- personal protective equipment (PPE).

### 6.1 Detection of fluorine leaks

The odour threshold for fluorine is less than 0.1 ppm and the TLV–TWA is 1.0 ppm. This means that personnel can quickly detect a release and vacate the area or prevent personnel from entering a room having dangerous levels of fluorine present, at times even before gas detectors can alarm. However, neither smell nor sensory irritation can be relied upon for warning of toxic concentrations, especially in the presence of other fumes, gases, or vapours.

Depending on the consequence of the release, based on a risk assessment, fluorine gas detectors that are interlocked into an alarm and shutdown system shall be used in areas where a leak would not easily be detected or if local regulations require

Electrochemical type gas detectors for fluorine are readily available for portable and fixed location applications.

NOTE Most available detectors show cross sensitivity to other acid gases (for example, hydrogen chloride, hydrogen fluoride).

The location of fluorine leaks can be detected by the use of indicating paper moistened or impregnated with a solution of potassium iodide (KI) of approximately 5% in water. The paper is held near or over the fitting and will quickly turn brown if fluorine is present. Potassium iodide/starch indicating paper can also be used and is more accurate in the colour change.

A solution of ammonia/water spray for fluorine leak detection is not recommended. The solution produces a white cloud when the ammonia and fluorine mix. Additionally, hydrogen fluoride is formed that can lead to corrosion and the ammonia content can lead to cracking of vulnerable metals, particularly brass.

Coaxial tubing may be used for fluorine leak detection. Coaxial tubing is a secondary pipe covering the inner (primary) pipe, which carries the fluorine. It is sometimes used for fluorine piping, based on specific codes, risk analysis, or end user requirements.

The inside surface of the secondary pipe shall be designed and prepared to guard against fluorine reaction in the event the primary pipe suffers a leak or ignition. Normally, the secondary pipe is constructed of the same material as the inner pipe, but in the case where Monel or nickel primary pipe are used, the installation of prepared stainless steel (or alternate material) secondary pipe may be justified. Cleaning the inner surface of the secondary pipe and the external surface of the primary pipe may be required and in some cases these surfaces may need passivation. For example, pure fluorine at high pressure in the primary pipe.

When required, the coaxial pipe is monitored for leaks. This provides a mechanism for sensing a breach anywhere along the distribution system within a facility, allowing for early warning and appropriate emergency action. There are several methods for monitoring the interspace between the tubing, for example:

- Vacuum—loss of vacuum is detected in the interspace and activates an alarm;
- Flowing inert gas with monitoring—the inert gas is continuously analysed and any fluorine activates an alarm. Very small leaks could be undetected by this method; or
- Pressurising with clean dry inert gas—the pressure of the inert gas is higher than the fluorine system and therefore fluorine leakage is minimized. A pressure transducer is used to monitor the space and activate an alarm if the pressure falls below normal set point.

## 6.2 Ventilation

In building ventilation design, consideration should be given to accommodate possible accumulation of fluorine. The ventilation design should keep the rooms containing the fluorine system at a negative pressure relative to surrounding rooms that are desired to be kept free of fluorine odour such as those occupied by personnel.

Any confined area where fluorine could be released shall be provided with ventilation, in particular all areas where personnel are involved in fluorine operations. This will provide personnel with sufficient time to escape an area where fluorine has been released. A minimum ventilation rate to meet local regulations/building codes or at least six (6) fresh air changes of the room volume per hour should be provided in all areas where personnel are present. Enclosures containing fluorine equipment should have a minimum ventilation rate of ten (10) fresh air changes per hour. The rate may be increased to higher rates per hour in the event a leak is detected. The emergency ventilation rate should be linked to a detection system and should be automatically activated.

Ventilated enclosures/barricades or gas cabinets should be used for all filling and supply operations involving cylinders depending on the concentration of fluorine and pressures being handled.

## 6.3 Personal protective equipment (PPE)

Fluorine reactions/leaks can result in chemical/thermal burns to personnel. Also, pulmonary injury can result from the inhalation of fluorine.

All surfaces that have the potential to be contaminated with fluorine shall be treated with extreme caution, as hydrofluoric acid could be present. Gloves shall be used at all times and these shall be cleaned or replaced after use to ensure no hydrofluoric acid is present.

At a minimum the following PPE shall be worn when removing the valve outlet plug/cap of a fluorine or fluorine mixture cylinder or connecting/disconnecting components:

- clean leather or neoprene gloves that can be quickly removed in the event of a fluorine fire;
- full face shield;
- long sleeve shirt (100% cotton recommended); and
- safety shoes.

A cartridge mask should also be available in close proximity in the event of an emergency.

Contact lens use shall be evaluated based on the given company policy but in general they are not used when handling fluorine.

## 7 Control of oxidizing/reaction hazards

As fluorine is a powerful oxidant, careful consideration shall be given to the following issues when designing systems to handle fluorine:

- building/site considerations;

- materials of construction of fluorine systems;
- fluorine system design;
- equipment selection;
- cleaning and passivation of fluorine systems;
- compression of fluorine;
- operating procedures and personnel training; and
- maintenance procedures.

### 7.1 Building/site considerations

Any building shall be of non-combustible construction, and the storage of combustible materials near the fluorine system shall be limited. Storage of non-compatible liquids and gases from the fluorine system shall follow separation distances specified in local regulations.

Whenever possible, pipes containing fluorine and fluorine mixtures shall be located away from non-authorized personnel access.

Fluorine piping systems are permitted to be buried if the piping system has been designed to be buried with such precautions including corrosion protection, leak detection, and requirements for inspection.

Systems containing fluorine and fluorine mixtures shall be located in the open air or in a forced ventilated enclosure or room.

Consideration shall be given to locate systems handling pure fluorine and mixtures of fluorine greater than 35% at greater than 4 bar in enclosures or behind barriers to protect personnel in the event of ignition. This is particularly relevant for those components at higher risk of ignition, for example, valves, components with moving parts, less resistant materials than Monel or nickel.

At lower pressures or concentrations, the designer shall review the site and regulatory requirements to determine the most practical means to protect personnel and meet local requirements.

- Gas cabinets/enclosures—limits the extent of fluorine gas release into an area by use of exhaust ventilation and also limits personnel exposure from leak/reaction and possible molten metal or direct impact from a pressure jet of fluorine;
- Equipment such as compressors and pumps handling fluorine shall be located inside isolated enclosures that personnel do not enter while the equipment is operating;
- Abatement systems are often used in the ventilation systems from enclosures/cabinets. See Section 10 for gas abatement system details;
- Barrier/shields—limits personnel exposure from leak/reaction and possible molten metal or direct jet of fluorine pressure. The barrier also can be used to limit surrounding equipment damage in the event of a reaction;
- Barriers and enclosures are constructed of fire-resistant materials (carbon or stainless steel, aluminium, concrete). Metal thickness for the enclosure or barrier should be at least 3 mm (0.12 in);
- Polycarbonate viewing windows, typically of approximately 10 mm (0.40 in) thickness, are used where required;

- Remote cameras can be used for viewing; and
- Coaxial piping can be used as a barrier for piping (see 6.1).

Due to the toxicity concerns of fluorine if released, the extent of the propagation of the materials from a fire is usually of secondary importance to designing a means to protect personnel from the localized impact and to quickly stop the fluorine flow.

## 7.2 Materials of construction of fluorine systems

### 7.2.1 Metals

Based on the reactivity, allowable temperature limits, and tenacity of the fluoride film the following piping/tubing materials (cleaned and passivated) are listed in order of decreasing suitability.

- Nickel;
- Monel;
- Copper;
- Stainless steel; and
- Carbon steel.

Since there are currently no known metals that will not ignite if the temperature and fluorine pressure are sufficient, a risk assessment shall be undertaken to review the likelihood of ignition and understand the consequences of the system failure.

While nickel and Monel provide the best resistance to fluorine ignition and propagation at all fluorine pressures and concentrations, they are sometimes not used, because of availability, or application requirements (for example, trace metal contaminants in the system).

Refer to 5.2.1.1 for ignition and temperature data of metals.

Monel and nickel piping are recognized as the best materials for use in fluorine systems at greater than 4 bar especially at elevated temperature.

Stainless steel piping can be used in applications with fluorine at less than 4 bar. However, stainless steel has also proven successful for many years of service at pressure up to 30 bar where additional safeguarding based on risk analysis has been applied.

Stainless steel piping/tubing is commonly used for mixtures of 20% fluorine in inert gas at pressures up to 150 bar.

Carbon steel piping is usually limited to low pressure fluorine production equipment (1 bar or less), but it is also used in some applications for fluorine at 4 bar or less. Gas cylinders of carbon steel alloys are used for fluorine up to 30 bar pressure.

Brass materials shall be used with caution, as they are susceptible to de-zincification and subsequent cracking, which can lead to complete component failure. Also brass components are susceptible to leak detection or other solutions containing ammonia, which can cause stress corrosion cracking (SCC). However, cylinder valve bodies made from brass material are used successfully for fluorine (see 8.2.2).

Copper has good ignition resistance but the copper fluoride film upon exposure to moisture readily dissolves to form hydrofluoric acid, which leads to accelerated corrosion. For example, copper is used as seals/washers.

Lead or silver is used for seals/gaskets where exposure to fluorine is minimized and not in the direct flow path.

Aluminium is not typically used for fluorine systems due to its low melting point and high heat of combustion (see 5.2.1.5).

### 7.2.2 **Metal corrosion**

Due to the formation of a metal fluoride film on the metal surface, corrosion of metals and alloys used in fluorine service is usually negligible if the operating temperature is maintained well below the temperature where the film can start to modify and/or vaporize.

Corrosion of the metal can be accelerated if any moisture is present due to the formation of hydrofluoric acid. Very minor leaks can react with moisture in the air and form hydrofluoric acid causing corrosion to the exterior surface of the piping/component. Diligence in inspection and correction of any small leaks is important to maintain system integrity.

### 7.2.3 **Non-metals**

Fluorinated polymers are constantly evolving and are subject to variations in formulations. If there is not proven performance in the fluorine application for the intended use, it is recommended to conduct testing to ensure that the non-metal component is acceptable for the application.

Consideration shall be given to the compatibility of lubricants, seals, and sealing compounds that may come into contact with fluorine under normal or failure conditions.

#### 7.2.3.1 **Lubricants**

Fluorine can react violently with hydrocarbon-based lubricants. Equipment for handling fluorine such as pumps or compressors, shall only use fluorinated oils/greases and design of the equipment shall be so excess exposure of the lubricant to fluorine is minimized. An example is a compressor that employs metal diaphragms to separate the oil from the fluorine. Only chlorotrifluorethylene (CTFE) or perfluoropolyether (PFPE) oils and greases should be used.

#### 7.2.3.2 **Pressure regulators seats**

For pure fluorine and mixtures above 35%: a diaphragm pressure regulator is used with all metallic parts in Monel and bronze and with filled PTFE seat with minimum plastic surface exposed to fluorine and a high percentage of filling material such as aluminium silicon bronze (ASB), nickel, or calcium fluoride.

For fluorine mixtures between 10% and 35%: a pressure regulator with bronze filled PTFE seat, having minimum plastic surface exposed to fluorine and a high percentage of filling material such as ASB, nickel, or calcium fluoride.

For fluorine mixtures at and below 10%: stainless steel pressure regulators with seats containing fluorinated plastic materials are used. The regulator shall be designed, cleaned, and tested to meet high pressure oxygen compatibility requirements.

#### 7.2.3.3 **Valve seats**

Industry practice for material of valve seats at ambient temperature is as follows:

- fluorine mixtures 10% fluorine or less up to 200 bar—fluorinated plastic seat;
- fluorine mixtures above 10%, up to 200 bar maximum—metal seats; and
- fluorine at low pressures (pressure of less than 0.3 bar) have successfully used PTFE valve seats.

NOTE Fluorinated polymeric materials used for seat materials in fluorine are PCTFE, PTFE, or PFA, based on industry experience under specific conditions or testing of components in fluorine. The testing methods will typically follow standard tests for oxygen service (for example, adiabatic compression testing) but should be done at the conditions (pressure, concentration of fluorine, and temperature) for the given fluorine service being proposed.

High flows of fluorine shall be avoided because the fluorinated polymers could be destroyed.

#### 7.2.3.4 Sealing compounds

PTFE is used, out of the flow path, for systems of fluorine and fluorine mixtures such as for valve packing, gasket material, and pipe thread sealant.

### 7.3 Fluorine system design

#### 7.3.1 General considerations

In addition to the control of the oxidizing reaction hazards, the toxicity hazards shall also be controlled.

Pure fluorine systems or mixtures that are classified as Acute Toxic Category 1 or Category 2 based on the LC<sub>50</sub> calculation shall be designed to meet the requirements of a code in agreement with national regulation for highly toxic fluids such as ASME B31.3, *Process Piping*, Category M Fluid Service [19]. The equipment shall be designed to withstand the maximum pressure and temperature at which it is to be operated including upset conditions.

Leak testing shall be performed prior to introducing fluorine. The leak test shall meet the requirements of the applicable piping code based on the toxicity classification of the mixture. A helium leak detector can be used to detect any leakage points.

Leak detection fluids that contain ammonia used for inert gas pressure testing (soap solutions) shall not be used on copper based alloys as it can cause SCC [20].

To prevent releases of fluorine and contact with personnel, double valve isolation is recommended on all pipes containing fluorine unless a risk assessment justifies otherwise.

Mechanical joints on fluorine or fluorine mixture systems shall be kept to a minimum. A welded piping system is preferred. Non-destructive weld testing is recommended prior to pressure testing of the system.

Isolation valves used in fluorine systems should be globe or needle pattern type with bellows seal or diaphragm design.

Secondary containment (for example, ventilated enclosures, coaxial piping) should be considered for fluorine systems and should be based on a risk assessment.

#### 7.3.2 Minimisation of the effects of adiabatic compression

Adiabatic compression can occur, for example, when a valve is opened and a system is rapidly pressurised with fluorine leading to increased heat and also increased pressure/gas density making non-metals particularly vulnerable to ignition. Techniques used to minimize the effects of adiabatic compression are:

- selection of materials of construction;
- slow opening of any valves; and
- downstream pressurization using an inert gas prior to opening a valve (reduces both adiabatic compression and velocity concerns).

Ball valves and rapidly acting pneumatic valves are not recommended.

**7.3.3 Fluorine gas velocities**

High velocity in a fluorine system leads to higher kinetic energy of a potential particle resulting in higher temperature upon particle impingement, which can result in ignition of the fluorine system.

Tests indicate that in non-impingement areas of clean systems, the ignition threshold temperature for common metals is not significantly affected between sonic versus sub-sonic fluorine gas velocity [21]. However, common practice for oxidizing gases is to limit velocity to as low as practical and use more resistant materials especially in impingements areas when velocity reduction is not viable (see Table 7). These limits are exceeded in some production applications and when performing cylinder and bundle filling because these operations are always performed with experienced personnel under controlled conditions with safeguards in place to lessen the occurrence of an uncontrolled fluorine release.

**Table 7 Guidelines for velocity limits in pipelines for fluorine and mixtures greater than 35%**

| Pressure                    | Material   | Impingement area               | Non-impingement                |
|-----------------------------|--|--------------------------------|--------------------------------|
| Less than or equal to 4 bar | Carbon steel   | Less than or equal to 15 m/sec | Less than or equal to 30 m/sec |
|                             | Stainless steel (greater than or equal to 3 mm wall thickness) | Less than or equal to 15 m/sec | Less than or equal to 30 m/sec |
|                             | Copper, Monel 400, nickel                                      | No limits                      | No limits                      |
| Greater than 4 bar          | Carbon steel   | Material not recommended       | Material not recommended       |
|                             | Stainless steel (greater than or equal to 3 mm wall thickness) | Less than or equal to 2 m/sec  | Less than or equal to 4 m/sec  |
|                             | Copper, Monel 400, nickel                                      | No limits                      | No limits                      |

NOTE Due to lack of data on particle impingement ignition mechanism in fluorine systems, the velocity guidelines presented in this table were developed by using approximately 50% of the maximum design velocities (using a cut-off value of pressure of 4 bar) defined in accepted oxygen design criteria, EIGA Doc 13, *Oxygen Pipeline and Piping Systems* [3].

For fluorine mixtures in inert gas at concentrations equal to or below 20% of fluorine, there are no velocity restrictions for Monel, nickel, copper, or stainless steel systems.

**7.3.4 Separation from flammable gases**

To ensure that there is no risk of inadvertent mixing of fluorine with flammable gases or other flammable materials:

- Fluorine handling equipment shall be dedicated to fluorine service and shall not be used for any other purpose;
- Precautions shall be taken to ensure any purge gas (for example, nitrogen), is not contaminated with flammable materials (for example, from another process). A dedicated purge system for the fluorine system shall be used. A dedicated purge system may consist of a cylinder, a bundle, or a separate high-pressure supply line that may be a part of a larger system;
- To prevent backflow of fluorine into the purge gas system, pressure differential (higher purge gas pressure than maximum fluorine system pressure) should be used along with non-return (check) valves and double block and bleed systems in material compatible with fluorine; and
- A specific design break in material selection relative to fluorine compatibility needs to be defined based on where fluorine backflow is expected to be stopped and all components to that point, even if not normally exposed to fluorine, shall be designed and installed as if they were in fluorine service.



## 7.4 Equipment selection

### 7.4.1 Valves

Where possible, valves shall be selected so the velocity through the valves, when fully open, is no greater than the design velocity of the system based on the fluorine concentration and material of construction. See Table 7. The design shall be so the valves can be opened and closed slowly and in a controlled manner.

When required to be behind barriers or inside enclosures, valves shall have extension handles that protect the operators hand from direct exposure of a fluorine reaction in the stem packing/bellows.

Valves shall be purchased cleaned and packaged to oxygen standards.

Packless valves such as bellows seals or diaphragm valves are used routinely for fluorine applications. While local regulations or company piping design codes may dictate the use of packless valves, packed stem valves (using PTFE stem packing) are also routinely used for cylinder valves in fluorine applications.

Globe style valves are used for fluorine service. A globe style valve is designed to incorporate linear motion to a stem that fits against the valve seat. Moving the stem away from the seat allows fluid from the inlet port to flow past the seat and to the valve outlet port.

Bellows stem sealed valves with secondary packing seals of PTFE should be considered for critical applications in case of bellows failure. Leak detection ports on this type of valve are used for early leak detection in critical applications.

NOTE Historically, bellows manufactured via hydroforming process have been preferred to those bellows of welded disc/diaphragm design.

Ball or plug style valves are usually not recommended for general use in fluorine service because:

- Typical design includes non-metallic seals with large surface areas that are in the direct flow path, making them susceptible to ignition; and
- Valve style is prone to rapid opening and the resulting risk of heat from adiabatic compression in the downstream system can lead to ignition.

Dissimilar metal hardness is recommended between the stem and the seat to prevent galling and to achieve better seating. Stellite® hard-facing is often used for stainless steel valve stems.

For cylinder valves, see 8.2.2.

### 7.4.2 Pressure regulators

Pressure regulators or pressure control valves are used to limit the pressure in the user's system. Pressure regulators shall be designed for fluorine service using materials that are fluorine resistant based on the intended maximum pressure and fluorine concentration (see 7.2). Regulators shall be cleaned for oxygen service. Inlet filters shall be made of compatible materials (see 7.4.3).

### 7.4.3 Filters

Due to their high surface area to mass ratio, filters increase the risk of ignition in fluorine systems so their use is discouraged especially in high pressure fluorine applications (for example, greater than 4 bar). If a filter is used, it shall be made of Monel or nickel and procedures shall be in place to guard against accumulation of system contaminants on the filter (for example, PTFE thread tape), which can further increase ignition potential.

If filters are used in high pressure/high concentration fluorine service, shields/barriers shall be used to protect personnel in the event of ignition.

## 7.5 Cleaning and passivation of fluorine systems

To ensure that the surfaces in contact with fluorine are at minimal risk of ignition, systems for handling fluorine shall be prepared during construction/fabrication or after maintenance (as required) as follows:

- cleaned to oxygen service cleaning levels or better (See EIGA Doc 33 and CGA G-4.1) [16, 17];
- dried to remove any residual cleaning agents and moisture; and
- passivated with increasing pressures and/or concentrations of fluorine ensuring that all wetted areas are exposed to fluorine.

### 7.5.1 Cleaning

Components such as valves and pipe/tubing are recommended to be specifically cleaned for fluorine service and purchased from a qualified vendor as cleaned and packaged to oxygen cleaning standards.

Cleaning for fluorine typically follows the same criteria used for oxygen components. See EIGA Doc. 33 and CGA G-4.1 [16, 17].

It is very important that the cleaning agent is thoroughly removed from the system particularly if it does not vaporize quickly. Cleaning agents that leave minimal residue should be selected for fluorine systems.

Extreme care shall be taken in maintaining the cleanliness level during assembly/fabrication of the system.

Cleaning verification methods such as wipe tests and ultraviolet (black light) inspection are commonly used during the fabrication process. Quantification of the levels of oil/greases can be obtained via solvent wash/analysis for complex components where visual means are not possible; however, solvent washing should be well understood before using, since this method can increase the risk of ignition if all the solvent is not adequately removed.

### 7.5.2 Purging and drying

The purging and drying processes shall ensure that all of the cleaning agent residue is removed from the system and that any moisture in the system is removed to the targeted levels. Compressed air shall not be used.

Purge and vent the system with inert gas. If possible, use vacuum and heat as part of the process to evacuate the system to assist in the air/moisture removal. Attention shall be paid to branches that do not allow flow-thru (for example, dead ends) of a piping system to ensure they are purged.

Determine the moisture level of the system by obtaining a dew point temperature at atmospheric pressure that meets the following guidelines:

- Less than or equal to 1 bar fluorine system pressure:  $-60\text{ }^{\circ}\text{C}$  [ $-76\text{ }^{\circ}\text{F}$ ] (10 ppm of moisture in purge gas); and
- Greater than 1 bar fluorine and mixtures system pressure:  $-75\text{ }^{\circ}\text{C}$  [ $-103\text{ }^{\circ}\text{F}$ ] (1 ppm of moisture in purge gas).

### 7.5.3 Passivation

Passivation shall not be considered a substitute for cleaning and degreasing of the system. Inadequate cleaning can result in undesired reactions during the passivation steps. Tests performed for the United States Air Force in the late 1960s have shown that under certain conditions, organic contaminants did not react when initially exposed to fluorine [22].

Studies have shown that the development of the passivation film on most metals, using pure fluorine at room temperature and one atmosphere pressure, is reported to achieve approximately 75% of its limiting film thickness within the first 10-15 min of exposure [23].

While theoretically it would be possible to passivate individual components of a system, it is more effective to passivate the entire system as a whole, to ensure all portions have received passivation. This also allows for operation of items such as valves to ensure all areas are wetted.

The basic steps listed below are meant to be guidelines for safe and effective passivation using increasing fluorine mixture concentrations and pressure as the technique. Variations from these guidelines, based on each unique installation and user practice, are acceptable after review by those experienced with handling fluorine.

Ensure that:

- The system has passed the required leak and pressure tests with inert gas;
- All components such as gauges and relief devices have been installed in the system as required for operation before performing passivation;
- Non-essential personnel are restricted from the area while performing the passivation steps; and
- Emergency procedures are in place, including plans for the quick venting of the fluorine gas should it be required.

Suggested procedure:

- a. Introduce the starting concentration of fluorine into the system under vacuum, to a pressure at or near atmospheric pressure, making sure all parts of the system are exposed. Allow the system to remain pressurised for at least 30 minutes;
- b. Pay attention for any signs of a fluorine reaction. Infrared (IR) temperature monitoring devices can be employed to assist in determining any hot spots on the surface of the components;
- c. Monitor any system pressure gauges for fluctuations while introducing fluorine and during the hold periods;
- d. Slowly operate valves as required at each increment to ensure all surfaces of the components are exposed;
- e. Slowly increase the pressure of fluorine until the next pressure increment is reached and then repeat the 30 minutes hold/monitoring sequence. The pressure increments are typically obtained by dividing the system design pressure by 3 or 4. Continue these steps until the final system design pressure is reached; and
- f. If the system is designed for fluorine concentrations of more than 20%. Increase the concentration of the fluorine and repeat the incremental pressure/hold steps. Repeat in increasing concentrations of fluorine per Table 8 until both the final concentration and the system design pressure are reached.

**Table 8 Passivation guidelines versus fluorine design conditions**

| System design fluorine concentration                               | System design pressure        | Initial fluorine concentration |
|--|-------------------------------|--------------------------------|
| Less than or equal to 5% fluorine /inert gas                       | All pressures                 | 5%                             |
| Less than or equal to 10% fluorine /inert gas                      | All pressures                 | 10%                            |
| Less than or equal to 20 % fluorine /inert gas                     | All pressures                 | 20%                            |
| Greater than 20% to 100% fluorine                                  | Less than or equal to 0.3 bar | 100%                           |
|  | Greater than 0.3 bar          | 20% <sup>1)</sup>              |
| 1) Fluorine concentrations increase from 20% to set concentration. |                               |                                |

**7.6 Compression of fluorine**

During compression, two main factors can create heat that can increase fluorine reaction potential:

- adiabatic compression; and
- friction from mechanical moving parts.

Compressors using multiple metal diaphragms are typically used to separate the fluorine gas from the hydraulic part of the compressor. The compressors are equipped to detect a leak of either the fluorine gas diaphragm or the hydraulic side diaphragm.

Heat dissipation and compression ratio are important considerations when compressing fluorine. Cooling may be required to limit the gas temperature to limits defined in the Table 6. Design of the cooling system shall include means to prevent contact of the incompatible coolant from the fluorine.

**7.7 Operating procedures and personnel training**

Written operating procedures shall be prepared to ensure that the equipment is operated within its design parameters and shall include actions to take in an upset condition. Due to the oxidizing and toxic properties of fluorine, the written procedures and training of personnel shall include (at a minimum):

- emergency procedures including how to safely close off the supply of fluorine;
- identification, storage, and handling of components to ensure that they do not become contaminated;
- system cleanliness to minimize ignition potential;
- passivation of new components;
- the need to slowly open valves in fluorine service;
- use of clean oil-free gloves and valve handle extensions when opening valves and handling components;
- risk of use of non-compatible material with fluorine;
- PPE (see 6.3); and

- management of change (MOC) process.

Refresher training shall be performed at regular intervals.

## 7.8 Maintenance procedures

Prior to any maintenance activity, the system shall be verified safe to perform the work.

It is essential to ensure that fluorine handling equipment is maintained in a manner commensurate with a highly reactive and highly toxic gas and to ensure that routine maintenance is conducted in a controlled and safe manner. Written maintenance procedures shall be developed. Maintenance of fluorine systems shall only be performed by personnel with proven experience.

Particular consideration shall be given to ensuring that the cleanliness of the system is maintained and that replacement parts are compatible with fluorine.

Replacement of components shall be made with exactly the same make-model ("like-in-kind"), unless approved through a MOC process.

After maintenance, the system is to be purged and leak tested. It could be necessary to passivate the system again depending on the extent of the maintenance.

Components added and/or replaced during maintenance will need to be cleaned and passivated (see 7.5.3 for details).

Materials that are to be used in fluorine service shall be kept clean (free from oil, particles, etc.) and stored in a clean environment. Care shall be taken when changing gas-wetted components to avoid contamination from oil that can be on the operator's hands (for example, cylinder valve outlet gasket washers). Consideration should be given to wearing suitable clean gloves to prevent contamination of the operator's hands.

Used components from fluorine systems are to be cleaned immediately after dismantling and prior to handling or disposal in order to remove any hazardous materials such as hydrogen fluoride.

Consideration should be given to wearing suitable protection equipment during maintenance or dismantling of gas-wetted components of fluorine systems (gloves).

Care shall be taken so that contaminants are not introduced during maintenance and that the passivated system is not exposed to excess moisture. Moisture is not only a possible source of fluorine ignition but can also hydrolyse the passivation layer resulting in formation of hydrogen fluoride. Hydrogen fluoride can lead to accelerated corrosion in the system. For this reason, it is not advisable to use a vacuum pump or fan to allow air to be sucked into a fluorine system as a means to prevent escape of fluorine when the system is opened to atmosphere. To minimize air infiltration when a system shall be momentarily opened, consider the use of low flow inert gas purge (for example, a trickle purge) as protection against moist air infiltration.

Piping systems that use fluorine can become contaminated with a powdery residue over time. This material is composed of metal fluorides and should be handled with caution since the material can contain hydrofluoric acid and should be neutralized. It should also be assumed that any liquids or moisture found in these fluorine systems contains hydrofluoric acid. This material is very corrosive to skin and many other materials of construction.

Use precautions such as protective canopies, if a fluorine system is opened to the atmosphere while it is raining or snowing.

Install blank flanges, pipe caps, etc., on any open ports of a fluorine system during maintenance.

## 8 Cylinder filling

### 8.1 Filling facility considerations

Filling of fluorine cylinders shall only be carried out by specially equipped centres with qualified and trained staff using documented and approved procedures.

Local fire codes and other applicable regulations shall be met.

Cylinders, cylinder bundles, tubes, tube modules, and systems containing fluorine shall be protected against fire risk. This can be achieved by storing them at least 5 m (16 ft) away from flammable materials or by separation using fire resistant walls.

Cylinders shall be stored in open air or in well ventilated rooms.

Filling operations should be located inside ventilated rooms. A risk assessment shall be done to verify adequacy of the room exhaust system (dispersion analysis). Abatement for building exhausts for emergency release may be required based on the risk assessment or local codes.

Fluorine detectors shall be placed in areas such as ventilation exhausts or near critical high pressure fluorine equipment to detect a leak as soon as possible. It can be difficult to approach or get access to the source of fluorine in the event of a leak to enable isolation of the source of fluorine. An actuated valve on the manifold line from the outlet of the fluorine source shall be installed. This valve shall be closed remotely by manual intervention or a signal from a gas or fire detector in the event of an incident. Wherever practicable, this valve shall be used exclusively for emergency shutdown of the system.

Equipment designed for fluorine and systems designed for fluorine mixtures with inert gases containing more than 35% fluorine above 4 bar shall be mounted behind barriers to protect operators. Remote operation of these systems shall be undertaken wherever practical (see 7.1).

### 8.2 Gas containers and associated equipment

#### 8.2.1 Cylinders, tubes, and bundles

Gas cylinders for fluorine are normally of carbon steel construction (carbon-manganese or chromium-molybdenum). The cylinder manufacturing process, internal degreasing/cleaning, and passivation are important to reduce ignition concerns. Cylinders formed by spinning steel tubes or the cold drawn method are the preferred manufacturing methods for fluorine cylinders. It is recommended to use seamless cylinders when authorized by the authority having jurisdiction (AHJ).

The forged billet technique for forming cylinders can allow carbon residue to be trapped under slag leading to a reaction in the future even after degreasing and passivation. Cylinders manufactured by the forged billet method shall be internally cleaned (such as by shot blasting) to bare metal before use in pure fluorine service. In this case, shot blasting residual material shall be removed.

Aluminium alloy cylinders shall not be used.

Only dedicated cylinders shall be used for fluorine service. The change of inert gas cylinders (nitrogen, argon, helium, etc.) to fluorine service is acceptable, if the history of the cylinders is well documented and confirms that they have only been in inert gas service.

See ISO 11621 Gas cylinders -- Procedures for change of gas service and CGA C-10, Guidelines to Prepare Cylinders and Tubes for Gas Service and Changes in Gas Service for further information on change of service from other gases to fluorine service [24, 25].

Cleaning, degreasing, and passivation shall be undertaken prior to introduction of fluorine (see 7.5).

The internal cleanliness of the cylinders is extremely important. The cleaning and inspection procedure shall include the removal of any materials likely to react with fluorine (particles, slag, rust, organic materials, etc.) and the appropriate final controls. Traceability of each operation procedure is important to ensure that all necessary steps have been taken.

The cleaning and inspection procedure shall be comprised of the following steps (as a minimum):

- a) internal treatment to produce a bare, pure metallic surface;
- b) removal of residual materials and particulates;
- c) visual examination of the inner surface of every cylinder by experienced personnel;
- d) sealing of cylinder inlets immediately after approval of inner surface preparation;
- e) leak and pressure testing of the cylinder(s) with dry, oil-free inert gas;
- f) vacuum baking, purging, and drying with oil-free inert gas; and
- g) pressurizing the cylinder with dry, oil-free inert gas.

Only trained, experienced, and authorized personnel shall perform the cleaning and inspection procedure.

### **8.2.2 Cylinder valves**

Cylinder valves for fluorine service shall be designed taking into account the requirements contained in Section 7.

Cylinder valves for fluorine require a dedicated choice of materials, design, and approval procedure. It is strongly recommended not to use valves that were designed for other toxic, oxidizing, or corrosive gases (for example, nitrogen trifluoride, oxygen, or chlorine) without a design review.

For selection of cylinder valve seat materials at varying pressures and concentrations of fluorine, see 7.2.2. Cylinder valves with packed needle stem design have been used extensively for applications of fluorine and fluorine mixtures.

ASB alloys (UNS C64210, VA10) are used for cylinder valve bodies to 30 bar for fluorine and to 200 bar for fluorine mixtures (fluorine greater than 35%).

Monel cylinder valves are used for high pressure fluorine applications in some specific cases.

Brass (UNS C38000) is used for cylinder valve bodies to 30 bar for fluorine and to 150 bar for fluorine mixtures (fluorine greater than 35%).

Stainless steel cylinder valves (316L) are used for mixtures of fluorine of 20% and below.

Cylinder valve designs shall be tested before being used for fluorine or fluorine mixture service. Such tests may include adiabatic testing with oxygen as well as endurance testing according to ISO 10297, *Gas cylinders—Cylinder valves—Specification and type testing* [26].

### **8.2.3 Cylinder filling pressure**

Local applicable regulations shall be met.

Pure fluorine cylinders and fluorine mixture cylinders are usually filled by pressure (manometric filling). For accurate mixtures, a gravimetric procedure should be used.

International transport regulations limit the filling pressure of pure fluorine to 30 bar at 15 °C, see Section 11, although historical practice in the U.S. has been to limit the pressure to 28 bar (400 psig) as required by DOT regulations [1, 27].

The following fluorine mixtures (with their respective manufacturing blending tolerances) are commonly supplied:

- 5% max fluorine in inert gases (laser applications) at pressures up to 200 bar;
- 10% fluorine in nitrogen at 150 bar; and
- 20% fluorine in nitrogen at 100 bar and 140 bar.

Other mixture concentrations and filling pressures are possible.

### 8.3 Cylinder filling equipment

#### 8.3.1 Filling manifold

Manifold components, valves, and equipment creating a higher velocity due to pressure drop shall be designed, constructed, cleaned, and passivated according to the requirements contained in Section 7. Particular attention shall be paid to filters and valve seat materials.

It is recommended to have a totally welded system for fluorine service. Use of compression fittings shall be minimized.

The design of manifold pigtailed shall ensure that the fluorine velocities are in accordance with 7.3.3. Under certain conditions, (for example, a full cylinder being vented) it may not be possible to comply with 7.3.3, however, such operations can be safely achieved by operating valves remotely (extension handle for valve actuation through a barrier) and by ensuring the system is clean.

Rigid tubing pigtailed are used for pure fluorine. Flexible hoses of Monel or stainless steel can be used for handling fluorine mixtures with a maximum concentration of 20%. Convolute flexible hoses shall not be used for pure fluorine.

Once a manifold is prepared for fluorine service (cleaned, dried, and passivated), contamination by particulates or moisture (ambient air, rain, snow) shall be avoided as they can damage the integrity of the system. When not under fluorine pressure, manifolds shall be plugged and pressurized with an inert gas to ensure that any contaminants are excluded and/or under constant inert gas flow-through purge, with venting to a safe location.

The system design shall permit inert gas purging prior to and after a fluorine cylinder replacement and prior to opening the system for maintenance.

It is recommended to apply an evacuation and inert gas purge sequence several times before opening the system. If a vacuum pump is used, the system shall include safeguards to prevent fluorine or high pressure inert gas exposure to the pump. Purge gases shall be vented into an abatement system.

It is recommended that a purge sequence is started on operator demand and is carried out automatically.

When making fluorine mixes in a cylinder by first adding pure fluorine and then adding inert gas at high pressure, there is potential for the inert gas to act as a piston and compress the initial charge of fluorine to a much higher pressure in the bottom of the container. Increased ignition potential due to this compression of the pure fluorine as well as the added heat from compression shall be evaluated in the design of a mixing/blending system.



When it is not in operation, the system should be depressurized, purged, and pressurized with an inert gas.

### **8.3.2 Compressors**

Consideration shall be given to the location of a fluorine or fluorine mixture compressor in a separate enclosure, provided with remote start up and shutdown capability. Diaphragm compressors are commonly used with fluorine and fluorine mixtures.

Compressors shall be specifically designed for fluorine service. High temperature wetted parts (for example, valves) should be made of nickel, Hastelloy®, or Monel, where practical. Compressors for fluorine shall use a fluorinated fluid such as PFPE or CTFE oil.

The heat generated by the compression of fluorine shall be considered and the compressor design shall minimise the fluorine gas temperature. This can be achieved by:

- Limiting the compression ratio and, if necessary undertaking the required compression in several stages, possibly cooling the gas between each stage;
- Choosing materials with high thermal conductivity for components that are in contact with the gas;
- Limiting the rate at which the gas is compressed is particularly important where high compression ratios are used; and
- Introducing a high temperature interlock to shut down the system automatically in the event of excessive temperature being reached.

### **8.3.3 Vacuum pumps**

Vacuum pumps shall be specifically designed for fluorine service. To protect the vacuum pump from fluorine, it is recommended to install a fluorine dry scrubber prior to the vacuum pump (see 10.2). Vacuum pumps in contact with fluorine shall be either dry pumps or pumps using a fluorinated fluid such as PFPE oil. The fluorine system vacuum pump exhaust shall be routed to an abatement system.

Vacuum pumps shall be protected from overpressure sources from the fluorine system.

The use of pump shields and enclosures to protect personnel shall be considered.

### **8.3.4 Pressure gauges and transmitters**

Gauges with Monel bourdon tubes or pressure transmitters designed for fluorine service shall be used.

Special care shall be taken to ensure that pressure gauges are cleaned internally to a standard equivalent to that used in oxygen service, that they are dried and passivated, and of adequate pressure range before installation and use.

Consideration should be given to the protection of the operator in the event of a pressure gauge failure by possibly using shields if the gauge is in a location near operators.

If liquid filled gauges (for dampening) are used, the fill fluid shall be compatible with fluorine.

Transmitter seals and transmitter fluids shall be fluorine compatible.

## 9 Supply to point-of-use

The supplier of fluorine gas shall review the facility capabilities of a new user of fluorine including verification that the equipment is designed for fluorine use and that the auxiliary equipment is available (abatement equipment, etc.) for normal processing and for emergency conditions.

The information mentioned in 7.7 and 8.3 also applies to gas supply equipment to point-of-use.

In addition, the following information shall be considered for those systems.

### 9.1 Facility considerations and storage

Facility considerations and storage shall meet applicable local regulations.

The storage area shall be locked and secured and access to the storage area shall be permitted only to trained and authorized personnel.

Cylinders shall be stored in the open air or in well ventilated rooms.

### 9.2 Gas supply manifolds

The pressure reducing system (regulator) shall be as close as possible to the source cylinder so that there is a minimum amount of piping exposed to high pressure fluorine.

Gas manifolds shall be located inside ventilated rooms or ventilated gas cabinets. If a ventilated room or gas cabinet is not available, then an outdoor installation may be used if permitted by local code and supported by a risk assessment.

Gas manifolds operating above 4 bar of fluorine or mixtures of fluorine greater than 35% shall be mounted behind barriers to protect operators. Remote operation of these systems shall be undertaken wherever possible.

The supply manifold shall prevent a backflow into the fluorine cylinder (for example, using check valves or differential pressures with process interlocks).

The supply manifold shall permit an inert gas leak/pressure test of the connection to the fluorine cylinder to ensure tightness after change over.

Cleaning, drying, and passivation of the manifold shall be undertaken to ensure it is safe to introduce fluorine (see 7.5).

At the point-of-use, the number of cylinders should be limited to those required for continuous supply.

It is recommended that all valves of the fluorine system be closed when no flow is required (for example, end-of-shift).

Consideration shall be given to firefighting and the arrangements to keep gas supply containers cooled in the event of a fire.

Fluorine detectors shall be placed in areas such as ventilation exhausts, near critical fluorine equipment (fluorine cylinder in use), and working areas to detect a leak as soon as possible. It can be difficult to approach or get access to the source of fluorine in the event of a leak to enable isolation of the source of fluorine. It is recommended that a remotely-actuated valve on the manifold outlet of the fluorine source be installed. This valve could be closed remotely by manual intervention or a signal from a gas or fire detector in the event of an incident. Wherever practicable, this valve should be used exclusively for emergency shutdown of the system.

Provision shall be made to deal with emergencies such as leaks and reactions within the fluorine supply systems (see Section 12).

## 10 Gas abatement system [28,29]

### 10.1 Abatement for processing

Because of its toxic properties, venting of fluorine or fluorine mixture systems shall be in compliance with local regulations.

Vents associated with the processing of fluorine shall be directed to an abatement system as required by local regulations.

### 10.2 Abatement for emergency release

Consideration shall be given to abatement systems for an accidental release of fluorine, which may also be required by local regulations. The abatement system shall be sized to treat the contents of the largest vessel in the process.

All discharges from process emergency venting such as, pressure relief devices (PRDs), etc., that do not go to an abatement system shall be:

- piped to the outside of buildings; and
- discharged to a safe area well away from personnel; and
- confirmed acceptable by use of dispersion analysis.

Gas abatement equipment shall be designed, constructed, cleaned, dried, passivated, and maintained according to the same considerations as other fluorine equipment, when relevant.

### 10.3 Basic principles of abatement

The method of abatement depends on the application in which the fluorine is being used.

Since fluorine is a strong oxidizer, there are numerous chemical reactions that can consume fluorine. A scrubber system can be used in order to convert fluorine into products that are easy and safe to dispose. The major issue is to control the exothermic reactions to achieve both a low enough temperature and the chemical efficiency of the abatement.

The size of the scrubber (fluorine quantity and fluorine release rate) is also very important. It shall be large enough:

- to destroy the quantity of fluorine coming out from the largest source, in case of emergency release; and
- to handle the largest possible flow of fluorine for both process and emergency release.

A system shall be in place in order to monitor the degree of saturation of the abatement system, for example, fluorine detector and colour change.

There are two categories of scrubbers, dry and wet, as detailed in 10.4 and 10.5.

### 10.4 Dry scrubbers

There are a number of solid state abatement systems available. These systems are usually designed to fit into the process exhaust and generally are designed for a dilute fluorine concentration. Examples are:

- Alumina scrubbers—Fluorine reacts with dry activated alumina ( $\text{Al}_2\text{O}_3$ ), producing oxygen and solid aluminium fluoride. The reaction is very exothermic and precautions shall be taken to avoid an excessive increase of temperature. Temperature can be controlled by external cooling of the

scrubbers and/or by control of the fluorine flowrate or by dilution of fluorine with inert gas prior to entering the scrubber. Activated alumina contains moisture, which can generate very toxic oxygen difluoride gas by reaction with fluorine. The activated alumina shall be dried to remove any trace of moisture; and

- Calcium hydroxide and calcium carbonate scrubbers—These solid state scrubbers are used when process streams containing fluorine are mixed with air. The resulting hydrogen fluoride is then scrubbed.

Carbon is not used because of the potential for explosion (see 4.3).

Since the solid bed can be subject to obstruction, a method shall be used (for example, differential pressure) to monitor and control the system.

## 10.5 Wet scrubbers

Typically, wet scrubbers use solutions of potassium hydroxide or sodium hydroxide. Attention shall be paid to the size and design of such scrubbers and to the concentration of the caustic solution to avoid fluorine salt precipitation and the production of very toxic oxygen difluoride gas (OF<sub>2</sub>). Oxygen difluoride is produced as a side reaction between fluorine and aqueous hydroxide. Too high or too low concentrations of caustic lead to greater amounts of oxygen difluoride generated. Addition of a mild reducing agent such as sodium thiosulfate is a very efficient way of reducing oxygen difluoride formation.

## 11 Transportation

### 11.1 Land transport

Compressed fluorine and fluorine mixtures in inert gases are authorized for shipment in containers having the appropriate service pressure.

However, the LC<sub>50</sub> of the mixture is used to determine the hazard class of the gas and establishes certain shipping restrictions per international transport regulations [1], namely:

- Pure fluorine is transported under UN 1045 Fluorine, compressed. The transport is not authorized in tubes or pressure drums. The filling pressure is limited to 30 bar and the quantity of fluorine to a maximum of 5 kg in a single cylinder or in a group of cylinders in a bundle. Bundles containing fluorine may be divided into assemblies (groups) of cylinders not exceeding 150 L total water capacity;

In the United States, 49 CFR 173.302a(e) requires that pure fluorine packages not exceed 6 lb (2.7 kg) and 400 psi at 21 °C (70 °F) [27];

- Mixtures containing fluorine with a LC<sub>50</sub> less than 200 ml/m<sup>3</sup> (200 ppm) (for example, 92.5% or more of fluorine in nitrogen) are transported under UN 3306, Compressed gas, toxic, oxidizing, corrosive, N.O.S. The transport is not authorized in tubes or pressure drums;
- Mixtures containing fluorine with a LC<sub>50</sub> greater than 200 ml/m<sup>3</sup> (200 ppm) but less than 5000 ml/m<sup>3</sup> (5000 ppm) (for example, between 3.7% and 92.5% of fluorine in nitrogen) are transported under UN 3306, Compressed gas, toxic, oxidizing, corrosive, N.O.S. but are authorized to be transported in tubes and pressure drums; and
- Mixtures containing fluorine with a LC<sub>50</sub> greater than 5000 ml/m<sup>3</sup> (5000 ppm) are not classified as toxic for transport but remain oxidizing down to 0.6% of fluorine in nitrogen and are transported under UN 3156, Compressed gas, oxidizing, N.O.S. and are also authorized to be transported in tubes and pressure drums.

## 11.2 Air transport

International Air Transport Association (IATA) *Dangerous Goods Regulations* prohibit the shipment of dangerous goods identified by UN 1045 and UN 3306 (see 11.1) [30].

## 11.3 Sea transport

Compressed fluorine and fluorine mixtures of all concentrations are permitted for sea shipment following provisions detailed in the *International Maritime Dangerous Goods Code (IMDG)* [31].

## 12 Emergency response

### 12.1 Leaks of fluorine

In the event of a fluorine leak/reaction the following basic steps are to be taken immediately:

- vacate the unsafe area;
- do not re-enter the unsafe area;
- activate the emergency stop buttons; and
- notify the local emergency centre.

Additional emergency measures are to be taken only by personnel trained and qualified for emergency response.

Caution shall be used to prevent direct exposure to a concentrated fluorine leak during an emergency response, as there is potential for ignition of the chemical resistant clothing, including gloves.

Trained personnel responding to an emergency involving a fluorine release should use a self-contained breathing apparatus (SCBA) with a full face-piece and positive pressure mode and a chemical resistant suit. Air purifying respirators are not recommended as they are not effective in fluorine service.

In the event of a large leak not in an enclosure, water fog/fine spray can reduce the impact of the cloud, but the runoff water is acidic (hydrofluoric acid). Since system design normally will minimize the fluorine mass being stored and rapid shutdown systems are used, the duration and quantity of a release usually does not warrant the use of a fixed water spray system.

Cylinder recovery vessel(s) for leaking fluorine cylinders shall be designed and cleaned for fluorine gas. However, since the external surface of the leaking cylinder contains materials (paint, labels, adhesives, oil/grease) which are incompatible with concentrated fluorine, the use of containment vessels for fluorine cylinders is recommended only for those that fully understand the oxidizing potential of the leaking cylinder.

### 12.2 Firefighting

Fire due to ignition in a fluorine system usually ceases when the flow of fluorine is stopped. Applying the extinguishing agent directly to the fire is not recommended, as the agent (even water) can react with the fluorine. Water spray can be used to cool surrounding equipment, if required.

In the event containers of fluorine are involved in a fire;

- Move cylinders and/or bundles from fire area if it can be done without risk; and
- Cool containers with water spray until well after the fire is out.

Cylinders exposed to high heat or flame can rupture violently.

Pure fluorine cylinders are usually not equipped with PRDs. Cylinders of 20% or less mixtures can be equipped with PRDs in the cylinder valves. These safety devices can release the contents of the cylinder and minimize the potential for cylinder failure under fire conditions

Hydrogen fluoride and other toxic fluorides can be produced as products of combustion. Besides the danger these products pose to personnel, they can also contaminate the runoff water from firefighting.

### 12.3 First aid measures

Delayed effects are possible. Even if no obvious signs of injury are present, it is important that a person exposed to fluorine be monitored for any delayed health effects.

First aid for exposure to fluorine and fluorine mixtures is treated the same as the specialized treatment for exposure to hydrogen fluoride. It is very important to preplan first aid and treatment for fluorine and hydrofluoric acid exposures because of their unique properties. Supply local medical facilities with information on treatment, and ensure that materials and procedures for treatment are in place.

For both fluorine and hydrogen fluoride exposure, it is important to neutralize the fluoride ion as soon as possible and to seek advanced medical treatment [32, 11].

#### 12.3.1 Skin exposure

- Remove the injured person from the contaminated area as soon as possible;
- Cleanse the fluorine from skin by flushing with running water;
- As water flushing is being done, remove any contaminated clothing from the victim;
- As soon as possible while wearing gloves, continuously rub calcium gluconate, 2.5% gel or benzalkonium chloride, 13% solution to the exposed area;
- Seek advanced medical treatment while continuing to apply calcium gluconate gel or benzalkonium chloride solution; and
- If calcium gluconate gel or benzalkonium chloride solutions are not available, continue flushing until medical treatment is rendered.

#### 12.3.2 Eye exposure

- Remove the injured person from the contaminated area as soon as possible;
- If the person is wearing contact lenses, the lenses should be removed, if possible;
- Immediately flush with gently flowing water for at least 15 minutes while holding eyelids open and away from the eye;
- If sterile 1% calcium gluconate solution is available, the water flush period may be reduced to 5 minutes, after which the 1% calcium gluconate solution should be repeatedly used to flush the eyes;
- Do not use calcium gluconate gel, benzalkonium chloride solutions, or other hydrogen fluoride skin treatments in the eye;
- Rubbing of the eyes is to be avoided; and
- Seek advanced medical treatment.

### 12.3.3 Inhalation exposure

- Immediately move injured person to fresh air and get medical attention;
- If not breathing, begin artificial respiration, but do not use mouth-to-mouth or mouth-to-nose cardiopulmonary resuscitation (CPR) techniques, due to exhalation of toxic gases. A bag valve mask (BVM) or artificial manual breathing unit (AMBU) breathing bags should be used. 100% medical oxygen (if available) should be administered by a trained individual;
- Seek advanced medical treatment;
- Under the company physician's direct instruction, users of fluorine typically have on-site supplies and personnel trained to administer additional first aid/treatment in order to quickly treat a person with inhalation exposure. The specific treatment varies based on the given country, company and physician. Some accepted treatments include:
  - As soon as available, administer 2.5% to 3% calcium gluconate solution using a nebulizer [10]
  - To minimise swelling and allow other treatments, inhalation steroids such as beclomethasone dipropionate are used (sometimes even in the absence of immediate symptoms); and
  - Because inhalation can be associated with bronchospasm, bronchodilators may be administered as necessary [11].

## 13 References

Unless otherwise specified, the latest edition shall apply.

[1] *UN Recommendations on the Transport of Dangerous Goods-Model Regulations*, [www.unece.org](http://www.unece.org)

[2] *NIOSH Pocket Guide to Chemical Hazards*, National Institute for Occupational Safety and Health, [www.cdc.gov/niosh](http://www.cdc.gov/niosh)

[3] EIGA Doc 13, *Oxygen Pipeline and Piping Systems*, [www.eiga.eu](http://www.eiga.eu)

NOTE This publication is part of an international harmonization programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

[4] ASTM STP 1395, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres*, [www.astm.org](http://www.astm.org)

[5] *TLVs® and BEIs® Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, [www.acgih.org](http://www.acgih.org)

[6] EIGA Doc 169 *Classification, and Labelling Guide in accordance with EC Regulation 1272/2008 (CLP Regulation)* [www.eiga.eu](http://www.eiga.eu)

[7] CGA C-7, *Guide to Classification and Labeling of Compressed Gases*, Compressed Gas Association, [www.cganet.com](http://www.cganet.com)

[8] *Code of Federal Regulations*, Title 29 (Labor) Parts 1900-1910, [www.gpo.gov](http://www.gpo.gov)

[9] *Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 8*, The National Academies Press, [www.nap.edu](http://www.nap.edu)

[10] ISO 10298, *Determination of toxicity of a gas or gas mixture*, [www.iso.org](http://www.iso.org)

[11] *Honeywell Hydrofluoric Acid—Recommended Medical Treatment for Hydrofluoric Acid Exposure*, [www.honeywell.com](http://www.honeywell.com)

[12] ISO 11114-3, *Gas cylinders—Compatibility of cylinder and valve materials with gas contents—Part 3: Autogenous ignition test for nonmetallic materials in oxygen atmosphere*, [www.iso.org](http://www.iso.org)

[13] ASTM STP 1267, *Flammability of Metals in Fluorine and Nitrogen Trifluoride*, ASTM International, [www.astm.org](http://www.astm.org)

[14] Godwin, T.W. and Lorenzo, C.L., *Ignition of several metals in fluorine*, American Rocket. Soc. Meeting, New York, November 1958, Paper No. 740–58. 3. [www.aiaa.org](http://www.aiaa.org)

[15] Daniel, P.L. and Rapp, R.A., “Halogen Corrosion of Metals”, *Advances in Corrosion Science and Technology*, Volume 5, Fontana M.G., et. al. (eds.), Plenum Press, New York. [www.link.springer.com](http://www.link.springer.com)

[16] EIGA Doc 33, *Cleaning of equipment for oxygen service — Guideline*, [www.eiga.eu](http://www.eiga.eu)

[17] CGA G-4.1, *Cleaning Equipment for Oxygen Service*, Compressed Gas Association, [www.cganet.com](http://www.cganet.com)

[18] ISO 10156, *Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets* [www.iso.org](http://www.iso.org)

[19] ASME B31.3, *Process Piping*, American Society of Mechanical Engineers, Three Park Ave., New York, NY, 10016 USA. [www.asme.org](http://www.asme.org)

[20] EIGA Doc 78, *Leak Detection Fluids Cylinder Packages*, [www.eiga.eu](http://www.eiga.eu)

NOTE This publication is part of an international harmonization programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

[21] Anderson, R.E., “Dynamic Compatibility of Fluorine with Metals”, *Fluorine Systems Handbook*, Section VI, Prepared for Air Force Rocket Propulsion Laboratory, October 1972. [www.dtic.mil](http://www.dtic.mil)

[22] The Properties and Handling of Fluorine, Technical Documentary Report No. ASD-TDR-62-273, October 1963, Air force Materials Laboratory, Table 5-3, p.71

[23] Halogen Passivation Procedural Guide, Air Force Rocket Propulsion Laboratory, Technical Report AFRPL-TR-67-309, December 1967

[24] ISO 11621, *Gas cylinder—Procedures for change of gas service*, [www.iso.org](http://www.iso.org)

[25] CGA C-10, *Guidelines to Prepare Cylinders and Tubes for Gas Service and Changes in Gas Service*, Compressed Gas Association, [www.cganet.com](http://www.cganet.com)

[26] ISO 10297, *Gas Cylinders—Cylinder valves—Specification and type testing*, [www.iso.org](http://www.iso.org)

[27] *Code of Federal Regulations*, Title 49 (Transportation) Parts 100-199, [www.gpo.gov](http://www.gpo.gov)

[28] EIGA Doc 30, *Disposal of gases*, [www.eiga.eu](http://www.eiga.eu)

NOTE This publication is part of an international harmonization programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

[29] EIGA Doc 80, *Handling Gas Container Emergencies*, [www.eiga.eu](http://www.eiga.eu)

[30] *Dangerous Good Regulations*, International Air Transport Association, [www.iata.org](http://www.iata.org)

[31] *International Maritime Dangerous Goods Code*, International Maritime Organization,



[32] *Management of hydrogen fluoride injury—Notes for health professionals*, Eurofluor—Comite Technique Europeen du Fluor (CTEF), A Sector Group of the European Chemical Industry Council (CEFIC), [www.eurofluor.org](http://www.eurofluor.org)

## Appendix A—Audit checklist

It is recommended that facilities handling fluorine undergo periodic audits to assess their compliance with this publication and with other recognised safe working practices. The nature and detail of such audits are determined by the type of work undertaken at the facility, its level of involvement with fluorine, and compliance with local regulations.

The checklists given in the following pages are not exhaustive for all fluorine facility audit applications; however, they provide a helpful starting point. There are separate checklist sections that only cover fluorine cylinder filling and fluorine systems; however, the other checklist sections are likely to be applicable to all fluorine handling facilities. The “Ref” column gives, where appropriate, the section of this publication where more information on the checklist item can be found.

| No       | CHECKLIST ITEM   | Ref             |
|----------|--|-----------------|
| <b>1</b> | <b>Fluorine storage area</b>   | <b>Ref</b>      |
| 1.1      | Are fluorine cylinders and other containers stored in a well-ventilated area, at least 5 m away from flammable materials (or separated by a fire <u>resistant</u> wall)?   | 8.1             |
| 1.2      | Does the fluorine storage facility meet local fire regulations (where applicable)?   | 8.1             |
| 1.3      | Is the storage area labelled?  |                 |
| 1.4      | Are cylinders in the <u>storage area</u> secured or nested to prevent them falling over and are their valve protection caps fitted?  | ---             |
| <b>2</b> | <b>Fluorine filling procedures and equipment</b>   | <b>Ref</b>      |
| 2.1      | Has the fluorine filling equipment been designed by engineers, who are familiar with the properties of fluorine, and the precautionary measures and material requirements necessary for its safe handling (as set out in this publication)?  | All             |
| 2.2      | Has a risk assessment been carried out on the system?  | 8.3             |
| 2.3      | If there is any uncertainty with respect to 2.1 or 2.2, detailed and documented reviews of the process equipment drawings, system design, and all component specifications <u>should</u> <u>be</u> carried out to confirm compliance with this publication.  | All             |
| 2.4      | Is the fluorine cylinder filling system and all its component parts located in a well ventilated place away from fire risk?  | 8.1             |
| 2.5      | Are there <u>written</u> operating procedures for fluorine cylinder filling equipment? Do these procedures take into account all the recommended operational precautions set out in this publication?  | 7.7             |
| 2.6      | Is the fluorine cylinder filling equipment dedicated to fluorine service?  | 7.3.4           |
| 2.7      | Are all flammable gases separated from the fluorine cylinder filling equipment?  | 7.3.4           |
| 2.8      | Is there a fluorine compressor? Does it comply with the recommendations in this publication?   | 7.6,<br>8.3.2   |
| 2.9      | Is there a purge gas associated with the fluorine cylinder filling equipment? If so, is it a dedicated supply? If it is not a dedicated supply (for example, house supply), are precautions <u>taken</u> to ensure the purge gas is not contaminated with flammable materials or cannot become contaminated with fluorine? | 8.3.1           |
| 2.10     | Are all lubricants that could come into contact with fluorine compatible with fluorine (for example, vacuum pump and compressor oils)?   | 7.2.2,<br>8.3.2 |
| 2.11     | Are fluorine cylinders approved for and dedicated to fluorine service? If not, are <u>cylinders</u> prepared prior to filling to ensure they are not contaminated with any materials that <u>can</u> react with fluorine?  | 8.2.1           |
| 2.12     | Have the fluorine cylinder valves been approved for fluorine service by an expert within the gas company and/or an external authority?   | 8.2.2           |

| <b>2</b> | <b>Fluorine filling procedures and equipment</b>  | <b>Ref</b>    |
|----------|---|---------------|
| 2.13     | Are cylinder valves prepared prior to use to ensure they are not contaminated with any materials that can react with fluorine?                                  | 8.2.2         |
| 2.14     | Are only approved compatible gaskets used for sealing valve outlet connections? Do operators take care to ensure they are in a good clean condition before use? | 7.2.2         |
| 2.15     | Are there checks to ensure fluorine containers are not overfilled?  | 11            |
| 2.16     | Are there checks and controls <u>in place</u> to prevent unauthorised modification of equipment and operating procedures?                                       | 7.7,<br>7.8   |
| 2.17     | Are precautions taken to prevent the contamination of equipment, particularly when it is not in use?  | 7.8,<br>8.3.1 |
| 2.18     | Are precautions taken to detect and act upon fire or fluorine leakage (for example, installation of detectors, automatic valve shutoff, etc.)?                  | 8.1,<br>11.2  |
| 2.19     | Has the system been cleaned, inspected, and passivated prior to operating with fluorine?  | 7.5           |

| <b>3</b> | <b>Fluorine supply and supply equipment (for cylinder filling or use)</b>   | <b>Ref</b>  |
|----------|---|-------------|
| 3.1      | Has the equipment been designed and installed in accordance with this publication?  | 7.3         |
| 3.2      | If there is any uncertainty with respect to 3.1, detailed and documented reviews of the process equipment drawings, system design, and all component specifications <u>should be</u> carried out to confirm compliance with this <u>publication</u> .   | 7.3         |
| 3.3      | Are fluorine supply cylinders located in a well-ventilated area away from fire risk?  | 8.1         |
| 3.4      | Are there <u>written</u> operating procedures for fluorine supply equipment? Do these procedures take into account all the recommended operational precautions set out in this publication?   | 7.7         |
| 3.5      | Is the fluorine supply equipment dedicated to fluorine service?   | 9.2         |
| 3.6      | Are cylinders connected for use secured to prevent them falling over?   | ----        |
| 3.7      | Are all flammable gases separated from fluorine supply equipment?   | 9.2         |
| 3.8      | Is there a purge gas associated with the fluorine supply equipment? If so, is it a dedicated supply? If it is not a dedicated supply (for example, house supply), are there precautions to ensure the purge gas is not contaminated with flammable materials or cannot become contaminated with fluorine? | 9.2         |
| 3.9      | Are all lubricants that could come into contact with fluorine compatible with fluorine (for example, vacuum pump oil)?  | 8.3.3       |
| 3.10     | Are only approved compatible gaskets used for sealing valve outlet connections and do operators take care to ensure they are in good clean condition before use?  | 7.2.2       |
| 3.11     | Are there checks and controls to prevent unauthorised modification of equipment and operating procedures?   | 7.7,<br>7.8 |
| 3.12     | Are precautions taken to prevent the contamination of equipment, particularly when it is not in use?  | 7.8         |
| 3.13     | Does the fluorine supply/storage system include a remotely activated shutoff valve?   | 8, 9.2      |

| <b>4</b> | <b>Fluorine abatement and abatement equipment</b>  | <b>Ref</b> |
|----------|--|------------|
| 4.1      | Has a risk assessment been carried out to confirm that the arrangements for the disposal of waste fluorine ensure the safety of people and minimise any impact on the environment? | 10.1       |

| <b>5</b> | <b>Maintenance procedures</b>  | <b>Ref</b> |
|----------|--|------------|
| 5.1      | Are there documented procedures to cover the maintenance of fluorine handling equipment? Are records kept of work carried out? | 7.8        |

| <b>5</b> | <b>Maintenance procedures</b>  | <b>Ref</b> |
|----------|--|------------|
| 5.2      | Is fluorine equipment maintenance covered by a permit-to-work procedure, where appropriate?  | ----       |
| 5.3      | Are materials and components that can be used during the maintenance of fluorine equipment clearly specified/identified?   | 7.8        |
| 5.4      | After maintenance work, is there a cleaning and purging (plus passivation where appropriate) procedure to be implemented before the equipment is returned to fluorine service?   | 7.8        |
| <b>6</b> | <b>Personnel</b>   | <b>Ref</b> |
| 6.1      | Is there a recorded training programme on gas handling for all personnel involved in handling fluorine and maintaining fluorine equipment?   | 7.7        |
| 6.2      | Are all personnel involved with fluorine trained to cover their degree of involvement?<br>NOTE It is recommended that representative samples of operational personnel are interviewed during the audit to assess their understanding of the properties of fluorine | ---        |
| 6.3      | Do personnel who handle fluorine have access to a fluorine <u>SDS</u> ?  |            |
| 6.4      | Do personnel who handle fluorine wear/use appropriate <u>PPE</u> ?   | 7.7        |
| <b>7</b> | <b>Emergency response</b>  | <b>Ref</b> |
| 7.1      | Is there a fluorine specific emergency response procedure <u>readily available and are personnel trained in this procedure</u> ?   | 12         |
| 7.2      | Is there firefighting and <u>PPE</u> readily available in the event of a fluorine ignition <u>and subsequent fire</u> ?  | 12.2       |
| 7.3      | Is the local <u>fire department</u> aware of the location of and hazards arising from fluorine on-site?  | ----       |
| 7.4      | Is there first aid information and specialised supplies available <u>on-site</u> ?   | 12.3       |