CODE OF PRACTICE

COMPRESSED FLUORINE AND MIXTURES WITH INERT GASES

AIGA 053/08

GLOBALLY HARMONISED DOCUMENT

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Acknowledgement

This document is adopted from the European Industrial Gases Association IGC 140/07 ‘Code of Practice – Compressed fluorine and mixtures with inert gases’. Acknowledgement and thanks are hereby given to EIGA for permission granted for the use of their document

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1. Introduction

Fluorine is a highly toxic and oxidizing gas which presents safety risks, such as poisoning by inhalation of the gas, or by ignition of the handling equipment.

The risks involved with fluorine compression and handling can be minimized to an acceptable level, if equipment is properly designed and if appropriate handling precautions are taken, as described in this document.

The information which is contained in this document is based mainly on the experience in compressing and handling fluorine within the member companies who prepared it and on published literature.

Input from German Federal Materials Testing Institute (BAM) assisted the preparation of this document.

2. Scope & purpose

This Code of Practice is for gaseous fluorine and mixtures of fluorine with inert gases where the resulting fluorine concentrations of 0.5% fluorine and above are considered to present a risk of reaction due to the oxidizing potential.

It is intended for the use of Suppliers, Distributors and Users of fluorine and fluorine mixtures and the associated handling equipment.

It sets out to provide a good understanding of the potential hazards involved in storage, use and transportation of compressed fluorine and its mixtures with inert gases and the approach to be taken to minimise the risk of incidents.

This document does not cover the manufacture, purification, liquefaction, or analysis of fluorine or its mixtures with inert gases, although the general guidance given is also relevant to these processes.

Within the Appendix of this document is an audit check-list.

3. Definitions

Auto-ignition temperature: The temperature at which a substance will spontaneously ignite in air. The term also can apply to a specified oxidant at a given pressure.

Bundle (of cylinders): Assembly of cylinders that are fastened together and which are interconnected by a manifold and carried as a unit.

Cylinder: A cylinder is defined as a transportable container of up to 150 litres water capacity that can be filled with gas under pressure.

Cylinder recovery vessel: Commonly known in the gas industry as “containment vessel”. A pressure vessel which is designed to safely contain a cylinder and its content for transportation and storage until it can be safely emptied. A cylinder recovery vessel is often fitted with a gauge to indicate internal pressure and with valves to enable purging Note - Due to the strong oxidizing potential of fluorine the use of a containment vessel for pure fluorine or high concentrations of fluorine mixtures may not be appropriate. Consult operating instructions for the containment vessel and follow specific guidelines that are provided and applicable to the situation. Also refer to Section 11 for details.

EEL: Emergency Exposure Level.

F_2: Chemical formula for fluorine

Gas cabinet: A 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 and process gas pressure reducing regulators and control systems. The gas cabinet can be quite complex in design, often being equipped with automatic microprocessor control.

*IDLH***:** Immediately Dangerous to Life or Health: The maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects. IDLH values are published by the USA National Institute for Occupational Safety and Health Standards Completion Program

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 (reference 12).

LC_{50}: Lethal Concentration is the concentration of airborne material, which results in the death of 50% of the test group after a fixed period of exposure within the observation period.

MAK: Maximum Concentrations at the Workplace: the maximum admissible concentration of a chemical substance present as gas, vapour or aerosol in the workplace air which, according to current knowledge, does not have any adverse effects on the health of the workers concerned even if they are exposed for eight hours daily. Set by Federal Republic of Germany

Monel: Monel is US registered trademark for an alloy of copper and nickel, UNS N04400

Oxipotential: The oxidizing power of a gas compared to that of oxygen, given as a dimensionless number, where oxygen = 1 (reference 14).

Passivation: Passivation is a procedure that is applied when there is a possibility of a reaction between a reactive gas and the container or system into which it is going to be introduced. Passivation is usually carried out using a mixture containing a reactive gas diluted in an inert gas, sometimes followed by the pure reactive gas. As an example, in the specific case of fluorine or fluorinated gases, passivation ensures that any residual contaminants will react in a controlled manner and will create an inert fluoride layer.

PEL: Permissible Exposure Limit. An 8-hour time weighted average exposure set by OSHA (Occupational Safety and Health Administration, United States)

PPE: Personal Protective Equipment

Pressure: In this publication, “bar” shall indicate gauge pressure unless otherwise noted – i.e. “bar*a*” for absolute pressure and “bar, dif” for differential pressure.

Risk assessment: A documented exercise to assess 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 personnel protective equipment provided. Sometimes, it may be deemed appropriate to improve operational safety controls after undertaking a risk assessment.

SCBA: Self Contained Breathing Apparatus.

Shall: The use of the word “shall” in this document implies a very strong concern or instruction.

Should: The use of the word “should” in this document indicates a recommendation.

SOP: Standard Operating Procedure

STEL: Short Term Exposure Limit. A time weighted average concentration, usually averaged over 10 minutes, aimed at avoiding acute effects.

Swarf: small strips or particles of metal that can arise from machining operations.

TLV-TWA : The concentration to which a person may be exposed, 8 hours a day, 40 hours a week, without harm (This is the definition from ACGIH – American Conference of Governmental Industrial Hygienist)

Tube: For the purposes of this document, a *tube* is a large cylinder, with a water capacity of greater than 150 litres. Tubes are often connected together in a manner similar to that for bundles and mounted on a vehicle trailer for transport, storage and use. These are known as tube trailers or ISO tube modules (known also as 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.

4.1 Fluorine identification

Chemical formula: F_2

CAS No.	07782-41-4
EC No.	231-954-8
UN No.	1045

4.2 Physical properties

4.2.1 Physical properties of pure fluorine

molar mass:	37.997g/mol
melting temperature	-219.6 °C
latent heat of fusion @ m.p.	13.4 J/g
boiling temperature	-188.1 °C
gas density @ 0 °C, 1.01 bara	*1.696* kg/m^3
gas density @ 15 °C, 1.01 bara	*1.608 kg/*m^3
relative gas density (air = 1)	1.312
latent heat of vaporization @ b.p.	173 J/g
critical temperature	-129.0 °C
critical pressure	52.2 bara
critical density	570 kg/ m^3
heat capacity @ 25 °C	0.82 J/(g*K)
entropy @ 25 °C,1.01 bara	5.34 J/(g*K)

4.2.2 Physical properties of F_2/N_2 mixtures (10/90 mol%) – ideal mixture

molar mass (mean value):	29.012 g/mol
gas density @ *0* °C, 1.01 bara	*1.295* kg/m^3
relative gas density (air = 1)	1.002

4.2.3 Physical properties of F_2/N_2 mixtures (20/80 mol%) – ideal mixture

molar mass:	30.010 g/mol
gas density @ 0 °C, 1.01 bara	1.340 kg/m^3
relative gas density (air = 1)	1.036

4.3 Chemical reactivity

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

Fluorine reacts with many organic substances even at room temperatures and often accompanied by combustion and possible explosion.
The reactivity of fluorine is dependant on the pressure and temperature of the system. Dilution with inert gas has shown to reduce the oxidizing potential.

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 °C) = -271.7 kJ/mol]. Even at very low temperatures (solid fluorine, liquid hydrogen) a violent reaction is produced.

Reaction with water
Fluorine reacts with water to form oxygen, oxygen difluoride (OF_2) and hydrogen fluoride (HF). Small quantities of ozone and hydrogen peroxide may also be formed. OF_2 is much more toxic than fluorine.

Reaction with halogens
If fluorine is combined with any of the other elements in Group VII of the periodic table, it produces a highly exothermic reaction, from which a series of interhalogen compounds are formed (such as ClF_3, ClF_5,BrF_3, and IF_5). Halogen fluorides are also widely used as fluorinating agents.

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

Reaction with other non-metals
Boron, silicon, phosphorus, sulphur, selenium and tellurium all react with fluorine to cause combustion and the formation of fluorides of the highest valency. Normally, oxygen and nitrogen do not react with fluorine, but reactions may occur under special conditions. Of the noble gases, radon and xenon react readily with fluorine while krypton reacts only under special conditions.

Reactions with hydrocarbons and other organic compounds
All organic compounds, including the hydrocarbons, react with fluorine. Ignition usually occurs, and under certain circumstances the reaction may be explosive. The end product of the reaction is invariably carbon tetrafluoride. Under suitable reaction conditions, organic compounds may 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, can be used as construction materials or sealants, provided reaction conditions (purity of the materials, pressure/temperature and concentration of fluorine) are controlled.

Reaction with metals
Fluorine reacts with many metals and alloys at room temperature, but it must be emphasized 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 classified as 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. Listed below are some of the more common established maximum limits (in volume)of fluorine exposure to personnel used in the industrial gas industry.

TLV - TWA	*1ppm*
STEL	*1ppm*
PEL	*0.1ppm*
MAK	*0.1ppm*

The following are established maximum exposure limits to personnel under emergency conditions:

Emergency Exposure Level (EEL):	25ppm for 5 min
IDLH (NIOSH)	25ppm

The following are established LC_{50} values:

LC_{50} (1h, rat) (pure F2)	185ppm (reference 13)
LC_{50} (1h, rat) (for 20%fluorine in nitrogen)	925ppm (calculated per reference 13)
LC_{50} (1h, rat) (for 10%fluorine in nitrogen)	1850ppm (calculated per reference 13)

Routes of exposure
As fluorine forms HF on contact with moisture in the air or in the body, exposure to fluorine must be treated as an exposure to hydrofluoric acid.
The substance can be absorbed into the respiratory tract when inhaled.

Inhalation risk
A harmful concentration of this gas in the air may be reached very quickly on loss of containment. Inhalation produces hydrogen fluoride HF as the fluorine reacts with moisture in the lungs and respiratory tract.

Skin contact
Fluorine is extremely corrosive to the eyes and skin. The effects may be delayed. Medical observation is indicated.
Skin burns are of two types:

- Caused by hydrogen fluoride (HF) formed by fluorine in moist conditions
- Caused by fluorine in dry conditions

The latter is similar to a second-degree thermal burn. Hydrofluoric acid burns can be more severe and are slower to heal than fluorine burns.

Hydrofluoric acid is one of the most hazardous chemicals used in industry. It is unlike other acids because it cannot be rapidly neutralised 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. Exposure can be fatal if not treated immediately.

4.5 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. Fluorine is however expected to be highly toxic and reactive on environmental release. Because of its toxic properties fluorine or fluorine mixtures should not be vented directly to the atmosphere and should be treated through a properly designed abatement system.
Contact with water will form hydrofluoric acid, which creates aquatic toxicity concerns at very low concentrations (e.g. 50 to 60ppm).

5. Oxidizing/reactivity hazards

The information presented 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 & explosion hazards

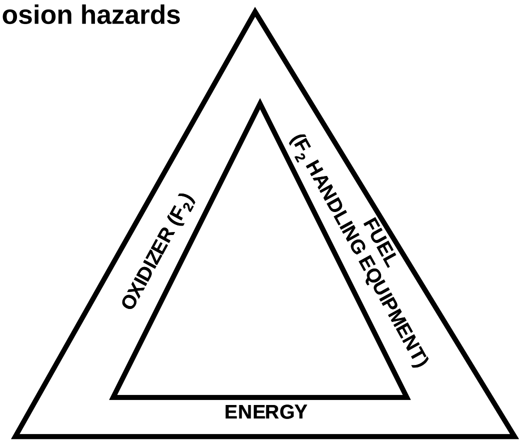

Figure 1 : ”Triangle of fire”

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

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

Because of its very high oxidizing ability the fluorine molecule can spontaneously react with most of the 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 less resistive 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 must 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:

- The Resistance of the Material to Fluorine See Section 5.2.1
- Size and Configuration of Equipment – See Section 5.2.2
- Cleanliness of the Equipment and Passivation with Fluorine - See Section 5.2.3
- Fluorine Pressure – See Section 5.2.4
- Concentration of Fluorine in Inert Gas- See Section 5.2.5
- Gas Temperature – See Section 5.2.6.
- Dynamic Exposure of Materials to Fluorine – See Section 5.2.7

5.2.1 The Resistance of the material to fluorine

Most metals offer far better resistance than plastics to fluorine ignition. Metal composition, mass and heat conductivity (ability to dissipate heat) are some factors that influence the potential for ignition. Use of plastics in a fluorine system significantly increases the risk of fluorine ignition and their use is limited to specific applications. Ignition of even the most resistive metals with Fluorine can occur if a less resistive material (e.g. plastics, 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, which 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, the testing for fluorine ignition and combustion is not standardized and in many cases tests were performed many years ago. It is clearly recognized that the relative auto-ignition temperatures in fluorine are much lower than the auto ignition temperatures in oxygen (Reference 3).

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

Auto-ignition Temperature of Metals
It must be emphasized that **any** metal can ignite in fluorine under specific conditions.

Temperature effects on common metals used for fluorine systems

Metal	**Recommended temperature limits for 100%F$_2$ Service based on Industry practice.** (° C) *Note 6*	**Test Data from Published Literature**			
		Average Ignition Temperature (° C) *Note 1* *Reference 1*	Threshold Temperature for Low Probability of Failure (° C) *Note 2* *Reference 2*	Threshold Temperature for High Probability of Failure (° C) *Note 3* *Reference 2*	Temperature where metal-fluoride film may vaporize causing accelerated corrosion *Reference 1* (° C)
Copper	150	692	588	863	No data
Carbon Steel	150	672 (iron)	No data	No data	
Stainless Steel	150 (300 series)	681 (302 grade)	696 (304L grade)	1054 (304L grade)	Note 4
Monel	400 (UNS N04400)	Note 5	924 (UNS N05500)	1041 (UNS N05500)	648
Nickel	600 (UNS NO2200)	1162	>957 At sonic velocity	>957 At sonic velocity	648

Note 1 – Tests were with thin wire (0.25 mm (0.01 inch) to 0.50 mm (0.20 inch) diameter) in static fluorine at atmospheric pressure.

Note 2 - 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.*

Note 3 - 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.*

*Note 4 – Chromium in the stainless steel can form four types of fluorides. Below 150°*C *a protective CrF2 scale forms, but this may be converted to a more volatile form above 150°*C*, which may compromise the protective ability of the film.*

Note 5 – 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 (Reference 1) and possible presence of detrimental minor alloying elements (Reference 2). Industry experience suggests Monel (UNS N04400) auto ignition temperature is greater than that of stainless steel, but precise measurements are not available.

References

1. *T. Godwin and C. Lorenzo; Ignition of Several Metals in Fluorine. Paper No. 740-58, ARS, 1958*
2. *P. Daniel and R. Rapp , Halogen Corrosion of Metals , Advances in Corrosion Science and Technology, Volume 5, Plenum Press, New York , 1976*

Note 6 - Temperatures approaching the listed temperature may result in rapid corrosion to the metal even with only short term exposure. It is imperative that the user fully analyze (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.

Auto-ignition temperature of non-metals

Ignition tests on plastics and lubricants in static and dynamic conditions have shown that the ignition risk increases with pressure and temperature elevation. Most plastic materials will spontaneously react upon exposure to fluorine. While some historical test results may indicate little or no reaction under a given condition, it must be understood that 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) may be enough to initiate ignition even after an extended time in fluorine service.

Highly fluorinated polymers such as PCTFE, PTFE, PFA, including metal-filled (e.g. bronze) types exhibit the best resistance to ignition in fluorine systems, but even their use must be carefully reviewed and exposure minimized. Refer to Section 7.2.2 for additional details of non-metal use in fluorine service.

5.2.1.2 Propagation of metals fires

The propagation of metal fires ignited in fluorine is also an important factor, which needs to be considered when selecting metal equipment components, in particular if there are components with low auto ignition temperatures (e.g. plastics). The consequences of the auto-ignition of sensitive materials (i.e. plastics) are aggravated when a metal may propagate 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 higher density than non-metals and therefore absorb significantly more heat with a lower temperature increase. Hence, the preferred materials are metals

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, therefore 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 (e.g. Monel), have a 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.

Materials with a low specific heat of combustion should therefore 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 fluorine handling systems.

5.2.2 Size & configuration of equipment

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.
Very careful material selection is therefore necessary for equipment components with a low mass and a high surface area that may be exposed to an ignition in contact with fluorine (e.g. filters).

Minimization of less compatible materials:

Less compatible materials are those that are easy to ignite with high specific heat of combustion (e.g. non-metallic materials such as plastics and polymers), which may 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 (e.g. 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 may be generated by the ignition of the non-metallic material.

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

This is a key factor 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 (e.g. particles, dirt, grease, water).

All components must 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 (reference 7) and ensuring strict control of the fabrication process.

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 proper cleaning of the system.

5.2.4 Fluorine pressure

The gas pressure is an important parameter and influences directly the rate of reaction and ignition likelihood. In practice according to the experiences of the gas industry the 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 by some companies based on their experience as a threshold pressure where different design criteria is used (materials of construction, shielding, etc.).
Note: The 30 bar limit is given by the ADR and DOT transport regulations and is valid for the European countries and the United States. According to these regulations it is prohibited to ship gas cylinders with higher filling pressures of pure fluorine. This requirement is likely to be binding under the P200 packaging instruction in the UN Orange Book.

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 volume concentration of less than or equal to 0.5% are considered to be non-oxidizers according to the UN classification regulations (ISO 10156). See Note below.

Typical mixtures on the market are approximately 1% in rare gases, and 10 % and 20% fluorine in nitrogen. In addition to the toxicity, these mixtures are classified by transportation guidelines as “oxidizing” and have to be handled carefully.

According to experience mixtures of less than 35% fluorine are less reactive than pure fluorine at a pressure, which 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.).

Due to lack of any operating history, mixtures of greater than 35% fluorine in inert gas should be handled in systems designed for 100% fluorine.

Note: ISO 10156-2 specifies a test and a calculation method to be used to estimate whether or not a gas or gas mixture is more oxidizing than air for the purpose of classification and labelling of gases or gas mixtures according to the transport and dangerous goods regulations (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

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 a fluorine system, higher velocity leads to higher kinetic energy of the particle and therefore higher temperature upon particle impingement, which may 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 Chapter 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 should 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
- Personal Protective Equipment (PPE)

6.1 Detection of fluorine leaks

The odour threshold for fluorine is less than 0.1ppm and the TLV limit is 1.0 ppm. This means that personnel normally 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 may alarm.

Depending on the consequence of the release, 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.

Location of fluorine leaks can be detected by 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. Commercially available 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 practice produces a white cloud where the ammonia and fluorine mix. However hydrogen fluoride is formed leading 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 the end user requirements.

The inside surface of the secondary pipe must be designed and prepared to guard against fluorine reaction in the event the primary pipe suffers a leak/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 properly 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. (e.g. 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 inter-space between the tubing e.g.:

- Vacuum (loss of vacuum is detected in the inter-space 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)
- 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

Fluorine is a gas that has no global warming or ozone depletion properties.

Any confined area where fluorine could be released must be provided with adequate 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.

Consideration should be given in building ventilation design to accommodate possible accumulation of fluorine.

A minimum ventilation rate *to* meet local regulations/ building codes based on the fluorine toxicity, or as a guideline at least 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 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.

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

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 breathing of fluorine gas.

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

At a minimum the following PPE must be worn when removing the valve outlet plug/cap of a fluorine /fluorine mix 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)
- Safety Shoes

Self Contained Breathing Apparatus (SCBA) should be available in close proximity in the event of an emergency.

Note: The use of contact lens should be evaluated based on the given company policy. In general contact lenses are not used when handling fluorine.

7. Control of oxidizing/reaction hazards

As fluorine is a powerful oxidant careful consideration must 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
- Maintenance procedures

7.1 Building/Site considerations

Any building used for the storage, processing or use of fluorine shall minimise the use of combustible materials of construction, and limit storage of combustible materials near the fluorine system. 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 should be located away from normal personnel access.

Fluorine piping systems should not be buried underground.

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

Consideration should be given to locate systems handling pure fluorine and mixtures of fluorine >35% at >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 (e.g. valves, components with moving parts, less resistive materials than Monel or nickel).
At lower pressures or concentrations the designer must 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 limit 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 abatement system details.

Barrier/shields – limit 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.

Polycarbonate viewing windows, typically *of* approximately 10 mm thickness, are used where required.

Remote cameras can be used for viewing.

Coaxial piping can be used as a barrier for piping – See Section 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.

1. nickel
2. Monel
3. copper
4. stainless steel
5. 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, cost, or application requirements (e.g. 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 fluorine at greater than 4 bar systems especially at elevated temperature.

Stainless steel piping can be used in lower pressure applications for 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 have been applied.
Stainless steel piping/tubing is commonly used for mixtures of 20% fluorine in inert gas at pressures to 150bar.

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 to 30 bar pressure.

Brass materials must 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.

However cylinder valve bodies made from brass material are used successfully for fluorine (See Section 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. Copper is used for example 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.

Metal corrosion

Due to the formation of 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 may 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. It must be cautioned that 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.

7.2.2 Non-metals

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

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

Lubricants:

Fluorine will 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 such that 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.

Pressure regulators seats:

For fluorine: 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 metal fill.

For fluorine mixtures above 10%: pressure regulator with bronze filled PTFE seat, having minimum plastic surface exposed to fluorine and a high percentage of metal fill.

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.

Valve seats:

Industry practice for material of valve seats at ambient temperature is as follows (See Note hereafter):

- Fluorine mixtures 10% F_2 or less up to 200bar, fluorinated plastic seat.
- Fluorine mixtures above 10 %, up to 200bar maximum, metal seats
- Fluorine at low pressures (pressure of less than 0.3bar) has successfully used PTFE valve seats.

Caution: When a mixture is prepared and pure fluorine is added as the first component, the valve should have a metal to metal seat to prevent ignition. This is true even if a final concentration is less than 10%.

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

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 must also be controlled.

It is recommended that pure fluorine systems or mixtures that are classified as toxic based on the use of LC_{50} calculations, should be designed to meet the requirements of a code in agreement with national regulation for highly toxic fluids, such as ASME B31.3 Category M Fluid Service. 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 may be used to detect any leakage points.
Leak detection fluids used for inert gas pressure testing (soap solutions) containing ammonia shall not be used on copper based alloys as it can cause stress corrosion cracking (reference 11).

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 should 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 of globe or needle pattern type with bellows seal or diaphragm design.

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

7.3.2 Minimisation of the effects of adiabatic compression

Adiabatic compression may 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:

- Proper selection of materials of construction.
- Slow opening of any valves
- 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 may 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 (Reference 2). However common practice for oxidizing gases is to limit velocity to as low as practical and use more resistive materials especially in impingements areas when velocity reduction is not viable.(see Table hereafter). Historically the industry has exceeded these limits in some production applications and at times when performing cylinder and bundle filling. This is because these operations are always performed with experienced personnel under controlled conditions with safeguards in place to protect them from an uncontrolled fluorine release

Guidelines for Velocity Limits in pipelines for fluorine and mixtures of >35%

Pressure	Material	Impingement Area	Non-Impingement
≤ 4 bar	Carbon Steel	≤ 15 m/sec	≤ 30 m/sec
	Stainless Steel (≥ 3 mm wall thickness)	≤ 15 m/sec	≤ 30 m/sec
	Copper, Monel 400, Nickel	No limits	No limits
> 4 bar	Carbon Steel	Material not recommended	Material not recommended
	Stainless Steel (≥ 3 mm wall thickness)	≤ 2 m/sec	≤ 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 in a conservative means 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 , AIGA 021/05 Oxygen Pipeline Systems.

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.
- Adequate precautions shall be taken to ensure any purge gas (e.g. nitrogen), is not contaminated with flammable materials (e.g. from another process). A dedicated purge system for the fluorine system should be used.
- To prevent backflow of fluorine into the purge gas system, pressure differential (higher purge gas pressure than maximum fluorine system pressure) is recommended to be used along with non-return (check) valves and double block and bleed systems in material compatible with fluorine.
- 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, must be designed and installed as if they were in fluorine service.

7.4 Equipment selection

7.4.1 Valves

Where possible, valves should be selected such that 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 in section 7.3). The design should be such that 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 should be purchased cleaned and packaged to oxygen standards.

Packless valves, such as bellows seals or diaphragm valves are used extensively for fluorine applications. Due to the toxicity of fluorine local regulations or company piping design codes may dictate use of packless valves, however packed stem valves (using PTFE stem packing) are used extensively for cylinder valves and in fluorine systems.

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

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. Bellows manufactured via hydroforming process are preferred to those bellows of welded disc/diaphragm design.

Ball or plug style valves are usually not recommended for general use in fluorine service due to;

- the "typical" design includes non-metallic seals with large surface areas that are in the direct flow path, making them susceptible to ignition and,
- the valve style is prone to rapid opening and the resulting risk of heat from adiabatic compression in the downstream system that may 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 Section 8.2.2.

7.4.2 Pressure regulators

Pressure regulators or pressure control valves are used to limit the pressure in the users' system. Pressure regulators must be designed for fluorine service using materials that are fluorine resistive based on the intended maximum pressure and fluorine concentration. (Refer to material selection guide in Section 7.2) Regulators must be cleaned for O2 service. Inlet filters, if used are to be of compatible materials (see Section 7.4.3).

7.4.3 Filters

Due to the high surface area to mass ratio, filters increase the risk of ignition in fluorine systems and their use is discouraged especially in high pressure (e.g. above 4 bar) fluorine applications. If a filter is required it should be of Monel or nickel. If a filter is used, procedures must be in place to guard against accumulation of system contaminants (e.g. PTFE thread tape) on the filter, which can further increase its ignition potential.

Filters are considered high risk components, especially in fluorine service and shields/barriers should 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 must be prepared during construction/ fabrication or as required after maintenance, as follows:

- **Cleaned**, to oxygen cleaning levels or better
- **Dried** to remove any residual cleaning agents and moisture
- **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. Cleaning methods vary based on the user, but include using detergents or suitable cleaning agents (solvents) that are free from fine particles and metal chips. Refer to Doc. AIGA 012/04 (Reference 7).

Since the cleaning/degreasing agent is incompatible with fluorine, it is very important that the cleaning agent is thoroughly removed from the system. Cleaning agents that vaporize quickly and leave minimal residue are selected for fluorine systems.

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

Cleaning verification methods such as wipe tests and UV (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 Purge and drying

The process must insure that all the cleaning agent residue is removed from the system and that any moisture in the system is removed to the targeted levels. Compressed air must 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 must be given to branches that do not allow flow-thru (e.g. “dead ends”) of a piping system to ensure they are properly purged. Determine the moisture level of the system by obtaining a dew point temperature at atmospheric pressure that meets the following guidelines:

- ≤ 1 bar fluorine system pressure: -60°C (10ppm of moisture in purge gas)
- >1 bar fluorine and mixtures system pressure: -75°C (1ppm of moisture in purge gas)

7.5.3 Passivation

Passivation shall not be considered a substitute for proper 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 1960’s have shown under certain conditions, organic contaminants did not react when initially exposed to fluorine.
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 approx. 75% of its limiting film thickness within the first 10-15 minutes of exposure (Reference 6).
While theoretically it would be possible to passivate individual components of a system, it is desirable and usually more practical to passivate the entire system as a whole, to ensure all portions have received adequate 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 installations and user practices, are acceptable after careful review by those experienced with handling fluorine. An example may be to use only pure fluorine starting at a very low pressure and slowly increasing the pressure.

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.

- emergency procedures are in place, including plans for the quick venting of the fluorine gas should it be required.

Suggested procedure:

- 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 system to remain pressurised for at least 30 minutes.
- Pay attention for any signs of a fluorine reaction. IR (Infrared) temperature monitoring devices can be employed to assist in determining any hot spots on the surface of the components.
- Monitor any system pressure gauges for fluctuations while introducing fluorine and during the hold periods.
- Slowly operate valves as required at each increment to ensure all surfaces of the components are exposed.

- 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.
- Increase the concentration of the fluorine and repeat the incremental pressure/hold steps, if the system is designed for fluorine concentrations of more than 20%. Repeat in increasing concentrations of fluorine per Table hereafter until both the final concentration and the system design pressure are reached.

Passivation guidelines versus fluorine design conditions

System design fluorine concentration	System Design Pressure	Initial fluorine concentration
≤5% F_2 /Inert Gas	All pressures	5%
≤10% F_2 / Inert Gas	All pressures	10%
≤20 % F_2 /Inert Gas	All pressures	20%
>20% to 100% F_2	<0.3 bar	100%
	>0.3bar	20 % *

* 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
- 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 in section 5.2.1.1. Design of the cooling system must include means to prevent contact of the incompatible coolant from the fluorine.

7.7 Operating procedures & personnel training

Written operating procedures shall be prepared to ensure that operators understand that the equipment shall be 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 should include:

- emergency procedures including how to safely close off the supply of fluorine

- components shall be clearly identified, carefully stored and handled 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
- Personal Protective Equipment (see 6.4)
- Refresher training should be performed at regular periods
- Management of Change process.

7.8 Maintenance procedures

Prior to any maintenance activity the system is to be verified safe to perform the work.
It is essential that equipment in which fluorine is handled be maintained to a high standard and to ensure that this is conducted in a routine, controlled and safe manner. Written maintenance procedures should be developed for tasks that are routinely done. Maintenance of fluorine systems should only be performed by personnel with proven experience.

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

Replacement of components shall only be made with exactly equivalent parts, unless approved through Management of Change process.
After maintenance the system is to be purged and leak-test. It may be necessary to re-passivate the system depending on the extent of the maintenance.
Components added/replaced during maintenance will need to be cleaned and passivated. Refer to Section 7.5.3 for details.

Materials that are to be used in fluorine service must be kept clean (free from oil, particles etc.) and therefore stored in a clean environment. Great care must be taken when changing gas-wetted components to avoid contamination from oil that may be on the operator’s hands (e.g. cylinder valve outlet gasket washers). Consideration should be given to wearing suitable clean gloves to prevent contamination of the operators’ 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 must 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 hydrolyze the passivation layer resulting in formation of hydrogen fluoride The 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 must be momentarily opened, consider the use of low flow inert gas purge (a “trickle purge”) as protection against moist air infiltration.

Piping systems that use fluorine may become contaminated with a powdery residue over time. This material is composed of metal fluorides and should be handled with caution since the material may contain hydrofluoric acid and should be neutralized. It should also be assumed that any liquids or moisture found in these fluorine systems would contain 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 must be 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 appropriate 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 metres 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 appropriate areas such as ventilation exhausts or near critical high pressure fluorine equipment to detect a leak as soon as possible. It may 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 should be used exclusively for emergency shut down 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 Section 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 manufacture process and internal degreasing/cleaning and passivation are important to reduce ignition concerns. The forged billet technique for forming cylinders can possibly allow carbon residue to be trapped under slag leading to reaction in the future even after degreasing and passivation. Cylinders manufactured by the forged billet method must be internally cleaned (such as by shot blasting) to bare metal before use in pure fluorine service. In this case shot blasting residual material must be removed. Cylinders formed by spinning steel tubes or the cold drawn method are the preferred manufacturing method for fluorine cylinders.
It is recommended to use seamless cylinders only.

Aluminium alloy pressure cylinders shall not be used.

Only dedicated cylinders should be used for fluorine service. It is not recommended to change the service of cylinders, which have been in a different product service into service for fluorine. 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 they have only been in inert gas service.

Adequate cleaning, degreasing and passivation shall be undertaken prior to introduction of fluorine (see Section 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 made correctly.

The cleaning and inspection procedure shall comprise at least the following steps:

- internal treatment to produce a bare, pure metallic surface
- removal of residual materials and particulates
- visual examination of the inner surface of every cylinder by experienced personnel
- sealing of cylinder inlets immediately after approval of inner surface preparation
- leak and pressure testing of the cylinder(s) with dry, oil-free inert gas
- vacuum baking, purging and drying with oil-free inert gas
- pressurizing 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 Chapter 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 (e.g. Nitrogen trifluoride, oxygen or chlorine) without a proper design review.

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

Aluminium/Silicon/Bronze alloys (UNS C64210, VA10) are used for cylinder valve bodies to 30 bar for fluorine and to 200 bar for fluorine mixtures (fluorine <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 <35%).

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

Cylinder valve designs should 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 suitable standards such as ISO 10297 or EN 849 “Transportable gas cylinders (Reference 8).

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 (Reference 9) limits the filling pressure of pure fluorine to 30 bar at 15^{O}C (see section 11), although historical practice has been to limit the pressure to 28 bar.

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 N2 at 150 bar
- 20 % fluorine in N2 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 taken with filters and valve seat materials.

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

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

Rigid tubing pigtails are used for fluorine. Convoluted flexible hoses should not be used for pure fluorine. Flexible hoses of Monel or stainless steel may be used for handling fluorine mixtures with a maximum concentration of 20%.

Once a manifold is prepared for fluorine service (cleaned, dried and passivated), contamination by particulates or moisture (ambient air, rain, snow) must be avoided as they may damage the integrity of the system. When not under fluorine pressure, manifolds should 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 must include safeguards to prevent fluorine or high pressure inert gas exposure to the pump. Purge gases should be vented into an appropriate abatement system.

It is strongly recommended that an adequate 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 must be evaluated in the design of a mixing/blending system

When it is out-of-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 shut-down capability. Diaphragm compressors are commonly used with fluorine and fluorine mixtures.

Compressors shall be specifically designed for fluorine service. High temperature wetted parts (e.g. valves) should be made of Nickel, Hastelloy or Monel where practical.

The heat generated by the compression of fluorine should be considered and the compressor design should endeavour to 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 – this is particularly important where high compression ratios are used.
- Introducing a high temperature interlock to shut down the system automatically in the event of excessive temperature being reached.

Compressors for fluorine shall use a fluorinated fluid such as perfluoropolyether or chlorotrifluoroethylene oil.

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 Section 10.2).. Vacuum pumps in contact with fluorine shall be either dry pumps or pumps using a fluorinated fluid such as perfluoropolyether oil. Fluorine system vacuum pump exhaust should be routed to an adequate abatement system.
Vacuum pumps shall be protected from overpressure sources from the fluorine system.
The use of pump shields/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 should 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 adequately 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 must be compatible with fluorine.

Transmitter seals and transmitter fluids must be fluorine compatible.

9. Supply to point-of-use

Consideration should be given by the supplier of fluorine gas to review the facility capabilities of a new user of fluorine. This should include verification that the equipment is suitable for fluorine and that the auxiliary equipment is available (abatement equipment, etc.) for normal processing and for emergency conditions.

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

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

9.1 Facility considerations and storage

Local applicable regulations shall be met.

The storage area shall be locked, 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) should be as close to the source cylinder as possible so that there is a minimum amount of piping exposed to high pressure fluorine.

Gas manifolds should be located inside ventilated rooms or ventilated gas cabinets. If a ventilated room or gas cabinet is not practical, then an outdoor installation may be used if permitted by local code and supported by an appropriate 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 back flow into the fluorine cylinder by adequate means (e.g. using check valves or differential pressures with process interlocks).

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

Adequate cleaning, drying and passivation of the manifold shall be undertaken to ensure it is safe to introduce fluorine (see Section 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 (e.g. end-of-shift).

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

Fluorine detectors should be placed in appropriate 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 may 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 should 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 shut down 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

This section of the document shall be used in conjunction with Reference (10).

Abatement for processing

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

Vents associated with the processing of fluorine should be directed to a suitable abatement system as required by local regulations.

Abatement for emergency release

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

All discharges from vent stacks, pressure relief devices etc. that do not go to an abatement system should be piped to the outside of buildings and discharges in a safe area well away from personnel and confirmed acceptable by use of dispersion analysis.

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

10.1 Basic principles of abatement

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

Since fluorine is a strong oxidizer, numerous chemical reactions destroy fluorine and a scrubber system can be used in order to convert fluorine into products easy and safe to dispose of. 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 must be large enough:

- to destroy the quantity of fluorine coming out from the largest source, in case of emergency release
- 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 e.g. fluorine detector, colour change etc.

There are two categories of scrubbers, dry and wet, as detailed hereafter.

10.2 Dry scrubbers

There are a number of solid state abatement systems commercially available. Carbon is not used because of the potential for explosion (see section 4.3). These systems are usually designed to fit into the process exhaust, and generally are designed for a diluted fluorine concentration.

- Alumina scrubbers
  Fluorine reacts with dry activated alumina (Al_2O_3), producing oxygen and solid aluminium fluoride. The reaction is very exothermic and precautions must 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 flow rate or by dilution of fluorine with inert gas prior to entering the scrubber. The activated alumina shall be dried to remove any trace of moisture. Activated alumina contains moisture, which can generate very toxic oxygen di-fluoride gas by reaction with fluorine.
- Calcium hydroxide and calcium carbonate scrubbers
  These solid state scrubbers are used when process streams containing fluorine are mixed with air. The resulting HF is then scrubbed.

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

10.3 Wet scrubbers

Wet scrubbers normally use solutions of potassium hydroxide or sodium hydroxide. Attention must be taken 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 di-fluoride gas (OF_2). OF_2 is produced as a side reaction between fluorine and aqueous hydroxide. Too high or too low concentrations of caustic lead to greater amounts of OF_2 generated. Addition of mild reducing agent such as sodium thiosulfate is a very efficient way of reducing OF_2 formation.

11. Transportation

Land transport

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

However the LC_{50} of the mixture is used to determine the hazard class of the gas and establishes certain shipping restrictions per International transport regulations (Reference 9), namely;

- UN1045, 92.5% or greater fluorine concentration has a resulting LC_{50} (based on fluorine content) of 200 ppm or less are not authorised for drums or tubes.

- UN1045, 92.5% or greater fluorine concentration limits the filling pressure to 30 bar and the quantity to a maximum of 5 kg in a single cylinder or a group of cylinders in bundle. Bundles containing fluorine may be divided in assemblies (groups) of cylinders not exceeding 150 litres total water capacity.

- UN3306, less than 92.5% fluorine concentration can be transported in cylinder, bundles, pressure drums and tubes having the appropriate service pressure.

Air Transport
Compressed fluorine and fluorine mixtures follow IATA (International Air Transport Association) and prohibits air shipment of UN3306 and UN1045 class gases.

Sea Transport
Compressed fluorine and fluorine mixtures of all concentrations are permitted for sea shipment following provisions detailed in IMDG (International Maritime Dangerous Goods) Code.

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;

- Immediately vacate the unsafe area
- Do not re-enter the unsafe area
- Activate the emergency stop buttons
- Notify the Local Emergency Centre

Additional emergency measures are to be taken only by personnel properly trained and qualified for Emergency Response.

Caution must 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 Self Contained Breathing Apparatus (SCBA) with full face-piece and positive pressure mode and a chemical resistant suit. Air purifying respirators are not recommended.

In the event of a large leak not in an enclosure, water fog/ fine spray can reduce the impact of the cloud, but recognize that the run-off water may be 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.

Emergency response containment vessel(s) for leaking fluorine cylinders must 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 Fire fighting

Fire due to ignition in a fluorine system usually ceases when the flow of fluorine is stopped. Applying extinguishing agent directly to the fire is not recommended, as the agent (even water) may 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.
- Cylinders exposed to high heat or flame may rupture violently.
  Pure fluorine cylinders are usually not equipped with pressure relief devices.
  Cylinders of 20% or less mixtures can be equipped with pressure relief devices in the cylinder valves. These safety devices may release the contents of the cylinder and minimize the potential for cylinder failure under fire conditions.
- Cool containers with water spray until well after the fire is out.

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

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.

Exposure of fluorine to personnel results in the formation of hydrofluoric acid and therefore the first aid for exposure to fluorine and fluorine mixtures is treated the same as the specialized treatment for exposure to hydrogen fluoride (HF). 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 HF exposure it is important to neutralize the fluoride ion as soon as possible and to seek advanced medical treatment (references 15 and 16)

Skin exposure

- Remove the injured person from the contaminated area as soon as possible.
- Cleanse the fluorine from skin by flushing with water.
- As water flushing is being done, remove any contaminated clothing from the victim.
- As soon as possible wearing gloves, continuously rub calcium gluconate (2.5%) gel to the exposed area.
- Seek advanced medical treatment while continuing to apply calcium gluconate gel.

Eye exposure

- Remove the injured person from the contaminated area as soon as possible.
- Flush immediately with water for at least 15 minutes while holding eyelids open.
- 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.
- Seek advanced medical treatment.
- Do not use calcium gluconate gel or other hydrogen fluoride skin treatments in the eye.

Respiratory exposure

- Move injured person to fresh air.
- If not breathing, begin artificial respiration. Administer 100% medical oxygen by mask (if available).
- Seek advanced medical treatment.
- Under the company’s physician direction, 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 are :
  - As soon as available, administer 2.5% to 3% calcium gluconate solution using a nebulizer (Reference 16).
  - To minimize swelling and allow other treatments inhalation steroids such as beclomethasone dipropionate (Ventolair ®) are used (sometimes even in the absence of immediate symptoms).
  - Because inhalation may be associated with brochospasm, bronchodilaters may be administered as necessary. (Reference 16).

Appendix 1: References

Reference 1 - Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems, NASA SP-30307, 1967.

Reference 2 - Fluorine Systems Handbook, Section VI, Dynamic Compatibility of Fluorine with Metals, Roger E. Anderson, Aerojet Liquid rocket Company, prepared for Air Force Rocket Propulsion Laboratory, October 1972.

Reference 3 - Gugliemini, C.J., Kadri, S.H., Martrich, R.L., Slusser, J.W., Vora, J., Werley, B.L, and Woytek, A. J., Flammability of metals in Fluorine and Nitrogen Trifluoride, Flammability and sensitivity of Materials in Oxygen enriched atmospheres: Seventh Volume, ASTM STP 1267, Dwigth, D. Janoff, William T. Royals, and Mohan V. Gunaji, Eds, American Society for Testing and Materials, Philadelphia, 1995.

Reference 4 - Fluorine, George Shia, Honeywell Specialty Chemicals, Kirk-Othmer Encyclopedia of Chemical Technology, Copyright © 2003 by John Wiley & Sons, Inc.
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Reference 5 - 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

Reference 6 - Halogen Passivation Procedural Guide, Air Force Rocket Propulsion Laboratory, Technical Report AFRPL-TR-67-309, December 1967

Reference 7- AIGA 012/04 Cleaning of equipment for oxygen service

Reference 8 - EN 849 “Transportable gas cylinders – Cylinder valves – Specification and type testing” or ISO 10297 “Gas cylinders – cylinder valves – Specification and type testing”.

Reference 9 - P200 of the UNRTDG/ADR/RID/IMDG

Reference 10 - IGC doc.30/07 “Disposal of gases – Code of practice” and AIGA 021/05 “Handling gas container emergencies”.

Reference 11 - IGC doc. 78/08 Leak detection fluids use with gas cylinder packages

Reference 12 - AIGA 021/05 Oxygen pipeline systems

Reference 13 - ISO 10298 Determination of gas or gas mixture toxicity

Reference 14 - ASTM STP 1395 on oxidizing ability of gases.

Reference 15 – Management of Hydrofluoric acid injury (Notes for Health Professionals), CTEF Comité Technique Européen du Fluor,June 2004

Reference 16 – Honeywell Recommended Medical Treatment for Hydrofluoric Acid Exposure, Ver.1.0, Honeywell Industrial Fluorine G525-521, May 2000

Appendix 2: Audit checklist

It is recommended that facilities handling fluorine undergo periodic audits to assess their compliance with this code and with other recognised safe working practices. The nature and detail of such audits will be 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 3 pages are unlikely to be exhaustive for all fluorine facility audit applications, however they may provide a helpful starting point. There are separate checklist sections to 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 document where more information on the checklist item may be found.

No	CHECKLIST ITEM	Ref

1	**Fluorine storage area**	Ref
1.1	Are fluorine cylinders & other containers safely stored in a well ventilated area, at least 5 metres away from flammable materials (or separated by fire resisting wall)?	8.1
1.2	Does the fluorine storage facility meet local Fire Regulations (where applicable)?	8.1.2
1.3	Is the storage area properly labelled?	
1.4	Are cylinders in the store properly secured to prevent them falling over and are their valve protection caps properly fitted?	----

2	**Fluorine Filling procedures & equipment**	Ref
2.1	Has the fluorine filling equipment been designed by competent engineers, who are familiar with the properties of fluorine and the precautionary measures & material requirements necessary for its safe handling (as set out in this Code)?	whole code
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 , it is recommended that detailed and documented reviews of the process equipment drawings, system design and all component specifications are carried out to confirm compliance with this Code.	whole code
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 adequate operating procedures for fluorine cylinder filling equipment? Do these procedures take into account all the recommended operational precautions set out in this code?	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 Code?	7.6 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 (e.g. “house” supply), are there adequate precautions 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 (e.g. vacuum pump & compressor oils)?	7.2.2 8.3.2
2.11	Are fluorine cylinders approved for and dedicated to fluorine service or, if not, are they properly prepared prior to filling to ensure they are not contaminated with any materials that may react with fluorine?	8.2.1
2.12	Have the fluorine cylinder valves been approved for fluorine service by a responsible expert (competent) person within the gas company and/or a competent external authority.	8.2.2
2.13	Are cylinder valves properly prepared prior to use to ensure they are not contaminated with any materials that may react with fluorine?	8.2.2
2.14	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
2.15	Are there adequate checks to ensure fluorine containers are not overfilled?	11
2.16	Are there adequate checks and controls to prevent unauthorised modification of equipment and operating procedures?	7.7 7.8

2	**Fluorine Filling procedures and equipment**	**Ref**
2.17	Are adequate precautions taken to prevent the contamination of equipment, particularly when it is not in use?	7.8 8.3.1
2.18	Are precautions taken to detect & act upon fire or fluorine leakage (e.g. installation of detectors, automatic valve shut-off etc.)?	8.1 11.2
2.19	Has the system been properly cleaned, inspected and passivated prior to operating with fluorine?	7.5

3	**F_2 Supply & supply equipment (for cylinder filling or use)**	**Ref**
3.1	Has the equipment been designed & installed in accordance with this code?	7.3
3.2	If there is any uncertainty with respect to 3.1, it is recommended that detailed and documented reviews of the process equipment drawings, system design and all component specifications are carried out to confirm compliance with this Code.	7.3
3.3	Are fluorine supply cylinders located in well ventilated areas away from fire risk?	8.1
3.4	Are there adequate operating procedures for fluorine supply equipment? Do these procedures take into account all the recommended operational precautions set out in this code?	7.7
3.5	Is the fluorine supply equipment dedicated to fluorine service?	9.2
3.6	Are cylinders connected for use properly 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 (e.g. “house” supply), are there adequate 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 F_2 (e.g. 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 adequate checks and controls to prevent unauthorised modification of equipment and operating procedures?	7.7 7.8
3.12	Are adequate 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 shut-off valve ?	8 & 9.2

4	**Fluorine Abatement & abatement equipment**	**Ref**
4.1	Has a risk assessment been carried out to confirm that the arrangements for the disposal of waste fluorine are adequate to ensure the safety of people & to minimise any impact on the environment?	10.1

5	**Maintenance procedures**	**Ref**
5.1	Are there adequately documented procedures to cover the maintenance of fluorine handling equipment? Are records kept of work carried out?	7.8
5.2	Is fluorine equipment maintenance covered by a “permit-to-work” procedure, where appropriate?	----
5.3	Are materials & components that may be used during the maintenance of fluorine equipment clearly specified/identified?	7.8
5.4	After maintenance work, is there an adequate cleaning & purging (plus passivation where appropriate) procedure to be implemented before the equipment is returned to fluorine service?	7.8

6	**Personnel**	**Ref**
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 sufficiently trained to cover their degree of involvement? **Note:** It is recommended that representative samples of operational personnel are interviewed during the audit to assess their understanding of the properties of fluorine and the particular care that is necessary to avoid incidents.	
6.3	Do personnel who handle fluorine have access to a fluorine material safety data sheet?	
6.4	Do personnel who handle fluorine wear/use appropriate personal protective equipment?	7.7

7	**Emergency response**	**Ref**
7.1	Are there an adequate emergency response procedure and a training specific to fluorine in place?	12
7.2	Is there adequate fire fighting and personal protective equipment readily available in the event of a fluorine ignition?	12.2
7.3	Is the local Fire Brigade aware of the location of & hazards arising from fluorine on site?	----
7.4	Is there adequate first aid information and are specialised supplies available locally?	12.3