

JPL PUBLICATION 79-64

Experience with Fluorine and Its Safe Use as a Propellant

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National Aeronautics and
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ABSTRACT

This report is a survey of the extensive industrial experience with fluorine since the early 1940's and the propulsion experience with fluorine or its derivatives with various fuels since the late 1950's. Fluorine is extremely reactive with virtually all other elements, which makes it a good oxidizer but also means it is hazardous to handle. Hydrogen fluoride results from the immediate reaction of fluorine with atmospheric moisture in the event of a leak. High quality materials, scrupulously clean containers and lines, gaseous fluorine passivation, detailed procedures, and automatic detection devices have led to successful ground testing during recent years. These currently well-understood procedures fulfill the safety requirement during ground operations for the handling of fluorinated propulsion systems, and similar procedures will be implemented for use on board the NASA Space Transportation System (commonly called the Shuttle).

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SECTION 1

INTRODUCTION

This report presents the historical experience with fluorine and its compounds, the current safety status for ground testing, and a description of how fluorine payloads will be safely integrated into the STS (Shuttle Orbiter) through careful selection of materials and procedures.

The NASA Lewis Research Center first performed early promising fluorine propulsion studies for the Air Force, and the Jet Propulsion Laboratory soon began precursor studies on fluorine propulsion systems. Many other organizations also began similar studies in the sixties. The NASA barium salt upper atmosphere experiment was successfully flown in October 1970, marking the first time that liquid fluorine was used as an oxidizer in a space vehicle.

Fluorine is reactive with virtually all materials and is toxic for humans. Past usage of fluorine has resulted in damaged equipment and a few early serious injuries. A multitude of tests have been made by many organizations, and a high degree of safety in operation has been achieved in recent years. Compatible materials, extreme cleanliness of lines and components, and careful attention to handling procedures are prime requirements to preclude incidents.

Fluorine with hydrazine as a fuel is a high-performance combination for liquid chemical propulsion systems as compared with current spacecraft propulsion system propellant combinations. The increase in performance permits larger payloads and/or shorter trip times. Future potential fluorinated (space-storable)¹ propulsion missions include Venus Orbiting Imaging Radar, Comet Rendezvous Missions, Mars Sample Return, Mars Advanced Mission (Rovers), Saturn Orbiter/Dual Probe (Titan), Mercury Orbiter, Solar Probe, Jovian Satellite Orbiter, and Uranus Orbiter.

The safety of fluorine on board the Shuttle Orbiter will depend upon the use of a containment (nonleak) design, high-quality materials typically used in spacecraft, gaseous fluorine passivation, cryogenic storage, dedicated personnel and training, quality assurance supervision, and automatic detection and implementation devices such as those currently used in ground tests. With these procedures, there should be little difference between handling fluorine and an earth-storable¹ propellant on board the Shuttle Orbiter, except the need for cryogenic control of fluorine; this latter exception is being addressed. Tests will be required to gain confidence with fluorine, including performance tests, thermal verification, structural dynamics, leak detection, and an early experiment on board the Shuttle Orbiter.

¹See Definition of Terms and Abbreviations

1.1 SUMMARY OF RESULTS

Fluorine-hydrazine is the most promising space-storable propellant combination for advanced planetary spacecraft propulsion systems, and will provide larger payloads and/or shorter mission flight time advantages when compared with those of earth-storable propellant combinations. There has been extensive experience with fluorine in various forms, and many highly successful fluorine propellant tests have been conducted in recent years.

Fluorine is stored as a liquid at cryogenic temperatures and is highly reactive. A splash of liquid or gaseous fluorine on personnel is toxic and can cause burns. Hydrogen-fluoride gas becomes the primary pollutant when fluorine reacts with the moisture in the air. Inhalation of high concentrations of either gaseous fluorine or hydrogen fluoride can cause serious damage, whereas lower levels for shorter periods cause only temporary irritation. Even weak concentrations have a prominent odor and are easily detected by the nose, skin, tongue, and eyes.

A monitoring device should be continuously operating in any area where fluorine is in use, and automatic shutoff devices which activate NaOH water sprays are also recommended. Personnel in the vicinity of fluorine must be protected by complete splash suits, and breathing masks should be used to prevent inhalation of high concentrations of toxic gases. It is necessary that personnel working in hazardous areas be properly trained in protective measures and procedures. Shuttle-based procedures consistent with good ground-based procedures also need to be developed. A primary requirement will be to reduce the potential leak of fluorine to an extreme minimum through proper design and tests.

SECTION 2

BACKGROUND

2.1 DISCOVERY OF FLUORINE

The element fluorine is relatively abundant, comprising approximately 0.65% of the earth's crust. Most of the available fluorine is combined in various mineral compounds such as fluorspar (fluorite, CaF_2), villiaumite (NaF), or cryolite (Na_3AF_6).

Fluorspar is the most abundant form of a fluorine compound and has been used for centuries to increase the fluidity of melts and slags in the ceramic and glass industry. (Hence, its name, fluere: to flow.) The first recorded description of fluorspar was made by George Bauer, a German physician and mineralogist, in 1529. Crude hydrofluoric acid probably was first produced by an unknown English glassworker around 1720. Carl W. Scheele, the Swedish chemist, created hydrofluoric acid in 1771 by heating fluorspar with concentrated sulfuric acid in a glass retort. The corrosion suffered by the retort made it clear that further research was needed to determine materials suitable for handling this highly reactive acid.

Anhydrous hydrofluoric acid was obtained in 1809, and two years later Ampere suggested that it consisted of a combination of hydrogen with a new element, which he called fluorine.

Elemental fluorine was not produced until 1886, when Henri Moisson succeeded in obtaining it by electrolyzing a solution of potassium hydrogen fluoride in hydrofluoric acid.

2.2 PROPERTIES OF FLUORINE

Fluorine is the most highly reactive element known, combining with all other elements, except the first few noble gases. This is due to its atomic structure, which places it at the top of the halogen family. The electron configuration of fluorine is $1s^2 2s^2 2p^5$. The tendency to complete the second shell with eight electrons is the driving force for the extreme chemical activity of fluorine (known as the octant rule). This gives fluorine the highest electronegativity, with a potential of -2.85 V, compared with -1.36 V for chlorine and -1.22 V for oxygen (Refs. 2-1 through 2-3).

Reactions with fluorine sometimes need to be initiated but then proceed explosively or with a detonation since the energy evolved leads to a sharp temperature rise. For instance, the energy of the reaction $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$ is 538 kJ (128.4 kcal) compared with 484 kJ (115.6 kcal) for $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (Refs. 2-4, 2-5).

The high electronegativity makes fluorine a highly reactive oxidizer. Fluorine-oxygen mixtures and compounds have many similar characteristics since oxygen is also a reactive oxidizer, having the

third highest electronegativity. (Physical properties for these oxidizers are listed in Appendix A, and additional data can be found in Reference 2-6.)

The only compounds that will not react with fluorine are those which are already fully fluorinated. Teflon (R), Mylar (R), and Kapton (R),¹ which are partially fluorinated compounds, are also highly resistant to fluorine. Fluorine can safely be handled using containers of stainless steel, nickel, and certain other metals such as aluminum and titanium, due to the formation of a fluorine compound film (10-20 Å thick), which covers the surface on contact, preventing further fluorination of the parent material (Refs. 2-6, 2-7). Purity of the metal is important; a low-level contamination can act as a catalyst to initiate combustion with the metal.

2.3 USES OF FLUORINE AND ITS COMPOUNDS

In the past fifty years, myriads of new uses for fluorine and fluorine-containing compounds have been developed. (See Table 2-1 and Refs. 2-8 to 2-10.) Detailed below are the major applications of fluorine.

2.3.1 Fluorspar

Fluorspar has been used for hundreds of years as a fluxing agent in ceramics and glass production and in the production of various metals.

2.3.2 Refrigerants

In 1930 Midgley and Henne discovered that derivatives of methane and ethane, in which most or all of the hydrogen was replaced by fluorine and chlorine, had properties for practically ideal refrigerants. They were relatively nontoxic and nonflammable as well. Fluorocarbon refrigerants are used in many government applications.² These refrigerants have found further use as aerosol propellants, although this use has recently become environmentally questionable because of the chlorine in the chlorofluorocarbon aerosol.

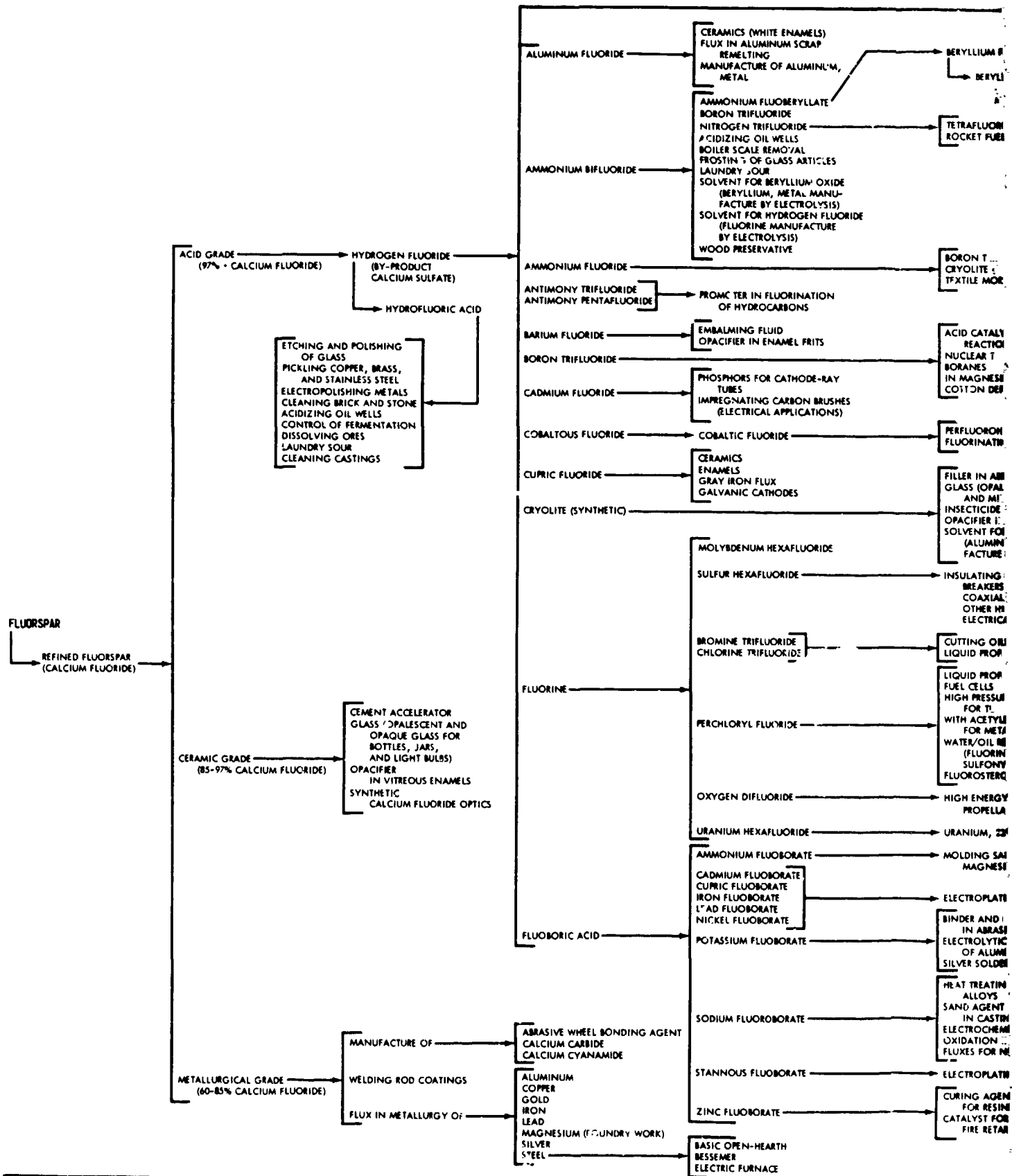
2.3.3 Lubricants

Much research and development of fluorine and its compounds took place during WWII in connection with the Manhattan Project. It was discovered that gaseous diffusion separation of uranium hexafluoride was the most efficient method of producing enriched Uranium-235. Due to the

¹Teflon, Mylar, and Kapton are registered trademarks of E. I. Du Pont de Nemours & Co., Inc.

²Trichlorotrifluoroethane also is used as a cleaning solvent for the Shuttle, and Monobromotrifluoromethane is used by the military (Ref. 2-11).

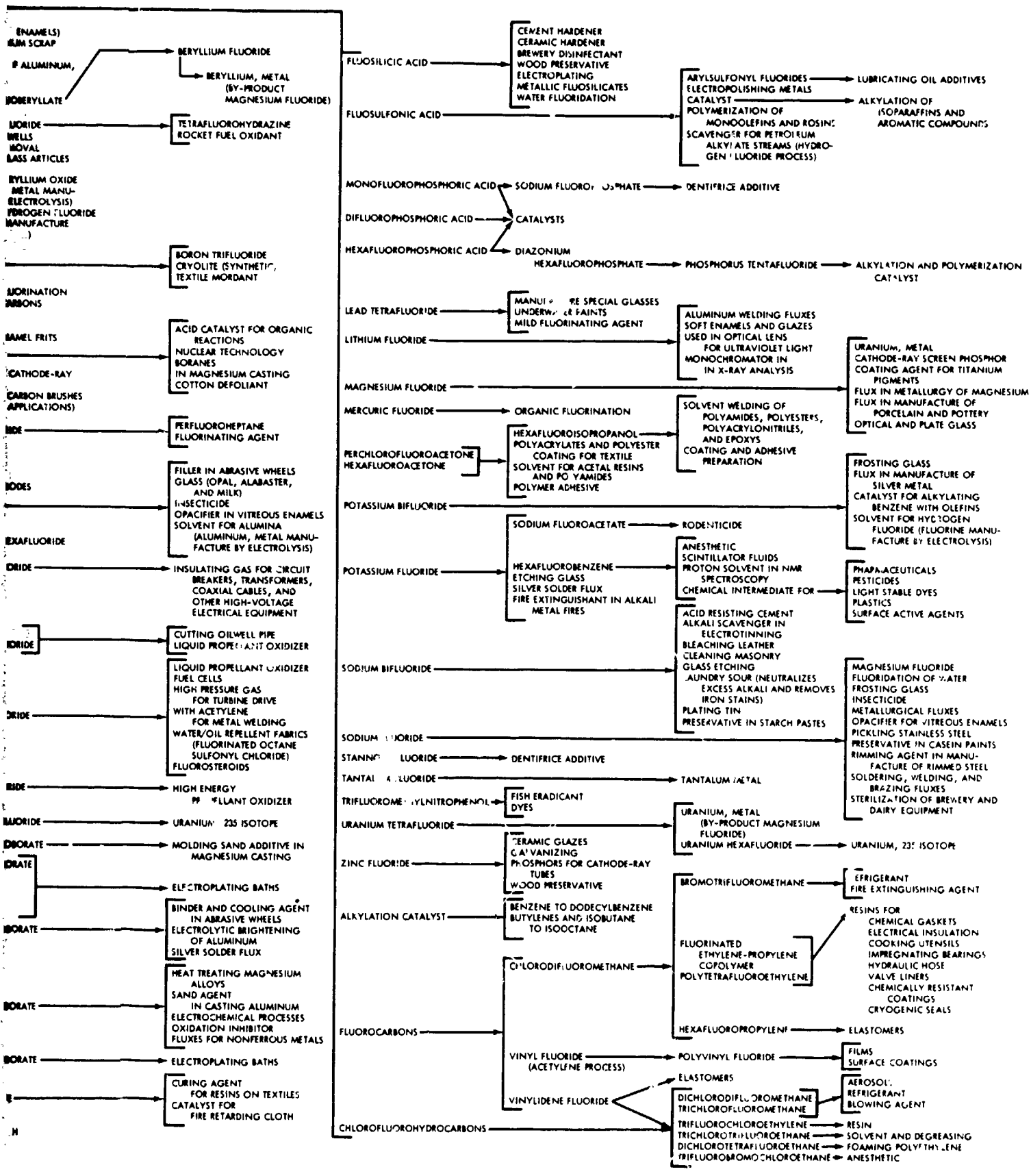
Table 2-1. Fluorine Derivatives



1Permission to reprint this table has been granted by Chemical Information Services, Stanford Research Institute

FOLDOUT FRAME

Fluorine Derivatives (Ref. 2-8)¹



reactivity of UF_6 , it was necessary to develop fluorinated oils to lubricate machinery used in handling this compound. These "fluorolubes" were soon replaced by "chlorofluorolubes", containing chlorine in place of some of the fluorine, as these could be produced more inexpensively.

These oils have found further use in the handling of liquid oxygen and a variety of highly oxidizing and corrosive propellants. They also serve as excellent flotation fluids in gyroscopic devices.

2.3.4 Dielectrics

In 1954 Olyphant and Brice discovered that, under the proper conditions, certain fluorocarbon liquids had ten times the heat transfer capability of transformer oil. This allowed substantial reduction in volume and weight of high-voltage power supplies.

Several gaseous fluorine compounds have excellent dielectric properties, as well as good heat conductivity and chemical inertness. Sulfur hexafluoride has successfully been used in high-power transformers, circuit breakers, and coaxial cables.

2.3.5 Surfactants on Liquids

Fluorocarbons as a group have the lowest surface tension of any known material. Many fluorocarbons display a high degree of surface activity. These compounds, when dissolved in a liquid medium, migrate to and orient on the surface, reducing the surface energy. These fluorocarbon "surfactants" can be used to inhibit evaporation of liquid in open containers. Under controlled conditions, a container of gasoline evaporated totally in three days. When 0.003% of a fluorocarbon surfactant was added, nearly 70% of the gasoline remained after a week's exposure. A dramatic decrease in flammability occurred as well, with no combustion taking place even when a lighted match was held to the surface of the liquid. Surfactants have also been found useful in decreasing the migration of plasticized vinyl polymers, asphalt, and adhesives.

Loss of chromic acid due to bursting gas bubbles was a major problem in chromium-plating processes until the development of surfactants. The surfactant allows the evolution of gas but prevents the violent bursting of bubbles and the resultant chromic acid spray. Since the surfactant is impervious to the acid, the only loss occurs in minor amounts when objects are removed from the chromic acid bath, requiring only infrequent additions to maintain the desired concentration. Fluorocarbon surfactants have also found use as "leveling" agents in floor waxes, as they require a smaller concentration (0.005% - 0.01% by weight) than hydrocarbon surfactants.

2.3.6 Surfactants on Solids

Surfactants can be either chemically or physically absorbed on a solid surface, resulting in films exhibiting oil and water repellency, lower coefficients of friction, low adhesive qualities, and other effects associated with low-energy films.

Textiles, paper products, and leather, when treated with various fluorocarbons, show marked improvements in water and oil repellency, stain resistance, and resistance to chemical corrosion. These fluorocarbon repellants also display greater durability and longer lifetimes than other repellants when undergoing repeated washing and/or dry cleaning. Fluorocarbons are used extensively in leather processing. Besides producing high quality leather, fluorocarbons impart a high degree of chemical resistance. Even concentrated hydrochloric acid and boiling caustics have no effect on fluorocarbon-treated leather. Fluorocarbon sizing agents are extremely useful in the production of hydrocarbon-resistant paper products. Paper can be treated for varying degrees of resistance to oil, grease, wax, and plastic-based lacquers. Inexpensive paper containers can now be used to contain a variety of substances previously requiring more elaborate containers.

2.3.7 Polymers

Fluorocarbon polymers and plastics have gained widespread usage due to convenient characteristics obtainable with various types of fluorocarbons. Polytetrafluoroethylene, better known as Teflon (R), can be found as a surface coating on a variety of kitchen utensils. Its chemical inertness, low coefficient of friction, and high stability over wide temperature ranges have made Teflon a household word.

Other similar fluorocarbon polymers have found a wide variety of uses as well. Fluorocarbon polymers display high dielectric strength and high heat resistance, making them excellent materials for electrical insulation. Their chemical stability makes them excellent static seals and gaskets for handling active chemicals, especially rocket and jet fuels. The low coefficient of friction of these materials makes them ideal as bearings and packings for sleeves in valves in relatively non-reactive fluids, especially when high loads are required. Fluorocarbon polymers also are useful in the field of cryogenics, as these products retain their flexibility even at temperatures as low as that of liquid helium, and will not react with liquid oxygen or other highly oxidizing agents in static usage. However, impurities in fluorocarbon compounds will cause these compounds to be highly reactive with oxidizers.

2.3.8 Rubber

Fluorocarbons of various types have proven useful when processed into natural or synthetic rubber. The finished product, besides displaying excellent rubber characteristics, also resists chemical and solvent attack and retains its characteristics over a broad temperature range. A copolymer of chlorotrifluoroethylene and vinylidene fluoride, a Kel-F (R)¹ brand elastomer, has been used as a liner in a chemical pump handling red fuming nitric acid continuously for 4,700,000 flex cycles without noticeable swelling or corrosion.

¹Kel-F, registered trademark of the Minnesota Mining and Manufacturing Co.

2.3.9 Fluorides for Teeth

Various fluorides have gained widespread acceptance as additives in toothpastes and drinking water to help strengthen tooth enamel and increase resistance to tooth decay.

2.3.10 Ion Sputtering

Fluorine ions, because of their high reactivity, are used to remove contamination from surfaces by sputtering the ions onto surfaces. Lunar surface samples coated with earth carbon monoxide molecules were cleaned recently by this process.

2.3.11 Propellants

Various forms of fluorine have been used as experimental propellants for nearly 30 years. The propellant performance and feasibility studies are covered in Sections 3.3 and 3.4. The safe use of fluorine as the oxidizer with hydrazine, transported by the Shuttle Orbiter, is the primary interest of this report.

In recent years fluorine, oxygen difluoride, and nitrogen trifluoride have been investigated by several contractors for the Department of Defense (Ref. 2-12). The Air Force is studying laser applications which require Shuttle transport of these fluorinated compounds. The Navy also is considering on-board ship use of fluorinated compounds.

2.4 FLUORINE PROCESSING

2.4.1 Production of Fluorine

Most commercial producers of fluorine use the same basic process of electrolyzing a solution of hydrogen fluoride in molten potassium fluoride. (The composition of the most commonly used electrolyte is $KF \cdot 2HF$.) A typical fluorine cell is illustrated in Figure 2-1. The anodes are usually carbon, and the cathodes and cell body are steel or monel. Cell life has been increased from a few thousand ampere hours in the 1940's (the first large-scale production of fluorine) to several million ampere hours in the 1970's. The process is shown in Figure 2-2, and some of the operating characteristics of actual fluorine cells are illustrated in Tables 2-2 and 2-3 (see also Refs. 2-13 through 2-17).

The impure fluorine gas evolved is purified by cooling to remove HF and CF_4 . Fluorine specification standards require that fluorine contain less than 1% impurities by weight. The purified fluorine is then either pressurized for use or liquified for storage and shipping.

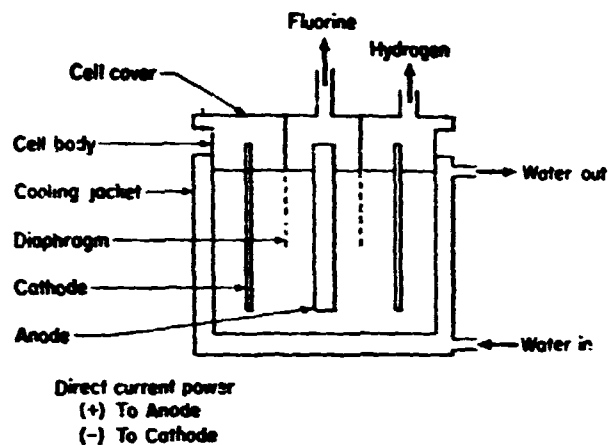


Figure 2-1. Typical fluorine cell (Ref. 2-13)¹

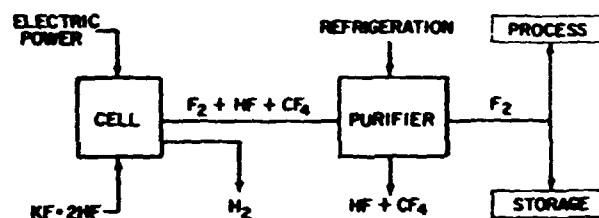


Figure 2-2. Fluorine process (Ref. 13)¹

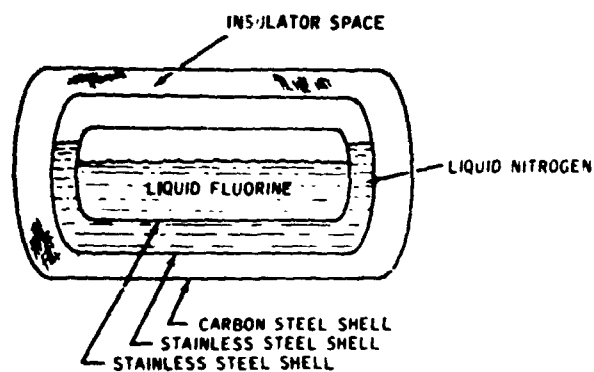


Figure 2-3. Liquid fluorine transport vessel (Ref. 2-13)¹

¹Reprinted with permission from Chemical Engineering Progress, N.Y.

Table 2-2. Cell Operating Characteristics (Ref. 2-16)¹

	Small Cell	New Cell	
	At 4000 A	At 4000 A	At 4000 A
Operating voltage, V	8-12	8-12	9-12
Cell operating temperature, °C (°F)	93-105 (200-220)	88-105 (190-220)	88-105 (190-220)
Hydrogen fluoride in electrolyte, %	40-42	40-42	40-42
Effective anode area, m ² (ft ²)	3.0 (32)	3.9 (42)	3.9 (42)
Anode current density, A/m ² (A/ft ²)	1,350 (125)	1,000 (94)	1,500 (140)
Anodes, number	24	32	32
L ² e, Ah	5 x 10 ⁶	16 x 10 ⁶	15.5 x 10 ⁶

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Table 2-3. Fluorine Cell (Ref. 2-17)¹

Operating Characteristics		
	Normal	Maximum
Operating current, A	4000	6000
Operating voltage, V	8	12
Cooling water temperature, °C (°F)		
Inlet	77±3 (170±5)	---
Outlet	79±3 (174±5)	---
Freezing point of electrolyte, 41% hydrogen fluoride, °C (°F)	72 (161)	---
Hydrogen fluoride in electrolyte, %	41.0	43.0
Fluorine, kg (lbm)		
Per 1000 Ah current	0.64 (1.40)	0.67 (1.47)
Per kg hydrogen fluoride	0.78	0.95
Life, millions of Ah	16	30

Cell Dimensions of Modified Cell

Effective anode area, m ² (ft ²)	3.9 (42)
Size, m (in.)	
Length, head flange	2.3 (89)
Width, head flange	0.97 (38)
Height, floor to top of head	1.04 (41)
Anodes	
Number	32
Dimensions	
m	0.05 x 0.2 x 0.52
(in.)	(2 x 8 x 20-5/8)

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Table 2-3. Fluorine Cell (Ref. 2-17)¹ (contd)

Materials of Construction	
Component	Material
Shell	Monel liner, steel jacket (ASTM-285)
Head	Steel plate, Monel skirt
Anodes	Carbon, Grade YBD
Cathode	Steel
Diaphragm	Monel
Anode support bar	Chrome-molybdenum steel (AISI-4140)
Anode support bolt	Chrome-molybdenum steel (AISI-4140)

2.4.2 Producers of Elemental Fluorine

American companies which produce or have produced fluorine include: Air Products and Chemicals, Allied Chemical Company, Liquid Carbonic Corporation, Matheson Gas Products, MG Scientific Gases, Precision Gas Products, Inc., and the Union Carbide Corporation. Large-scale fluorine production facilities exist at several of these companies. Currently the Allied Chemical Company is producing LF_2 and Air Products and Chemicals are producing GF_2 .

2.4.3 Shipping and Handling

Gaseous fluorine is packaged and shipped in steel cylinders under a pressure of 280 N/cm^2 (400 psia). The cylinders must conform to ICC specification 3AA-1000 and can contain no more than 2.7 kg (6 lb)/cylinder. Bulk shipment of liquid fluorine was authorized by the ICC under special permit in 1957. Tonnage quantities of the liquid are shipped in loss-free, Dewar-type tanks (Fig. 2-3). The Dewar-type tank design is based on the difference in boiling points of nitrogen and fluorine -196°C and -188°C (-320°F and -307°F), respectively. The fluorine is kept entirely loss free at the expense of boiling nitrogen. The system

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is designed so that it can be maintained for several days without the need for replacing liquid nitrogen. Sound and visual alarms are provided to warn of low liquid nitrogen level and to indicate high fluorine pressure.¹

The NASA Lewis Research Center, JPL, and Allied Chemical Co. are all experienced in the handling and transportation of liquid fluorine. As a result of its experiences with fluorine, Lewis Research Center has published a handbook on Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems (Ref. 2-6).

Below is a short check list from the experiences of the above organizations of key points in the handling of LF_2 :

- (1) Choose proven compatible materials, preferably an all metal system.
- (2) Minimize the number of potential leak points by use of welded joints.
- (3) Fabrication should not result in sharp edges within the flow passages, and all welded joints should be x-rayed to assure no occlusions are present.
- (4) Extreme cleanliness is required. Therefore, occlusions and dead-end crevices cannot be permitted.
- (5) The system must be leakproof.
- (6) Prepassivation with GF_2 is strongly recommended.
- (7) A link-wire shutdown sensing system for automatic closing of isolation valves is strongly recommended to minimize hardware loss and toxic releases in the event of a system element failure.

¹Containers for transport of fluorine do not have relief or burst devices, which can malfunction, but rely on the subcooling effect of the LN_2 to maintain the LF_2 at a low, safe pressure.

SECTION 3

TESTING AND USES OF FLUORINE AS PROPELLANTS

3.1 THEORETICAL STUDIES

During the 1950's, the National Advisory Committee on Aeronautics (NACA) conducted several theoretical performance studies involving liquid fluorine and oxygen-fluorine mixtures as oxidizers for various fuels. The results were uniformly encouraging. Calculations predicted specific impulses of over 3,900 N/kg/s (400 lbf/lbm/s), and some combinations had predicted specific impulses of over 4,900 N/kg/s (500 lbf/lbm/s). These theoretical calculations clearly indicated that significant increases in propellant performance could be obtained by use of fluorine, fluorine-oxygen mixtures, and fluorine compounds (Ref. 3-1).

3.2 MATERIAL COMPATIBILITY AND SAFETY STUDIES

In the late 1950's and early 1960's several studies were conducted to determine the types of materials best suited for storing and handling liquid fluorine and fluorine-oxygen mixtures. Much of this work took place at the NASA Lewis Research Center. The results of these and other tests have been compiled and published by NASA in Ref. 2-6. The Joint Army, Navy, NASA, Air Force Propulsion Committee (JANNAF) has published a Chemical Rocket/Propellant Hazards Handbook, which contains a brief but complete overview of recommended procedures for the handling, storage, and transportation of liquid and gaseous fluorine, fluorine-oxygen mixtures, and oxygen difluoride (Ref. 3-2, see also Ref. 3-3). Additional materials evaluation is currently being conducted by JPL.

3.3 PERFORMANCE STUDIES

Testing of various fluorine-liquid propellant systems has been conducted for almost 30 years. Although some of the more recent work is still classified, there is a large amount of experimental results available for review. The major problem in testing or use of fluorine-based oxidizers is that the same properties which make these attractive for use (i.e., extreme reactivity) also make them extremely hazardous. The utmost care must be exercised when dealing with such oxidizers. Despite the dangers and difficulties entailed in using elemental fluorine, successful research has been conducted under the sponsorship of NASA and the U.S. Air Force (see Air Force spill tests in Ref. 3-4, for example). It is encouraging to note that no serious personal injury has occurred in any of the tests conducted since 1970 and only a few before that time.

3.3.1 Fluorine-Hydrazine

Fluorine-hydrazine rocket engines have undergone tests on a small scale since 1949. The fluorine-hydrazine combination offers high specific impulse and high bulk density. The most complete study

of the performance characteristics of this bipropellant combination was compiled by Bell Aerosystems for the Air Force maneuvering satellite propulsion system (Ref. 3-5). Liquid fluorine was used in combination with BA-1014. (The composition of BA-1014 is 1 mole monomethylhydrazine, 1 mole water, 4 moles hydrazine.) A peak vacuum specific impulse of 4,120 N/kg/s (420 lbf/lbm/s) was predicted (see Table 3-1, from Ref. 3-5). The handbook contains data on vacuum and optimum specific impulse, optimum and vacuum thrust coefficient, combustion temperature as a function of mixture ratio, chamber pressure, and area ratio for shifting and frozen equilibrium. Calculated densities and enthalpies of combustion products are listed as well (see also Ref. 3-6).

3.3.2 Fluorine-Ammonia

Ammonia is similar to hydrazine in its performance characteristics. The Bell Aerosystems Handbook contains the same parameters for ammonia as for fluorine/BA-1014 (Ref. 3-5). Parameters for peak specific impulse are listed in Table 3-1.

3.3.3 Fluorine-Hydrogen

Liquid fluorine-liquid hydrogen propellant systems have the highest theoretical performance potential of all stable chemical sources of energy, making them extremely attractive as a liquid bipropellant combination. The NASA Lewis Research Center has published results of tests conducted with a 22,000 N (5000 lbf) thrust engine (Ref. 3-7). Using a combustion pressure of 200 N/cm² (300 psia), they obtained a specific impulse of 3450 N/kg/s (352 lbf/lbm/s) with a 13.8% hydrogen mixture. They experienced no difficulties in engine operation. Further tests by NASA Lewis on the same engine ultimately resulted in a specific impulse of 4,410 N/kg/s (450 lbf/lbm/s) using 10 to 15% fuel and a chamber pressure of 500 N/cm² (750 psia) (see Refs. 3-8, 3-9). The Bell Aerosystems Propellant Performance Handbook (Ref. 3-5) also contains a section on the fluorine-hydrogen combination (Vol. II, Parts a and b). A vacuum specific impulse of 4,660 N/kg/s (475 lbf/lbm/s) was predicted (Table 3-1).

3.3.4 Lithium-Fluorine-Hydrogen

A lithium-fluorine-hydrogen tripropellant system has a theoretical vacuum specific impulse of 5,300 N/kg/s (540 lbf/lbm/s). A Rocketdyne study for NASA (Ref. 3-10) achieved a vacuum specific impulse of 4,990 N/kg/s (509 lbf/lbm/s) in experimental tests. However, systems analyses indicated that this system would not be as efficient as other fluorine systems, due to the weight of the lithium propellant feed system.

3-1. Peak Specific Impulse Performance Comparison¹

Propellant	O/F	Shifting I _{sp} vac		T _c °C(°F)	Specific Gravity	Storage (Liquid) Range	
		N/kg/s (lbf/lbm/s) (A _e /A _t = 50)	P _c =70 N/cm ² (100 psia)			P _{vap} max = 200 N/cm ² (300 psia)	Fuel °C
F ₂ /H ₂	14.0	4653 (474.5)	3924 (7094)	0.640	-220 to -146	-259 to -240	
O ₂ /H ₂	4.5	4492 (458.1)	2462 (4464)	0.304	-219 to -140	-259 to -240	
F ₂ /NH ₃	3.3	4089 (417.0)	3855 (6970)	1.157	-220 to -146	-78 to 50	
F ₂ /BA-1014	2.3	4119 (420.0)	3910 (7070)	1.297	-220 to -146	-19 to 236	
OF ₂ /B ₂ H ₆	3.6	4231 (431.5)	3745 (6773)	0.991	-224 to -90	-165 to -13	
N ₂ O ₄ /50-50							
UDMH-N ₂ H ₄	1.8	3338 (340.4)	2838 (5140)	1.182	-12 to 101	-6 to 95	

¹Data taken from Ref. 3-5

3.3.5 Fluorine-Oxygen Mixtures (FLOX)

Fluorine-oxygen mixtures (FLOX) have been developed and tested in the hopes of increasing specific impulse without necessitating the use of a pure-fluorine-compatible system. The U.S. Air Force conducted several studies to determine if a FLOX system could be used as the propellant system for an Atlas missile. The results should be declassified in a few years. A 30% F₂ FLOX mixture originally was used by the USAF.

A 1967 Pratt and Whitney Aircraft study (Ref. 3-11) was conducted to determine the amount of fluorine in oxygen necessary to achieve hypergolic ignition in a hydrogen-oxygen liquid propellant system (present hydrogen-oxygen systems need ignition devices). The percentage of fluorine necessary was high enough (46.5-53.4%) for the report to conclude that such vehicle and engine systems must be compatible with pure fluorine. JPL first used a 70% F₂ FLOX and later used an 88% F₂ FLOX.

Fluorine-oxygen mixtures have been tested with LPG (light petroleum gases) and methane as the fuel (Ref. 3-12). Rocketdyne, in conjunction with the NASA Lewis Research Center, did a comparative study of two proposed space-storable propulsion systems, one of which was a FLOX/methane bipropellant system using an 82.5% fluorine oxidizer. With an 11,000 N (2500 lbf) thrust engine and 70 N/cm² (100 psia) chamber pressure, a specific impulse of 3,800 N/kg/s (386 lbf/lbm/s) was achieved (Ref. 3-13).

Pratt and Whitney Aircraft recently studied the performance of various FLOX mixtures with light hydrocarbons such as methane, propene, and butene-1. The tests used a 22,000 N (5000 lbf) thrust engine and a chamber pressure of 70 N/cm² (100 psia). The fluorine concentration in the oxidizer was optimized for maximum theoretical performance with each fuel. The results were published in Ref. 3-14. Measured vacuum specific impulses of 3,600 N/kg/s (368 lbf/lbm/s) were achieved for FLOX/methane and 3,550 N/kg/s (362 lbf/lbm/s) for FLOX/butene-1.

3.3.6 Oxygen Difluoride-Diborane

The space-storable propulsion system comparison by Rocketdyne referred to above (Ref. 3-13) obtained results for an oxygen difluoride-diborane propellant system as well as the FLOX-methane system. The same system configuration was used for both. A specific impulse of 4,000 N/kg/s (412 lbf/lbm/s) was achieved with an oxidizer-to-fuel ratio of 4:1.

3.4 SPACE-STORABLE PROPULSION SYSTEM STUDIES

In the early 1960's, JPL undertook an effort to determine a propellant combination that should be adopted as its advanced development program for the next generation of spacecraft planetary propulsion systems. Oxygen difluoride (OF₂) and diborane (B₂H₆) were chosen initially because of a high performance of about 3,700 N/kg/s (380 lbf/lbm/s) and a common storage temperature of -135°C (-210°F). The cost of the

propellant was high, approximately \$100/kg (~\$50/lbm) in 1963 dollars, so FLOX (70 w/o F₂)¹ was used as the thermodynamic simulant for OF₂. In order to concentrate efforts on the oxidizer, monomethylhydrazine (MMH) was used in place of B₂H₆. The changeover to OF₂/B₂H₆ occurred in 1966 and the technology continued until 1971. JPL published a state-of-the-art report of injectors and thrust chambers for OF₂/B₂H₆ in Ref. 3-15. TRW also studied the thermal control technology required for this system for JPL (Ref. 3-16, Vol. 1).

During the time period from 1963 to 1970, it was anticipated that the price of OF₂ and B₂H₆ would decrease because of potentially high Air Force usage. However, this predicted Air Force usage never occurred, and the price of propellants rose to about \$200/kg (~\$100/lbm). In addition, the manufacturer planned to stop producing the propellants because the rates of production were so low.

Facing this situation along with the success with the FLOX (70 w/o F₂)/MMH, JPL and NASA-HQ decided to redirect the advanced development program. The redirection task took the form of two concurrent efforts in a Systems Technology Program mode. The first was termed the Feasibility Module, which was to use state-of-the-art technology and FLOX (70 w/o F₂)/MMH. Its objective was to demonstrate that a fluorine-containing propulsion system could be successfully designed, fabricated, and tested. This phase of the effort took 24 months and was completely successful. The objective of the concurrent program, which was called the Engineering Test Module and used both FLOX (88 w/o F₂)/MMH and F₂/N₂H₄, was to advance the state-of-the-art. The 88 w/o F₂ mixture is optimum for use with MMH.

Because of reduced funding, The Systems Technology Program was terminated after completion of the Feasibility Module, and then the work reverted to an R&T Base effort. Later, it was no longer possible to carry the R&T Base effort with two propellant combinations. After system-level trade-off studies were completed, hydrazine was found to be the best fuel to use for planetary spacecraft propulsion systems. This conclusion was based on the following reasons:

- (1) Hydrazine has high bulk density (1 g/cc).
- (2) Hydrazine is used as the fuel for the attitude-control propulsion systems (ACPS).
- (3) The fuel for the ACPS and main propulsion system can be stored in a common tank, thereby minimizing reserves and reducing inert mass.

¹w/o = weight percent fluorine

With hydrazine as the selected fuel, fluorine is the optimum oxidizer. The propellant combination of F_2/N_2H_4 delivers approximately 2% more specific impulse than FLOX (88 w/o F_2)/MMH. A comparison was made by TRW of F_2/N_2H_4 (space-storable) with N_2O_4/MMH (earth-storable) in Ref. 3-17, since there will usually be a bipropellant on board for planetary missions. A thermal evaluation of this space-storable propellant was also made by TRW in Ref. 3-16.

In 1975 JPL submitted a request for a program augmentation. This request for augmentation included a benefit/cost analysis, which indicated that the costs of the development effort could be returned in one flight project. The augmentation request was accepted, and a Systems Technology effort was begun in FY'77. This program is currently underway and is scheduled to be completed by the end of FY'82. Because of the concern for carrying fluorine as a Shuttle payload propellant, an effort is underway to ensure that all safety aspects of a flight system are factored into the current program.

Earlier, General Dynamics/Convair had studied the prelaunch operations for B_2H_6/OF_2 on Titan/Centaur (Ref. 3-18). Later, TRW Systems Group conducted a study for JPL of safety implications for Shuttle-launched spacecraft using fluorinated oxidizers (Ref. 3-19). This study, which used nitrogen-tetroxide (N_2O_4) as a basis for comparison in safety considerations, showed that with the proper design of flight and ground support hardware, adequate test and operation procedures, and thorough training of personnel, the hazards associated with fluorine can be reduced to a level equivalent to that of nitrogen tetroxide for Shuttle use.

3.5 MATERIALS COMPATIBILITY

This section covers aspects of material compatibility of oxidizer feed assembly components relative to the Space Shuttle during initial handling operations and prelaunch conditions. One of the major goals for the program is to provide an advanced system, which will utilize LF_2 for a mission duration of up to ten years. The necessity for compatibility of materials of construction with the finished components and system for LF_2 service cannot be over-emphasized in order to meet the mission and long-life requirements. It is necessary that the component and system materials exhibit inertness to the LF_2 environment.

3.5.1 Feed System Components

The feed system components identified by function in Table 3-2 provide for the containment within the propulsion system of the LF_2 from the initial propellant loading operation to the spacecraft launch. The primary and/or critical materials of construction are listed for each component. These materials were initially screened for the program by checking their compatibility from known experience and as reported in the literature (Refs. 2-6, 2-7, 2-12, and 3-20 through 3-36). The next step involved actual testing of the most critical items to verify the suitability of candidate materials for the application, and to ensure that the overall requirements would be met.

Table 3-2. Feed System Components and Candidate Materials of Construction Subjected to Fluorine (either liquid or vapor) Demonstrated on the Feasibility Module.

Component	Material
Propellant tank, LF_2	Titanium 6AL-4V Heat treated
Propellant management device (PMD) and cooling coil	Titanium 6AL-4V Heat treated
Propellant tank, LF_2 , outlet cover and seal	Titanium 6AL-4V Heat treated
Propellant feed lines	CRES 304L
Transition joint tank outlet to feed line	Titanium 6AL-4V Heat treated To CRES 304L
Isolation valve seat Poppet	Inconel 718 (may be gold-plated) Beryllium Copper Alloy 172, Temper H
Fill valve seat Poppet	Inconel 718 (may be gold-plated) Beryllium Copper Alloy 172, Temper H
Burst disc	Aluminum 2219-T87 or 6061-T6
Transducer, pressure sensing element	Inconel 718

Finally, a candidate all-metal shutoff valve was designed, fabricated, and tested with LF_2 . The testing demonstrated the ability of the valve to meet the design goals. Alternate all-metal valves are currently being tested (Ref. 3-38).

3.5.2 Fluorine Storage

This section describes the general characteristics of fluorine and the type of data available on which to judge the acceptability of specific materials of construction. Gaseous fluorine has

been produced and handled in industrial processes for many years. Experience, including the handling, transportation, and disposal of tonnage quantities of fluorine, has clearly demonstrated that fluorine can be handled over prolonged periods and in large quantities.

Many common materials of construction are compatible for use in a liquid fluorine environment in the temperature range of -173 to -200°C (-280 to -363°F). At these cryogenic temperatures, chemical reaction in general tends to take place slowly; thus corrosive attack by the liquid fluorine progresses at a slower rate. Another factor responsible for the low rate of attack by LF_2 and GF_2 on the common metals is that thin protective films of fluoride compounds form on metal surfaces and act as barriers to further reaction. The effectiveness of the protective film formed on the metals by LF_2 is based on the insolubility of the various metal fluorides present that form in the film in LF_2 .

To summarize, the use and satisfactory performance of fluorine are achievable and predictable. However, the highest standards are demanded in system design, maintenance, cleanliness, elimination of contaminants (particularly moisture), and operational techniques.

3.5.3 Compatibility Criteria and Available Data

The choice of metals for use in the Space-Storable Propulsion System is primarily based upon the mechanical property requirements for the given applications; this includes material strength and shock resistance at the cryogenic temperature. Other parameters considered include rate of corrosion resistance, ignition temperature of the metal in LF_2 , fluoride film retention, and impact sensitivity. Specific aspects of detail design, fabrication, and assembly practices are also considered.

The material compatibility data are based upon practical information accumulated under:

- (1) NASA general research and advanced development programs
- (2) USAF development programs
- (3) NASA-OAST Advanced Technology Programs directly related to the Space-Storable Propulsion System development. This also includes the breadboard system feasibility demonstration test program.

3.5.4 Materials Evaluation

3.5.4.1 Aluminum. Both aluminum alloys 2219-T87 and 6061-T6 have been tested in LF_2 . The results from prolonged corrosion (static) exposure tests lasting over one year and stressed specimens were satisfactory. A tenacious fluoride film was produced with a thickness in the range of 8 \AA . There were no deleterious effects as a result of the testing.

Aluminum is proposed for facility burst-disc applications with LF_2 because of its inherent characteristic of repeatability (less susceptible to effects of work hardening, thus narrowing the operating range band). The main consideration deals with an overpressure condition in the LF_2 system causing disc rupture and possible ignition of the aluminum alloy.

The advantage of this material is that the melting point is below its ignition point with fluorine gas, or about $600^{\circ}C$ ($1100^{\circ}F$). A series of mechanical property tests were conducted to verify tensile strengths in LF_2 . In some of these tests, the specimens were fractured in the propellant with no evidence of adverse effects. Based upon these results, the aluminum alloy is considered acceptable for application with fluorine.

3.5.4.2 Corrosion-Resistant Steel. Several alloys of corrosion-resistant steel (CRES) type materials have an extensive background of testing with LF_2 . They are used successfully in test systems handling fluorinated oxidizers, including LF_2 , and CRES type 304L is one of the more commonly used forms.

Results from immersion tests (static and stressed samples) revealed minimal rates of corrosion. Corrosion-resistant steel exhibits good resistance to attack by hydrogen fluoride; the stable fluoride films formed about 6 \AA thick are similar to those formed in Monel (a material generally used in systems employing hydrogen fluoride). During mechanical properties and ignition tests, there were no detrimental results.

During dynamic operation with fluorine flow, the propellant feed lines are subjected to a variety of conditions such as varying fluid velocities, turbulence, and increases in fluid friction adjacent to the walls. Another critical condition can occur during the engine shutdown when the propellant shutoff valve is closed. Relatively high transient pressures and shocks ("water-hammer") are imposed locally near the shutoff valve for several milliseconds.

The use of CRES 304L provides a suitable material that will maintain a uniform protective fluoride film against corrosion or other attack under these severe flow conditions and a material that will meet the needs of the application.

Flight system burst assemblies of an all-welded variety would probably use CRES similar to that used on Viking (VO-75), for repeatability of performance. The type of CRES selected would depend upon the mechanical rupture mode anticipated.

For data sources and/or summaries, see Refs. 2-6, 2-12, 3-21 through 3-29 and 3-31 through 3-33.

3.5.4.3 Inconel/Beryllium Copper. Comments about CRES above are applicable to this material combination, although these alloys are of different types.

Under NASA Contract NAS7-733, a bipropellant all-metal shutoff valve was developed for use on the system. Extensive testing with LF_2 at the component level and on the feasibility demonstration model demonstrated the ability of the valve to meet the design goals and material suitability and compatibility. For data sources and/or summaries see Refs. 2-6, 3-21, 3-22, 3-30, 3-32, and 3-33.

3.5.4.4 Titanium. Propellant tanks made of titanium alloy have been widely used on both manned and unmanned type spacecraft. The material offers the advantages of high strength-to-weight ratio, compatibility, low rates of corrosion, and well understood fabrication processes.

Studies and analyses of the system, considering both ferrous and nonferrous metals, were performed relative to the LF_2 propellant tank materials. These studies established that titanium was the preferred metal for the application.

Titanium, in particular the alloy 6A1-4V, has demonstrated excellent compatibility in contact with LF_2 . Titanium 6A1-4V samples have been subjected to long-term static exposure testing with LF_2 . After sixteen months' exposure, definitive information has been extracted from the test program regarding compatibility. Gross properties, such as mechanical properties, were not significantly affected. The most significant changes were in the form of microscopic pitting on the specimen surfaces. There was no evidence of embrittlement.

Test specimens representative of the propellant management device (i.e., surface tension vane type) are being tested for 36 months in liquid fluorine. Significant features include: test coupons fabricated from 6A1-4V titanium in both annealed and heat-treated conditions; investigation of surface effect using polished and machined finishes. The three-year storage test which will be completed June 30, 1979, has progressed satisfactorily.

Titanium is also being investigated to determine fracture toughness. Numerous tests have been conducted by JPL, using standard stress-crack corrosion procedures with parent metal and heat-affected zone (due to welding) samples in a highly stressed condition. Twenty-four hour and one thousand-hour duration tests were conducted with LF_2 exposure at 220 N/cm^2 (315 psia). The most important result is that there was no evidence of stress-crack corrosion growth as a result of this testing. Results have been reported and published in Ref. 3-37.

There is some indication in the literature that titanium in LF_2 may be sensitive to impact conditions. Typical tests involved the impact of various shapes of strikers on impact plates beneath the liquid surface. An arbitrary value of 98J (72 ft-lb) energy is used as the criterion for evaluation. The results reported are conflicting and inconclusive at this time.

The primary conclusion, resulting from a critical review of the flight operational functions and comparison with available data on reactivity, is that impact is only a secondary consideration in

the design of the fluorine propellant tank. Specifically, the impact source would result from shutoff valve operation during engine firing; since these effects for the most part would be damped out locally, the effect on the tank would be minimal.

Experimental dynamic flow tests were performed, duplicating service conditions. Test coupons of 6A1-4V titanium were subjected to LF_2 flow at 220 N/cm^2 (315 psia) internal pressure and impacts resulting from the shutoff valve operation in the 5-25 millisecond range. Transient pressure spikes peaked at $600\text{-}800 \text{ N/cm}^2$ (900-1200 psia). There were no deleterious effects on the titanium specimens as a result of these tests.

The use of titanium alloy is considered feasible for the fluorine propellant tank based upon compatibility and other data generated to date. For data sources and/or summaries, see Refs. 2-6 and 3-26 through 3-33.

3.5.4.5 Other Materials. Current valve and component development for the Space-Storable Propulsion System (both JPL in-house and contracted efforts, Ref. 3-38) has incorporated other candidate materials as well as those above. These other candidate materials include:

- (1) A286 high-strength steel
- (2) CRES stainless steels (17-4, selected 300 and 400 types)
- (3) Hastalloy B
- (4) Inconel 600
- (5) Monel
- (6) Tungsten carbide

SECTION 4

SAFETY CONSIDERATIONS

4.1 AREAS OF INVESTIGATION

Liquid fluorine would be used at infrequent intervals at NASA centers. Therefore, the exposure of center personnel would be rare, occurring only as the result of an accident. Fluorine could be released either as a slug of liquid fluorine or as a concentrated puff of gaseous fluorine. If a large spill were to occur, hydrogen fluoride gas would also be present as the result of neutralization processes and natural reaction with moisture in the atmosphere. The exposures could lead to relatively high vapor concentrations but for short time intervals.

It is the purpose of this section to show that the effects of potential fluorine ground spills are predictable and that safe operations can be achieved if proper procedures are followed. Extensions for safe Shuttle use also are covered. NASA must be concerned with both the acute, toxic effects of fluorine and the long-term cumulative toxic effects. The consequences of acute exposure to relatively high doses of air contaminants may be qualitatively and quantitatively quite different from long-term chronic exposure. Two types of exposure must be considered. First, the skin may be splashed with liquid fluorine, or a concentrated jet of fluorine gas may impinge upon it. Second, high concentrations of the toxic gas may be inhaled.¹ The target organs or body systems which are most sensitive to short-term exposure to the air contaminant must be identified. A full characterization of the nature of the effects upon the target area must be made, and the range of time-concentration relationships from those causing no effect to those causing severe injury to the target areas must be determined. The maximum exposure before severe or irreversible damage results should be noted. It must also be established whether any cumulative effects accrue from repeated short-term exposure.² First-aid procedures must be developed to treat both dermal burns and respiratory intoxication. These are the toxicology objectives that concern NASA, and they must be fulfilled to insure the highest standards of safety for personnel. Answers to these issues have enabled toxicologists to establish rational emergency exposure limits for fluorine or hydrofluoric gas. These limits are being used as maximum exposure limits at NASA centers.

If an accidental liquid fluorine release were to occur, automatic emergency shut-down systems should be a mandatory requirement. This assumes that a device for measuring the concentrations is in constant operation. NASA requires maximum exposure limits for various time

¹High concentrations cause a person to hold his breath, and the pungent odor forces him to find a quick exit.

²Cumulative effects are less than for N_2O_4 , where the nose becomes somewhat desensitized to N_2O_4 .

intervals after shutdown, in which personnel may safely work in the spill area, restoring it to normal operation. These values are to be emergency exposure levels only; regular occupational exposure limits would be significantly below these values. These emergency levels may create a discomfort for a short time and be irritating to the workers; however, they will not be so high as to cause injury of an irreversible nature.

4.2 CHRONIC EFFECTS OF FLUORINE

Most work dealing with fluorine toxicity has centered on the chronic effects caused by long-term exposure (many years) to abnormally high fluoride concentrations. Exposures of this type have been experienced, primarily by employees of industries that generate high concentrations of airborne fluorides, such as steel, aluminum, and phosphate fertilizer manufacturers. Of the fluoride absorbed, about 50 percent is retained in the body, while the other half is expelled from the body via the urinary system. Ninety-nine percent of the fluorine retained in the body is localized in the skeleton. Both the deposition and excretion of fluorides are very rapid, and tests with isotope fluorine 18 have shown that bone deposition is the faster process. Fluoride deposition occurs by an exchange mechanism, where fluoride in the extracellular fluids passively exchange with hydroxyl groups on the surface of the bone apatite. When too much fluorine has been absorbed, the symptoms of chronic fluorosis become apparent: vague pains in small joints; "poker back"; the calcification of ligaments in the back, resulting in the loss of movements; thickening of bone ends can be observed in X-rays; and in extreme cases bony outgrowth and spurs emanate from the bone surface.

To prevent chronic fluorosis, industrial threshold exposure limits have been established. These limits use the bone deposition of fluoride as the index to gauge the degree of poisoning. Exposure is assumed to occur for 8 hours a day, 40 hours a week and continue for many years. The threshold limit values, formulated by the American Conferences of Governmental Industrial Hygienists, Ref. 4-1, are 2, 2, and 2.5 milligrams per cubic meter for gaseous fluorine, hydrogen fluoride, and particulate fluorides, respectively; or 1 and 3 ppm for GF_2 and HF, respectively. Research and background material about the long-term chronic effects of fluoride are readily available. Two literature reviews containing extensive background information on the chronic effects of fluoride are given in Refs. 4-2 and 4-3. A summary of the effects is included in Appendix B.

4.3 EFFECTS OF SHORT-TERM EXPOSURE TO CONCENTRATIONS OF FLUORINE

Information about the pathological effects of fluorine dermal burns and the medical treatment of these burns is widely distributed. (See Air Force reports, Refs. 4-4 or 4-5).

Three stages or types of burning occur when the skin comes in contact with liquid fluorine or a jet of fluorine gas impinges on

it: (1) The fluorine reacts with the flesh, resulting in severe, deep-seated burns that are slow to heal. Upon contact, immediate oxidation or chemical burning of the flesh occurs, (2) Thermal damage to the skin results from the heat generated by the skin-fluorine exothermic reaction, and (3) Tissue poisoning may follow, caused by hydrofluoric acid which is produced by the reaction of higher concentrations of fluorine with the moisture of the skin, where the burning occurs rapidly. Tissue poisoning also can result at lower concentrations due to the fact that moisture on the skin readily absorbs fluorine gas. After exposure to fluorine gas puffs, several hours may elapse before the victim becomes aware of the pain or injury. These slow burns are similar to those that result from anhydrous hydrofluoric acid. The delay in pain and ulceration make treatment of even suspect burns necessary. Immediate medical attention will prevent ulceration of the skin.

Prior to NASA interest in the short-term acute effects of inhaled fluorine, little work had been done in the area. In 1968, a NASA-contracted report was published by Keplinger (Ref. 4-6). This is a comprehensive report dealing with all aspects of short-term exposure to gaseous fluorine and the acute toxic effects.

The extensive inhalation of high concentrations of fluorine is considered impossible because of the stifling effects of elemental fluorine. Choking and suffocation would result if relief were delayed beyond a few seconds. Laryngeal and bronchial spasms followed by bronchial obstruction and pulmonary swelling would result. Blockage is caused by swelling of mucous membranes and the secretion of tenacious mucous. Fluorine concentrations of lesser amounts can be inhaled, and the effects caused by this type of exposure have been studied.

It has long been thought by people in the fluorine industry that the industrial threshold limit values could be safely exceeded for short periods of time in emergency situations. However, no quantitative work supported this contention until the NASA-sponsored Keplinger study (see Appendix C). In 1969 the Advisory Center on Toxicology set emergency exposure limits for fluorine and hydrogen fluoride, shown in Figure 4-1 (Ref. 4-7). These emergency levels are not to be encountered daily. They may cause physical discomfort to those experiencing them, but they will not cause any serious or permanent physical injury. However, it must be remembered these are emergency limits, with exposure occurring only as the result of an unpredictable accident, and some minor physical injury may be incurred by personnel. For fluorine gas the Emergency Exposure Limits (EEL) are shown by the lower curve in Figure 4-1. The corresponding Threshold Limit Value (TLV) for long-term exposure is only 1 ppm, where the TLV applies to an 8-hour day, 40-hour week. The EEL's for hydrogen fluoride are shown by the dashed curve in the figure, and the TLV is 3 ppm. If excessive inhalation of fluorine does occur, the only recommended treatment is the administration of oxygen coupled with bed rest. Oxygen should be administered with a slightly positive pressure, forcing oxygen past the constricted windpipe and increasing pressure on the lung cells until the doctor arrives.

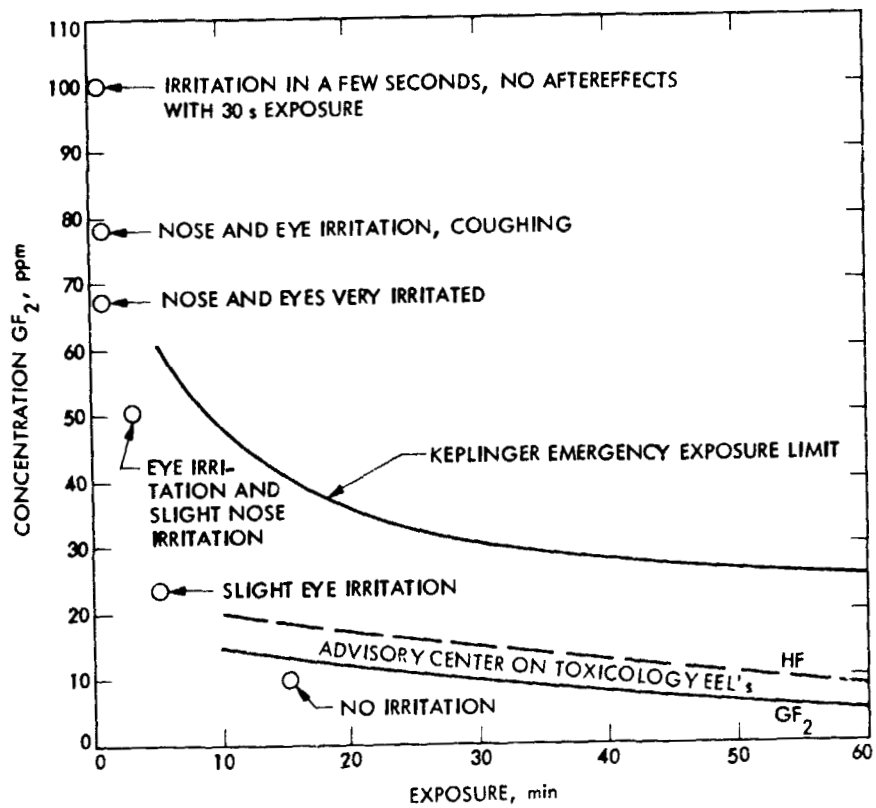


Figure 4-1. Keplinger Fluorine Gas Exposure Tests

The Keplinger test results are given in Appendix C and shown by points in Figure 4-1. These tests on volunteers were done with a mask over eyes and nose, which could easily be removed by the participant if too aggravated. Therefore, there is some question about the nose sensitivity since the volunteers could simultaneously breathe fresh air through their mouths.

Experience by JPL during exposures to low concentrations of fluorine and HF gases is that the nose is a more sensitive detector than the eyes. The sense of smell is very acute and the odors far more intense than from a chlorine or ammonia spill. The formation of hydrofluoric acid with moisture on the skin causes a tingling sensation at very low concentrations. The tongue can detect HF as a battery-acid-like taste, which also can provide an early warning of the presence of fluorine gas.

The acute toxic effects of fluorine are now well understood. The nose, eyes, skin, and tongue are the most sensitive detectors of fluorine. The physical damage caused by dermal burns and the pathological damage caused by the excessive inhalation of gaseous fluorine have been documented. Inhalation of excessive quantities of fluorine would primarily result in damage to the lungs. Minor damage may result to the kidneys and liver, but no instance of such damage has ever been found in humans.

First-aid procedures have been established for both dermal burns and respiratory intoxication. The Advisory Center on Toxicology, using the Keplinger paper, has established Emergency Exposure Limits for fluorine. The acute effects of fluorine gas are known, and the pathological damage caused by exposure to high concentrations has been studied. EEL's are the upper concentration-time exposures to which personnel may be exposed before it becomes necessary to evacuate or don self-contained breathing units. These values would be programmed into NASA monitoring systems at locations where liquid fluorine will be used. The EEL's can probably be exceeded safely to at least those values suggested by Keplinger, since the EEL's do contain a margin of safety, which is desired in all upper limiting values for toxic substances.

4.4 EFFECTS OF FLUORINE SPILLS

The accidental release of large quantities of liquid fluorine, while very unlikely, would cause a temporary increase of fluorides in the areas adjacent to the spill (see Appendix D). It is important to anticipate the ecological impact such a release would cause. The water deluge system and atmospheric moisture would rapidly convert most of the fluorine to gaseous hydrogen fluoride, the primary pollutant (see Appendix E), and the runoff water from the deluge system would contain hydrofluoric acid. While the major concern is with airborne fluorides (see Appendix F), the problems associated with water pollution must also be considered.

One of NASA's objectives has been to determine the response of plants, animals, and people to short-term, high exposures of hydrogen fluoride, similar to those accompanying a fluorine spill. The exposure limits at which phytotoxic (plant poison) damage first becomes apparent and the maximum exposures tolerable before economic loss is incurred must be determined. Domestic animals, particularly cattle, can suffer

a secondary effect caused by airborne fluorides absorbed by forage crops, which they then ingest.

How much damage will a liquid fluorine release cause? This question, as well as the specific concerns for the fluorine effects on the population, the environment, the plant life, and the animal life surrounding a spill site, will be discussed in the following section.

Eight studies which cover the biological effects of fluorine and hydrogen fluoride on plants, animals, and people are referenced in Appendix B. Also covered are the Emergency Exposure Limits allowed, concentrations that could be expected from a large spill at the Kennedy Space Center (KSC), and the decontamination of such a spill. Only temporary effects would be experienced in the event of a spill, and these would be minimized by scrubbing techniques; no permanent damage would result from a spill.

Emergency public exposure limits must be established, with the most susceptible segment of the population being the limiting factor. If exposure levels exceeding these limits have a probable chance of reaching uncontrolled areas and populations, consideration will be given to emergency and public awareness programs; otherwise complaints about bad odors and irritations could be anticipated. The presence of any long-term or residual effects must also be determined.

4.4.1 Effects on Surrounding Plant Life

Fluorine is everywhere in man's environment, constituting from 0.06 to 0.09 percent by weight of the upper layers of the lithosphere. Fluorine is usually found in mineral forms such as fluorspar, cryolite, and fluorapatite. Phosphate rocks (apatite) also contain a great deal of fluorine, often in various fluoride compounds, such as silicon fluoride, which are presently uneconomical to extract. In solid samples taken throughout the country, fluoride concentrations were found to range from 20 to 1620 ppm. In parts of Tennessee, solid fluoride concentrations as high as 8300 ppm are found. Fluoride concentrations in surface streams and rivers usually range between 0.02 and 0.10 ppm, but well water in areas containing fluoride minerals have concentrations from 1 to 7 ppm. Fluorine is a common element; however, even when high fluoride concentrations are found in the soil, plant life suffers no adverse effects.

During the normal growth and development of most plant species, very little fluoride is absorbed from the soil or water. In part, this is due to the insolubility of fluorides in the soil. When fluoride is absorbed through the roots, it moves through the vascular system of the plant and is deposited in the tips or marginal portions of the leaves. Airborne fluorides, particularly hydrogen fluoride, are readily absorbed by plant leaves, and it is by this means that concentrations causing phytotoxic (plant poisoning) damage are introduced into the plant. After absorption, the fluoride is transported to the apical (tips) or marginal portions of the leaves. Once the fluoride has been incorporated into the foliar (leaf) tissue, translocation to other parts of the plant generally does not occur.

Very low exposures to airborne fluorides are known to cause severe phytotoxic damage. Concentrations of hydrogen fluoride well below those tolerated by humans and animals will cause dramatic plant injury in less than eight hours. The plants of primary interest in the NASA Ricca study (Ref. 4-8), described in Appendix B, were citrus trees and various ornamental plants. In the area around KSC, several citrus groves are owned by the U.S. government, but they are leased to private concerns. The commercial importance of citrus trees in Florida necessitates their inclusion in this study. Ornamental plants grown in the area by private persons were also included in the study. Damage to these plants would be of less economic significance, but must certainly be considered. Further, the ornamental varieties span the spectrum of fluoride susceptibilities, enabling the identification of exposure limits encompassing a broad range of varying tolerances. The purpose of the NASA study was to determine the parts of the plant injured by excessive short-term exposures to hydrogen fluoride and to catalogue the nature and extent of damage done to the target area. It is important to explore a range of exposures, from levels at which no phytotoxic effects occur to levels causing severe damage and economic loss.

The TRW Systems and Boyce Thompson Institute for Plant Research studies (Ref. 4-9) of hydrogen fluoride effects on various plant species near KSC are described in Appendix B. A spill would damage leaves of plants and could cause the loss of a citrus crop if it occurs in the springtime.

In summary, airborne fluorides can cause temporary damage to citrus and ornamental plants, but no permanent damage would result.

4.4.2 Effects on Surrounding Animal Life

The introduction of airborne fluorides into the environment has a known secondary effect on foraging animals. When pastures are fumigated with fluorides, the forage crops absorb and store the fluorides in their leaves. Relatively high concentrations of hydrogen fluoride, a few ppm, may reach pastures in the event of an accidental release of liquid fluorine at KSC. While these exposures would not be high enough to cause acute damage to animals, it must be considered whether any chronic long-term damage would result.

This secondary effect, called fluorosis (fluoride poisoning), strikes primarily cattle and is observed in areas that have industries that daily introduce airborne fluorides into the environment. Industries shown to be responsible for the chronic toxicity problem in livestock are limited to aluminum, steel, phosphate, and brick. Symptoms of fluorosis include reduced food consumption, decreased milk production, calcification of ligaments, and increased incidence of lameness and bone exostosis (bone spurs). Since cattle are the most susceptible animals to fluorosis and most economic damage has occurred to the cattle industry, many studies have been done on the chronic fluoride poisoning of cattle. Fluoride concentrations of 93 ppm have been ingested for 2.5 to 3 years before the first visible symptoms of fluorosis appeared. Dietary poisoning is a long-term process.

The accidental release of fluorine at KSC is so unlikely that fumigation of fields with HF would be essentially a one-time occurrence (Ricca study, Ref. 4-8; see also Appendix 2). While the cattle would be consuming increased concentrations of fluorides for a short time, these levels would not be maintained for very long. Additional fumigation would not occur, and as the grass continues to grow and to be eaten, the concentrations decrease. Economic damage to dairy cattle in the KSC area would not result from this secondary effect. Concentrations of airborne HF that cause respiratory irritation will not reach cattle around KSC.

The incorporation of fluorides into plant foliar tissue is a very complicated process. No correlation between the amount of fluoride absorbed by the foliar tissue and the vapor concentration or duration of exposure has been determined.

In summary, there would be no short-term effect on cattle from a fluorine spill since fluorosis takes nearly three years to develop.

4.4.3 Effects on the Surrounding Population

Active volcanoes are the only known natural source of gaseous hydrogen fluoride. Many industrial processes release gaseous HF into the atmosphere. The gas is an effluent of industries such as aluminum reduction; phosphate fertilizer manufacturing; petroleum refining; manufacturing of fluorocarbon compounds; and the making of brick, pottery, glass, and ceramics. Within the past decade, another potential source of atmospheric HF has appeared: the liquid propellant rocket employing oxidizers containing fluorine. In the event of the accidental release of any of these liquid oxidizers into the atmosphere, which would almost certainly be attended by fire, one of the resultant products would be hydrogen fluoride.

Liquid fluorine spills may result in unpredictable short-term exposure of the general public to hydrogen fluoride. Unpredictable short-term exposures will occur when pollutants are released in an uncontrolled manner, at unpredictable times and places as the result of accidents such as damage to transportation equipment, fire in a chemical storage facility, or the rupture of a propellant tank. Even for such circumstances, it should be possible to predict with fair accuracy the variety of probable conditions of an accident and hence to predict the corresponding exposure parameters. An inadvertent release would be considered an accident in its effects upon Cape personnel, who would be trained in emergency procedures to minimize injury to themselves and facilities. Public emergency exposure limits relating to unpredictable exposures of the population surrounding the Cape should result in only minor and reversible injury to segments of the unprotected population. Undesirable esthetic effects (such as objectionable odors or clothing damage) should also be considered but on a lower priority basis.

Public exposure limits (PEL) have been formulated at half the Keplinger values by the Advisory Center on Toxicology with the above considerations in mind. The PEL's assume that some temporary

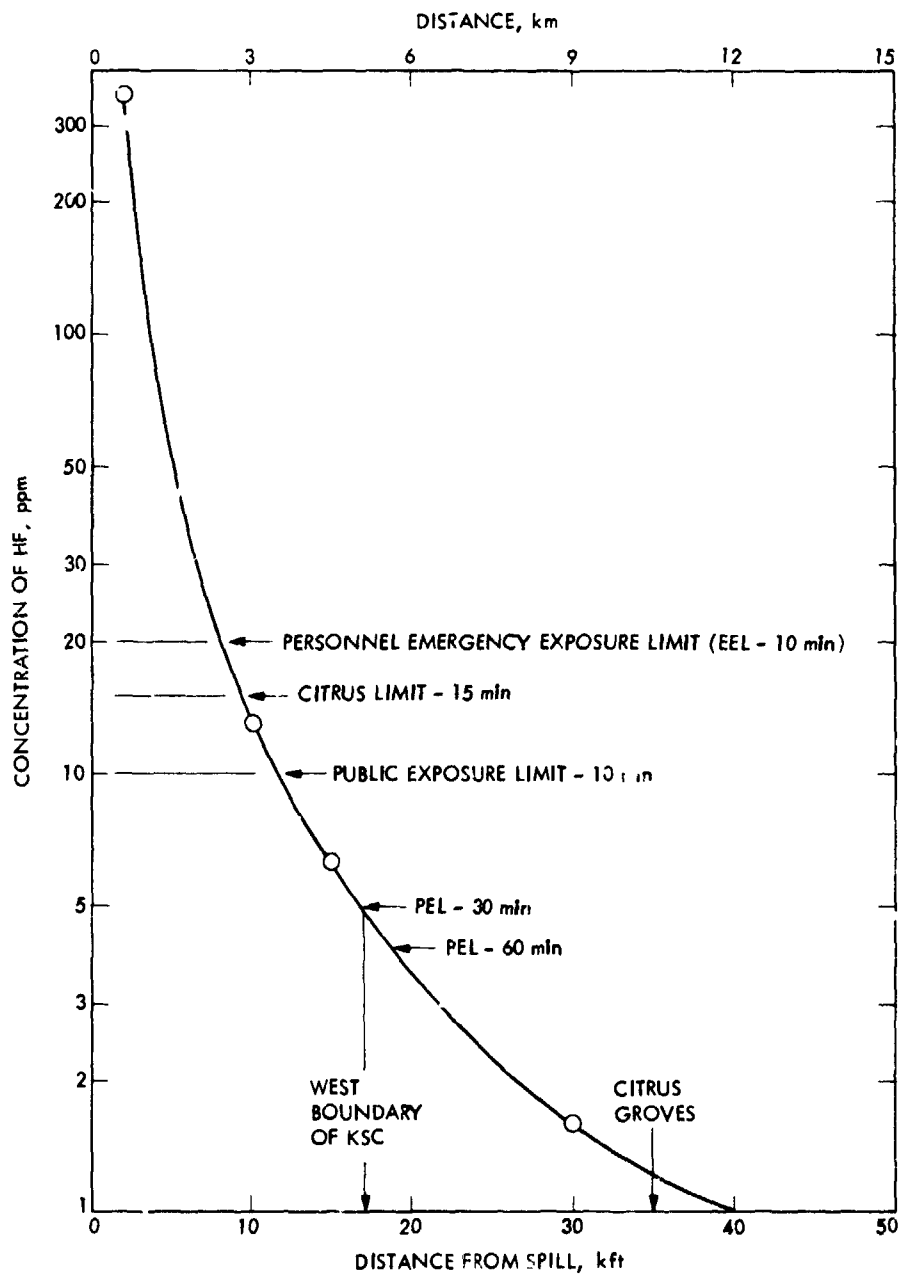


Figure 4-2. Concentration from LF_2 Spill

discomfort may occur to segments of the public but that any effect resulting from the exposure is reversible and without residual damage. The public exposure limits of the Advisory Center on Toxicology, which are shown in Figure 4-2, are not reached until 30 minutes after a spill, allowing time for local evacuation. An additional few hours would be required before the residents could return to the area.

The Ricca study also points out that hydrofluoric acid is formed from the water spray used to dilute the hydrogen fluoride from a spill. In the past $\text{Ca}(\text{OH})_2$ has been used to neutralize the acid but is difficult to clean up afterward. Charcoal scrubbers also have been used to absorb HF but need an initial dry nitrogen purge to minimize a tendency towards explosive burning.

More recent facility improvements at the Jet Propulsion Laboratory - Edwards Test Station (ETS) have utilized a 2% NaOH solution as a water fog spray. In a controlled closed-loop scrubber system, it has been demonstrated that 99.9% of the fluorine introduced into the system can be captured by reaction with the NaOH solution as a soluble NaF. All preplanned venting releases of fluorine at the JPL-ETS occur through this scrubber system. It is therefore recommended that a NaOH solution be used as the fog spray deluge for all fluorine testing. Much more fluorine would be trapped, resulting in a significant reduction of the airborne contaminants.

As previously stated, the release and disbursement occur in a very short period of time, making it mandatory to apply the controlling medium almost instantly (i.e., automatically) and to close off the release, if possible. A hot-wire (electrical) circuit has been incorporated by JPL-ETS on all of the fluorine-carrying elements. Therefore, if any unintentional fluorine release occurs, the hot-wire circuit is broken and an automatic predetermined emergency shutoff control system is activated, which can include a fog spray deluge. These techniques have been successfully used for several years. (See Appendix G for procedures used by JPL.)

In summary, automatic shutoff devices and water scrubbing with NaOH are recommended to minimize short-term effects from accidental fluorine spills.

4.5 FLUORINE ACCIDENTS AND INCIDENTS

There were a number of serious accidents with fluorine before 1970. Documentation on early accidents is, however, not readily available, and precise reasons are not always obvious; often several possibilities for the cause of these early accidents are hypothesized. References 4-10 and 4-11 are typical as are others, such as the early experiences of LeRC, MSFC, and Rocketdyne with FLOX, fluorine, and OF_2 /diborane. Component materials, lack of cleanliness, and procedures were listed as the primary causes of these accidents.

JPL has had access to these reviews and benefited from these early experiences of others and has also handled sizable amounts of fluorine since 1963, including tests for the Air Force, with only minor

incidents. Typical of an incident at JPL is Ref. 4-12, where the procedures were not followed. As a result, fluorine was trapped and pressure increased (a normal occurrence in any cryogenic system). Technicians nearby first heard sharp cracks. A facility valve and line leaked, spraying fluorine on a flowmeter, and a fire was initiated. Automatic shutoff precluded any extensive damage.

4.6 CURRENT INVESTIGATIONS

A number of investigations are currently under study which are of vital importance to the eventual use of a fluorine-hydrazine space-storable propulsion system on board the Shuttle. They are described briefly in this section to show the on-going fluorine safety activity required to provide confidence in fluorine operations.

Vapor detector evaluation, safety suit development, and cryogenic ground-support investigations are evaluations of various current equipment types in use at fluorine ground test facilities and are essential for safe handling of fluorine during integration into the Shuttle. The on-board temperature control investigation includes a study of applications for different propulsion configurations. The structural investigation includes a study of various structural concepts for retaining tanks during an emergency landing and the feasibility of integral and double-wall tank concepts. The need for compatibility of the Shuttle tiles with the fluorine is being investigated in the event the above structural investigation should show a propellant dump required to assure safety upon emergency landing. An environmental study is included to show possible effects from various potential fluorine atmospheric dumps. Support also is being given to Payload Safety Reviews with JSC (on the payload) and KSC (on ground) operations.

Results of these investigations are confirming that fluorine systems can be safely handled.

4.6.1 Fluorine Vapor Detectors

Experiences with fluorine toxic level detectors in the past have been unsatisfactory for various reasons. They either have the sensitivity required but are very inconsistent or prone to overload/malfunction due to the fluorine reactions degrading the delicate internal system, or are stable and compatible enough but lack the desired sensitivity. One unit, the TVM-1 Toxic Vapor Detector, built by General Electric at the Lynn, Massachusetts, plant, exhibits the best overall characteristics and chances for satisfying some of the safety requirements of the fluorine facilities and operations. It should give satisfactory historical data as to the toxic levels in multiple locations around a fluorine source, establishing and verifying the levels (to <1 ppm). A weakness in the present design is the time lag (approximately two minutes) from the taking of an air sample and the resultant readout. This is satisfactory for monitoring work areas for low levels to verify and establish working conditions. However, there is a need for a system with a much quicker response to indicate slightly higher toxic levels

of an emergency nature. The General Electric Co. is working on a sequencing valve with a quicker response for its system. The hot-wire detector previously discussed can provide an immediate response for critical locations.

Other systems tested included the "Billionaire" system from Mine Safety Appliances Co. and the "Draeger" unit from National Draeger, Inc. The "Billionaire" system is more sensitive but its repeatability is poor, requiring an elaborate purging process to reinitiate it. The "Draeger" unit is not sensitive enough and requires manual operation. A continuing search is being conducted to find a system that responds more quickly. Identification is being made of the development required to meet sensitivity, repeatability, rapidity, and automation specifications to assure fluorine operations that are safe for personnel and the facility.

Normal and emergency procedures currently being used by JPL at the Edwards Test Station "C" Stand are covered in Appendix G. This includes a description of the automatic and remote safety systems which have proven effective in service.

4.6.2 Fluorine Safety Suits

A continuing search for an improved fluorine safety suit of various materials has been carried out over the past several years. Personnel from ETR have contributed samples to JPL for evaluation and, in turn, have performed permeation tests on JPL-selected materials. Beta cloth (#389-7 Beta glass fabric) (R)¹ impregnated with Teflon (R),² has proven to be the most successful material to date, since it satisfies the requirements of compatibility and splash-penetration resistance (porosity) and is also reasonably light and flexible. Material was procured and shipped to Dixon Safety Products, Chicago, Illinois, and a prototype test propellant handling suit was fabricated and delivered to JPL. Exposure tests did show some reaction at the seams with the sewing threads originally used, and later a new Fluoroglass (R75:-18) thread was used. Some additional sealing of stitching may be accomplished with Teflon (R) coatings. It is expected that this suit will establish the material and design for use in the fabrication of LF₂-propellant handling suits. This application is for unconfined area activities but probably could also be used in the manufacture of astronaut type suits with head cover and air supply (scafe suits), if deemed a requirement.

Other materials which have been tested include Armalon (R),² Lawson material (R),² Viton (R),² Nomex (R)² (fire suit material), and various glove materials. Most of these were Teflon (R) impregnated or backed and resisted fluorine in varying degrees. Cleanliness is an ultimate requirement to prevent ignition; only Beta cloth (R), Lawson material (R) and Armalon (R) resisted fluorine burns when contaminated

¹Beta glass fabric is a trade name of Owens-Corning Fiberglass Corp.

²Teflon, Armalon, Lawson material, Viton, and Nomex are trade names of E.I. du Pont de Nemours & Co.

with glue (only the glue burned). Armalon with Teflon was too stiff, putting stress on the Teflon, whereas the Lawson material was too rubbery. Beta cloth has the best flexibility for suits.

4.6.3 Cryogenic Ground-Support Equipment (GSE)

Various approaches for maintaining the liquid fluorine at -193°C (80 K) or lower during prelaunch operations are being reviewed, including earlier investigations by other organizations on this subject. Other requirements to be met include prelaunch hold for several weeks, no venting or topping of fluorine, no frost buildup, portability at the Cape, and capability to integrate with the Shuttle on pad and after abort on the ground.

Different cooling approaches include LN_2 (open or closed loop), subcooling LN_2 (by venting or using helium), and refrigerators. The open loop LN_2 system is the least expensive, closed loop LN_2 is more costly, and subcooling, which may be beneficial because of the added thermal inertia of many hours, is additional cost. Refrigerators require considerable electrical power (1-2 kilowatts) and are the most expensive because of development cost.

The foam insulation (3.8 cm, i.e., 1.5 in. thick) on tanks and lines eliminates frost buildup. Both polyurethane and polybenzimidazole (PBI) foams (about 32 kg/m^3 , i.e., 2 lbm/ft^3) are being considered, where the latter, because of its resistance to fire in the event of a fluorine leak (Ref. 3-37), will be used on the LF_2 tank itself. Polyurethane will be used elsewhere because of its foam-in-place ease of installation, while PBI will be installed as precut blocks bonded together.

4.6.4 Temperature Control On Board the Shuttle

The warmup of the LF_2 after disconnecting the above GSE, through launch, in orbit, and during an abort return is being investigated under this task. Two generic spacecraft-type configurations consisting of two tanks and four tanks, respectively, as well as the integral pressurant tank concept, are included. Effects of shrouds (shielding), subcooling of LF_2 , or possible slushing are being considered for the best thermal inertia effectiveness. This results in the least rapid temperature rise to 130 K (-220°F) or a pressure of about 300 N/cm^2 (450 psia) before opening of doors and deployment from the Shuttle, or retrieval in an abort and return situation.

Several feasible approaches exist for this mission phase, and this task is to determine the best. Related temperature control studies are included in Refs. 4-13 and 4-14.

4.6.5 Structure for Emergency Landing

Structural approaches for containment of full tanks during an emergency landing, rather than prior dumping, are being investigated

under this task. Tension-cable support is an initial concept being studied, which promises to be lightweight. The tank-stiffening weight penalty required for launching unpressurized, double-walled tanks to minimize a fluorine leak and the possible benefit of a shroud are also being studied under this task. The integral pressurant and fluorine tank concept is the baseline for this investigation as well as for thermal control studies noted above in Section 4.6.4.

4.6.6 Shuttle Tile Compatibility with Fluorine

This investigation will be contingent upon the results from Section 4.6.5 above. If safe containment of fluorine in the event of an abort cannot be assured, then the effect of a prior dumping of LF_2 on the Shuttle thermal tile will be investigated.

4.6.7 Environmental Study

An environmental study of the effects from a possible atmospheric dump of fluorine in the event of an abort is reported in Ref. 4-15. Because of the relatively low concentrations involved, the predicted effect on the reduction of stratospheric ozone is extremely small. No adverse environmental impacts are predicted for an ionospheric injection of fluorine. Similar results were found for a possible dump of the space-storable hydrazine fuel.

4.6.8 Payload Safety Reviews

A preliminary Phase Zero Payload Safety Review was held at the JSC Shuttle Payload Integration and Development Program Office (SPIDPO) on October 18, 1978. Future meetings will be held with KSC on support equipment and ground operation safety and with JSC to further define hazards and testing required to give assurance of safe operations with fluorine, both on the ground and in flight.

SECTION 5

FLUORINE USAGE BY THE DEPARTMENT OF DEFENSE

The Department of Defense has been sponsoring chemical laser studies which use fluorine and its compounds for space applications (see Ref. 2-12). The Advanced Research Projects Agency (ARPA) earlier sponsored the Space Laser Experiment Definition (SLED) program, in which Rocketdyne studied the use of LF_2 , GF_2 , OF_2 , and NF_3 . Recently the Air Force has sponsored contracts to TRW and Bell Aerospace to study applications of NF_3 for lasers in space. From a safety viewpoint, the handling of sizable amounts of NF_3 on board the Shuttle will be almost as difficult as the handling of LF_2 . Impurities which can cause it to detonate are a basic problem for NF_3 . Transporting on board the Shuttle small amounts of LF_2 or GF_2 to be used as an igniter for the NF_3 is also considered. The safe handling procedures should be similar to those for the space-storable propellants above.

The Navy is investigating the use of fluorinated compounds for laser applications aboard ship. The safety of personnel will be enhanced by the readily available seawater, which can be used for emergency spills.

A comparison of NF_3 and F_2 is shown in Table 5-1, which includes thermal properties and other safety aspects for on-board Shuttle use (Ref. 5-1 contains extensive NF_3 data). Fluorine has a lower boiling point and a higher vapor pressure, but these disadvantages are offset by its higher heat capacity (warms up more slowly) and higher thermal conductivity (lower thermal gradients). An on-going study and design effort has been focused on the storability of liquid fluorine, which requires better thermal isolation from heat sources. The freezing point and critical temperature of F_2 are lower, whereas the rest of the thermal properties are about the same as for NF_3 .

Other safety aspects in the lower half of Table 5-1 show that both NF_3 and F_2 require careful selection of materials, cleanliness, and similar passivation procedures. Fluorine is reactive with more materials, whereas larger payloads of NF_3 are being considered, requiring attention to larger and more components for the NF_3 applications.

The toxicity level, emergency exposure limits, and threshold limit value for fluorine are lower but detectability is much higher, making it easier to discover small amounts (with the human nose and eyes). While special equipment is required to detect NF_3 , F_2 requires a faster response when detected.

Thus, from an overall safety viewpoint, similar procedures are required for handling both fluorine and nitrogen trifluoride in future Shuttle applications. A cooperation exchange of efforts in these two areas would benefit both NASA and DOD.

Table 5-1. Comparison of Nitrogen Trifluoride and Fluorine

Property	NF ₃	F ₂
Normal boiling point	144 K (-200°F)	85 K (-307°F)
Heat capacity of liquid	0.25 cal/g K	0.37 cal/g K
Density of liquid	1.53 g/cm ³	1.50 g/cm ³
Thermal conductivity of liquid	2.3 x 10 ⁻⁴ cal/cm s K	3.6 x 10 ⁻⁴ cal/cm s K
Heat of vaporization	39 cal/g	40 cal/g
Vapor pressure at NBP plus 25 K	47 N/cm ²	78 N/cm ²
Freezing point	66 K (-340°F)	54 K (-363°F)
Critical temperature	234 K (-39°F)	146 K (-200°F)
Critical pressure	490 N/cm ²	560 N/cm ²
Critical density	0.58 g/cm ³	0.61 g/cm ³
Reactivity	Most gases explosive with electrical spark or contaminants; most metals & nonmetals have low corrosion rates	High with most gases, nonmetals or metals with contaminants; low corrosion rates for pure metals
Shuttle payload mass	~10,000 kg	~2000 kg
Toxicity	4000 ppm	500 ppm
Emergency exposure limits (EEL)	2250 ppm for 10 min 750 ppm for 30 min 375 ppm for 60 min	60 ppm for 5 min 30 ppm for 30 min 25 ppm for 60 min
Threshold limit value (TLV)	10 ppm	1 ppm
Detectability	Odorless	Highly pungent

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

The general conclusion is that fluorine, when properly handled, presents no greater problem than any other cryogenic propellant. Specific conclusions and recommendations for proper handling follow.

6.1 CONCLUSIONS

- Many fluorine propellant combinations have been investigated, with fluorine/hydrazine being the most promising for advanced planetary spacecraft propulsion systems.
- Mission studies show larger payload and/or shorter mission flight time advantages compared with those for earth-storable propellants.
- Fluorine systems can be safely integrated into Shuttle-launched payloads.
- Extensive experience with fluorine and its derivatives exists.
- Many fluorine propellant tests have been conducted, with those in recent years being highly successful.
- Fluorine is highly reactive and when stored as a liquid must be maintained at cryogenic temperatures.
- Direct splash effects of liquid or gaseous fluorine on personnel would be toxic and could cause burns.
- Hydrogen fluoride gas formed by fluorine reacting with moisture in the air would become the main pollutant.
- The Ricca study (Ref. 4-8) shows that 20% of an accidental spill could be absorbed by water, with the remaining 80% going mostly into HF. No plant or public exposure limits would be exceeded by the latter, but hydrofluoric acid formed by the water needs to be neutralized. JPL uses a 2% NaOH scrubber at Edwards Test Station for this purpose.
- Inhalation of high concentrations (>500 ppm) of gaseous fluorine or hydrogen fluoride for extended periods (>5 min) can cause serious damage; at lower levels (<100 ppm) and shorter periods (<5 min), only temporary irritation would occur.
- Fluorine, even in weak concentrations, has a prominent odor; the nose, skin, tongue, and eyes are good detectors and sensitive to HF formed from body moisture.

- Plants are more susceptible to damage than humans and animals. A study was made of effects on citrus groves near KSC in Florida, showing a seasonal crop could be lost but no permanent damage would result in the event of a spill.
- Neither short-term inhalation nor long-term foraging of contaminated pasture land would be a problem for cattle in the KSC area in the event of a spill.

6.2 RECOMMENDATIONS

The extensive research work and conclusions have led to several recommendations as follows:

- Continuously operating monitoring devices should be used to detect the fluorine concentration levels in fluorine work areas.
- Automatic shutoff devices and water sprays (dilute with NaOH where practical) are required at test sites. JPL uses a hot-wire circuit to automatically shut off the fluorine supply at various stations in the event of a leak with good success.
- All venting must be through charcoal burners or appropriate gas scrubbers.
- Personnel in the vicinity of fluorine operations must be protected by a complete splash suit of an approved material.
- Inhalation of high concentrations of toxic gases can be prevented by use of a self-contained breathing air or mask and hose supply. Personnel working in hazardous areas must be properly trained in protective measures and procedures.
- Shuttle-based procedures need to be developed consistent with good ground-based procedures, and a requirement exists to reduce the potential of a leak to an extreme minimum through proper design and test, including investigation of the following:
 - (1) Selection of high-quality and fluorine-compatible materials.
 - (2) Design of a completely sealed propulsion system.
 - (3) Passivation of tanks, lines, and valves with GF_2 .
 - (4) Maintenance of a low positive GHe pressure in lines.

- (5) Vibration tests for launch and landing loads.
 - (6) Use of leak detectors and link-wire failure system on propulsion module.
 - (7) Use of an on-board LN₂ cooling system for thermal control (may be umbilically supplied).
 - (8) Development of safe loading and unloading procedures.
 - (9) Provision for an emergency dump on pad and a post-landing disposal or recovery of propellant.
 - (10) Availability of a fire control truck with NaOH water spray and a portable LN₂ supply.
 - (11) Consideration of needs for remote status monitoring.
 - (12) Provision for remote-storage sites before installation in the Shuttle and post-landing.
 - (13) Limitation of personnel access around ground loading and loaded tanks.
 - (14) Monitoring of weather for safe loading and unloading, and transportation of loaded systems.
- Completion of the phase II safety review with the STS Payload Review Panel (JSC) and the Safety Operations Office (KSC) for the current F₂ System Technology Program.

DEFINITION OF TERMS AND ABBREVIATIONS¹

Å	angstroms
ACPS	attitude control propulsion systems
AEC	Atomic Energy Commission, now a part of the Dept. of Energy
Apatite	phosphate rocks or in bone structure, mostly calcium phosphate fluoride
Armalon (R)	Du Pont fluorocarbon coated fabric
ARPA	Advanced Research Projects Agency
Beth cloth	glass fabric from Owens-Corning
B ₂ H ₆	diborane, fuel used with OF ₂ , a space-storable propellant
BTI	The Boyce Thompson Institute of Plant Research
"C" Stand	test stand at ETS capable of handling fluorine
cold spill	no fire resulting from a fluorine spill
contaminants	any substance causing F ₂ chemical reaction, such as moisture
corrosive	slow chemical reaction of fluorine on various materials
cryogenic	cold enough to store room-temperature gases as liquids (e.g., O ₂ , N ₂ , F ₂)
dermal	sensitive (deep) part of the skin
DoD	Department of Defense
double-wall tank	tank within a tank
earth-storable propellants	propellants stored as liquids at room temperature
EEL	emergency exposure limit, short-term emergency use

¹Some terms and abbreviations are defined locally in text where used

Engineering Test Module or Feasibility Module	early test module using FLOX (88 w/o F ₂)/MMH for Systems Technology Program
ETR	Eastern Test Range
ETS	Edwards Test Station
exothermic	heat produced in a reaction
F ₂	fluorine
Feasibility Module	see Engineering Test Module
FLOX	liquid fluorine and oxygen, 30% F ₂ originally used by the USAF and LeRC, 70% F ₂ used earlier by JPL, 88% F ₂ used later with MMH
fluorides	various chemical compounds of fluorine commonly occurring as minerals and in rock formations; they are easily absorbed by plants and in liquids or appear as gases (e.g., HF, SiF ₄ , or H ₂ SiF ₆).
fluorosis	fluoride poisoning
GCA	GCA Corp., Bedford, MA.
GF ₂	gaseous fluorine
GHe	gaseous helium
GSE	ground-support equipment
HCl	hydrochloric acid
HF	hydrogen fluoride
not spill	fire results, causing a cloud to rise
HQ	headquarters (NASA)
hypergolic	spontaneous combustion of a fuel and oxidizer
ICC	Interstate Commerce Commission
integral tank	pressurant tank imbedded in propellant tank
IUS	Inertial Upper Stage in Shuttle launch vehicle
JP-1, JP-4	hydrocarbon fuels
JPL	Jet Propulsion Laboratory

JSC	Johnson Spacecraft Center
Kapton (R)	Du Pont polyimide film
KSC	Kennedy Space Center
Lawson material (R)	Du Pont copolymer material
LC50	lethal concentration that would kill 50% of test animals
LeRC	Lewis Research Center
LF ₂	liquid fluorine
LN ₂	liquid nitrogen
LOX	liquid oxygen
MMH	monomethyl hydrazine, fuel used with FLOX
MSFC	Marshall Space Flight Center
Mylar (R)	Du Pont polyester film
NaOH	sodium hydroxide, used in water sprays to neutralize fluorine
NASA	National Aeronautics and Space Administration
necrosis	death of tissue
NF ₃	nitrogen trifluoride, oxidizer used by DoD for lasers
N ₂ H ₄	hydrazine, fuel used with fluorine in the Space-Storable Propulsion System
N ₂ O ₄	nitrogen tetroxide, an oxidizer for earth-storable propellants, common reference for safety comparison of fluorine
Nomex (R)	Du Pont aramid fiber and paper composite
OAST	Office of Aeronautics and Space Technology, NASA Headquarters
OF ₂	oxygen difluoride, a space-storable propellant
passivator.	process of creating a protective fluoride film using OF ₂ before loading with LF ₂
pathology	health condition of tissues
PBI	polybenzimidazole, insulating foam material fairly resistant to fluorine

PEL	public exposure limit
phytotoxic	plant poisoning
pollutants	fluorine or HF in air and water
ppm	parts per million
R&T Base	Research and Technology Base, NASA Headquarters advanced technology program
SAEF	Spacecraft assembly facilities at KSC, No. 1 -- Vertical Process Facility and No. 2 -- Payload Process Facility
scape suit	fully enclosed safety suit with hard head cover
scrubbing	diluting with water or chemical sprays or absorbing in charcoal reactors
Shuttle	STS Earth Orbital Spacecraft including IUS (but not booster)
space-storable propellant	propellant storable with passive thermal control in space, also stored cryogenically on the ground (e.g., F ₂ , FLOX, OF ₂)
Space-Storable Propulsion System	flight-like F ₂ /N ₂ H ₄ propulsion hardware being developed under the Systems Technology Program
STS	Space Transportation System (Shuttle)
Systems Technology Program	phased program to develop F ₂ /N ₂ H ₄ propellant system for flight-program readiness
Teflon (R)	Du Pont fluorocarbon elastomer
toxic	poisonous to humans, animals, or plants
TLV	threshold limit value, maximum long-term industrial exposure
TRW	TRW Space Systems
USAF	United States Air Force
Viking (VO-75)	Viking Orbiter launched in 1975 to orbit Mars
Viton (R)	Du Pont fluoroelastomer
w/o	weight percent oxidizer
WWII	second world war

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APPENDIX A

PROPERTY DATA FOR F₂, OF₂, AND FLOX

Physical properties for fluorine, oxygen difluoride, and fluorine-oxygen (FLOX) are included in the following tables.

Table A-1. Physical Properties of Fluorine

Property	English Units	Metric Units
Boiling point at 10 N/cm ²	-306.64°F	-188.13°C
Freezing point	-363.32°F	-219.02°C
Liquid density	12.5 lbm/gal at -306.64°F (94.1bm/ft ³)	1.50 g/cc at -188.13°C
Specific gravity of vapor relative to air at standard temperature and pressure		1.3
Critical density	5.1 lbm/gal	0.61 g/cc
Critical pressure	809.7 psia	558.3 N/cm ²
Critical temperature	-199.57°F	-128.65°C
Vapor pressure	19.7 psia at -300°F	13.58 N/cm ² at -184.4°C
	164.7 psia at -250°F	113.6 N/cm ² at -156.6°C
	794.7 psia at -200°F	547.9 N/cm ² at -128.8°C
	Kinematic	
	0.127 centistokes at -306.55°F	
Coefficient of viscosity		0.257 centipoises at -187.95°C
	Absolute	
		0.414 centipoises at -203°C
Density, solid	0.0686 lbm/in. ³	1.90 g/cc

Table A-1. Physical Properties of Fluorine
(Continuation 1)

Property	English Units	Metric Units
Transition point to white solid	-377.7°F	-227.61°C
Thermal conductivity		
at -188°C (-306°F) (gas, 10 N/cm ²)	0.004 Btu/ft h °F	1.7 x 10 ⁻⁵ cal/cm s°C
at -123°C (-190°F)	0.008 Btu/ft h °F	3.2 x 10 ⁻⁵ cal/cm s°C
at -188°C (-306°F), (liquid)	0.088 Btu/ft h °F	3.6 x 10 ⁻⁴ cal/cm s°C

Table A-2. Physical Properties of Oxygen Difluoride (OF₂)

Property	English Units	Metric Units
Boiling point at 10 N/cm ²	-230°F	-145.3°C
Freezing point	-371°F	-233.8°C
Gas density		
at 0°C (32°F)	0.14 lbm/ft ³	0.0023 g/cm ³
at 21°C (70°F)	0.13 lbm/ft ³	0.0021 g/cm ³
Liquid density		
at -145°C (-230°F)	12.7 lbm/gal (95 lbm/ft ³)	1.521 g/cm ³
Specific gravity of vapor (relative to air at standard temperature and pressure)		1.86
Critical volume	0.0376 ft ³ /lb	2.35 cm ³ /g
Critical pressure	719 psia	4.955 x 10 ⁶ N/m ²
Critical temperature	-72°F	-58.0°C
Vapor pressure equation at -182 to -146°C	Log P _{mm} = 7.4199 - 581.1/T _K ^a	

Table A-2. Physical Properties of Oxygen Difluoride (OF₂)
(Continuation 1)

Property	English Units	Metric Units
Density equation at -145 to -196°C	$\rho(\text{g/cm}^3) = 0.8225 - 0.004873T^{\circ\text{C}^a}$	
Viscosity equation (liquid) at -196 to -156°C and a pressure of 11 to 760 mm Hg	$\text{Log } \mu (\text{centipoise}) = 112.4/T_K^a - 1.4508$	
Thermal conductivity (liquid) at -196°C (-321°F)	0.14 Btu/ft h °F	5.8×10^{-4} cal/cm s°C
at -183°C (-297°F)	0.15 Btu/ft h °F	6.1×10^{-4} cal/cm s°C

^aTemperature in K or °C as noted by subscript; equations from Ref. A-1.

Table A-3. Physical Properties of Propellant FLOX
(Fluorine-Oxygen 70/30)

Property	English Units	Metric Units
Boiling point at 10 N/cm ²	-304°F	-186°C
Liquid density	11.6 lbm/gal at -304°F (87 lbm/ft ³)	1.24 g/cc at -186°C
Vapor pressure	16.8 psia at -300°F	11.6 N/cm ² at -184°C
	Kinematic	0.29 centistokes at -304°F
Coefficient of viscosity		0.24 centipoises at -186°C
	Absolute	

Table A-4. Appearance of Oxidizers

Oxidizer	General Appearance	
	Gas	Liquid
F ₂	Yellowish	Amber
OF ₂	Clear	Pale yellow-brown
FLOX	Yellowish	Amber

REFERENCE

- A-1. Thiokol Chemical Corporation, Reaction Motors Division, Investigation of Advanced High-Energy Space Storable Propellant System, RMD Report 5507-F, Contract NASw-449, June-November 1962.

APPENDIX B

STUDIES OF THE EFFECTS ON PLANTS, ANIMALS, AND PEOPLE

The general effects of fluoride poisoning on plants, animals, and people have been studied for many years. These studies have been conducted where various industries daily dump vast quantities of fluoride into the atmosphere, subjecting the surrounding environments to increased concentrations of airborne fluorides year after year. Literature reviews of these studies, with detailed background information are given in Refs. 4-2 and 4-3.

NASA's concern is primarily with the effects caused by shorter, more acute exposures. The target organs or systems may be completely different for acute poisoning than those affected by long-term chronic exposures. NASA sponsored two studies dealing specifically with the effects of short-term exposure to hydrogen fluoride and fluorine gas, one dealing with plants (Ref. 4-9), the other with animals and people (Ref. 4-6).

The Advisory Center on Toxicology and the Air Pollution Control Office of the Environmental Protection Agency have established emergency exposure limits for the public. These limits are described in Refs. 4-9, B-1, and B-2.

NASA conducted the Ricca study (Ref. 4-8) for the specific purpose of determining the environmental effects that an Atlas booster using 30 percent FLOX could conceivably cause in a normal launch, a total conflagration, and a fueling spill. The FLOX/Atlas booster was to use over 25,000 kg (55,000 lbm) of liquid fluorine per launch (plus 58,000 kg or 128,000 lbm of LOX), more than 20 times the quantity of LF_2 to be used in a planetary Shuttle mission (FLOXED TUG study in Ref. B-3). Unneutralized spill tests involving up to 450 kg (1000 lbm) of liquid fluorine have been conducted with no detectable ecological harm observed (Ref. 3-4, also Ref. B-4).

B.1 TRW-BTI STUDIES ON PLANTS NEAR KSC

TRW Systems and The Boyce Thompson Institute for Plant Research (BTI), under a NASA contract, studied the impact of toxic propellants on plant species on or near KSC (Ref. 4-9). The toxic pollutants of interest were hydrogen fluoride and nitrogen dioxide. The study was concerned only with the effects of high vapor concentrations, short-duration exposures of the type that might result from an accident involving liquid fluorine at KSC.

Several species of plants growing in the areas were identified. In the first phase of the study, two citrus varieties and two ornamental varieties were used to determine the range of the product of concentration and duration exposures necessary to induce visible plant response varying from no injury to severe damage. Eighteen HF exposure values were used, extending from 0.5 ppm-hours (0.5 ppm HF for one hour) to

40 ppm-hours (10 ppm HF for four hours). The lowest exposure caused slight damage to one of the citrus varieties, called the Hamlin Orange. There was slight tip damage and marginal chlorosis (blanding) on 20 percent of the young leaves. The most severe exposure resulted in damage to all of the plants. The citrus trees experienced complete defoliation of young leaves, death of succulent shoots, the dropping of all young fruit, and moderate intercostal (between "ribs") necrosis of the older foliage.

Gaseous hydrogen fluoride causes plant damage in proportion to the vapor concentration and the exposure time. It has not been possible to determine the interrelations between time and concentration. In some cases increased time and in other cases, increased concentrations, seem to cause the most dramatic phytotoxic response. Boundary levels for hydrogen fluoride range from 15 ppm for two hours to 8 ppm for four hours. If these threshold values are exceeded, the damage will be severe and can be expected to result in a partial or complete crop loss for the year. If HF concentrations reaching the commercial groves are higher than 15 ppm for over 15 minutes during the period of flowering and fruit development, it can be assumed that there will be no commercial citrus crop that season. The relatively high HF exposures did not kill any of the plants in this test. After a period of 4 to 6 weeks, new shoots had started to grow. The cumulative effects caused by these short-term exposures were not assessed. It is known that the fluorides are localized in the leaves, and when these leaves fall, the fluorides are expelled from the plant. It would be reasonable to assume that no further fluoride poisoning occurs after defoliation. The loss of leaves may cause a reduced yield in the next growing season; however, the long-term impact has not been assessed.

B.2. RICCA STUDY OF CONCENTRATIONS EXPECTED FROM A SPILL

The Ricca study noted earlier (Ref. 4-8), details the expected ecological impact that would result from the use of FLOX with Atlas boosters. The source of liquid fluorine will be transient, resulting in short-term, acute exposure, rather than chronic deterioration. Such damage manifests itself as vegetative leaf burn, respiratory irritation, and dermal irritation. Three types of atmospheric releases are discussed:

- (1) A total vehicle conflagration, consuming/releasing over 25,000 kg (55,000 lbm) of liquid fluorine in the fire (30 percent LF_2 plus 58,000 kg (128,000 lbm) of LOX for floxed Atlas).
- (2) A normal launch, introducing nearly 1,350 kg (3,000 lbm) of hydrogen fluoride into the atmosphere.
- (3) A cold spill involving from 1,350 to 2,700 kg (3,000 to 6,000 lbm) of liquid fluorine. This spill is neutralized with water fog, resulting in HF pollution.

The third release will be the mode discussed in this appendix because it is the closest approximation of release modes that would be

encountered in the Shuttle program. If a break in oxidizer lines were to occur while filling the Atlas booster, 1,350 to 2,700 kg (3000 to 6000 lbm) of liquid fluorine could be released. This compares with 900 to 1,350 kg (2000 to 3000 lbm) that would be released in a complete space-storable propellant Shuttle catastrophe.

A water deluge system would be activated in the event of a ground spill and would capture in solution an estimated 20 percent of the fluorine. The remaining 80 percent of fluorine would be introduced into the atmosphere, primarily as HF. The expected maximum concentrations as a function of distance are shown by the curve in Figure 4-2 presented earlier in Section 4.4.3 along with Public Exposure Limits. These estimates were calculated assuming the most stable of atmospheric conditions, which cause maximum ground-level concentrations. A strong inversion is assumed to exist; the breeze is sporadic and varies only slightly.

At a distance of 4 km (13,000 ft) from the launch site, the likely place for an accident is the KSC industrial area. HF concentrations of less than 13 ppm would fumigate this area for a very short period of time. The Emergency Exposure Limit for space personnel is 20 ppm HF for 10 minutes. The west boundary of KSC, the Banana River, is 5 km (17,000 ft) away (see Fig. B-1), and this is the closest boundary to the supposed flogged Atlas spill site. At this point, the HF concentration is estimated to be less than 6.2 ppm. This would also be for a very short term. The Public Emergency Limit is 10 ppm for 10 minutes, and it appears that this would not be exceeded. On Merritt Island the government leases citrus groves to private concerns. These groves are located 11 km (35,000 ft) from the launch sites, and HF concentrations could range from 1.6 to 0.9 ppm. These would be transient maximum concentrations, but they could possibly linger as long as one hour. This is far below the short-term exposure levels estimated to cause phytotoxic damage to plants. During flowering and fruit development, crop destruction does not occur until exposures of 15 ppm of HF for 15 minutes have been reached.

These maximum concentrations are not experimental facts; they are based on experience and the Ocean Breeze and Dry Gulch Diffusion program. The values tabulated are maximum concentrations that would occur only under conditions which greatly inhibit diffusion. This study, and spill experiments involving up to 725 kg (1600 lbm) of liquid fluorine, indicate that even if a total vehicle destruct were to occur to a fluorine-bearing payload, no established exposure limits would be exceeded.

For the purposes of the Ricca report, it was estimated that approximately 270 to 635 kg (600 to 1400 lbm) of fluorine would be absorbed by the deluging agent, water. This would form extremely toxic hydrofluoric acid. If this were released straight into the Banana River, it would result in a localized fish kill. The runoff water needs to be collected and treated with a chemical like $\text{Ca}(\text{OH})_2$ or NaOH (cleaner). This will precipitate the fluoride out as insoluble CaF_2 or soluble NaF and neutralize the acid. This treated water can then be safely discharged into the river.

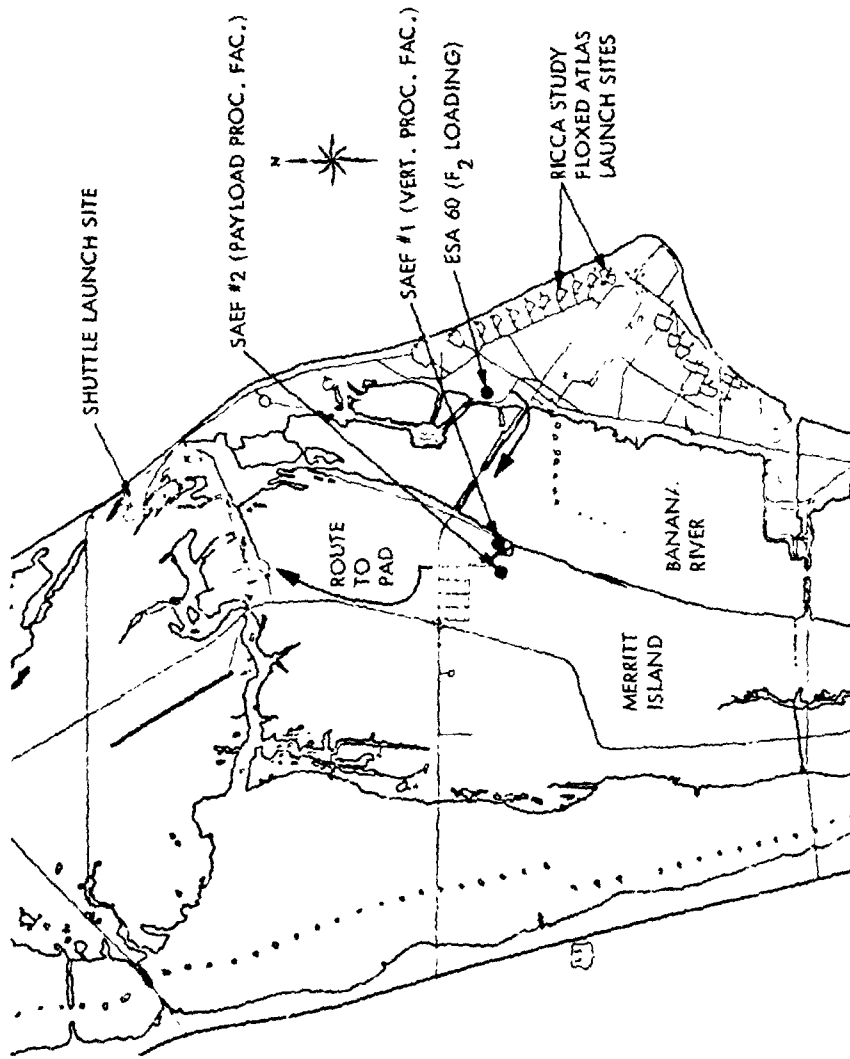


Figure B-1. John F. Kennedy Space Center and Cape Canaveral Air Force Station

If a systems or human failure were to occur, causing the release of liquid fluorine, the worst situation would involve a spill of approximately 1,350 kg (3000 lbm) of liquid fluorine. Such mishaps would be very rare and for environmental impact studies, it could be considered a one-time occurrence. In Polk County, Florida, before 1965, it was estimated that 6,000 to 18,000 kg (13,000 to 40,000 lbm) of gaseous fluorides, including HF, SiF₄, and H₂SiF₆, were dumped into the air per day for 350 days of the year. No harmful acute effects were observed in the populations living in the area. Citrus trees could be grown and successfully cultivated within 1-1/2 miles of one of the phosphate plants, the source of the gaseous fluorides.

The Shuttle launches will be 16 to 19 km (10 to 12 mi) up the coast (see Fig. B-1) from the floxed Atlas sites. Loading the fluorine would most likely occur at ESA-60, and the propulsion system would be mated with the spacecraft and the inertial upper stage (IUS) across the Banana River in the spacecraft assembly area and transported to the Shuttle launch site as indicated in Figure B-1.

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APPENDIX C

KEPLINGER FLUORINE GAS INHALATION TESTS

C.1. EFFECTS ON ANIMALS

The Keplinger paper (Ref. 4-6) is a comprehensive study dealing with the inhalation of fluorine gas. First, Keplinger determined lethal concentrations that killed 50 percent of the test animals (LC50's) for variable time exposures. The five-minute LC50's for mice, rats, and rabbits were 600, 700, and 820 ppm F₂, respectively. The survivors were sacrificed serially. From this part of the test the lungs and respiratory tract were identified as the primary targets, gross pathological changes were observed, and benchmark concentrations for other experiments were determined. Severe congestion and hemorrhaging of the lungs occurred in the worst cases. After 7 days, blemishes were observed on the kidneys and liver of some of the animals. By the time 14 days had passed, approximately 85 percent of the mice sacrificed on that day had kidney damage. At concentrations where no lung damage is observed, neither kidney nor liver damage is observed. It takes slightly higher fluorine concentrations to induce liver pathology than it does to cause lung and kidney damage. After six months had elapsed, the pathology of all organs had returned to normal. Outward manifestations of fluorine poisoning of test animals are dyspnea (difficulty in breathing), lethargy, red nose, and swollen eyes. These tests indicated that the acute effects of fluorine can be gauged by the irritation noted in the lungs, respiratory tract, nasal passages, and eyes.

Tests were later conducted to determine if cumulative effects occurred in the soft tissue as a result of repeated intermittent exposure to fluorine. Test animals were exposed repeatedly to the same concentration of fluorine gas at intervals ranging from 24 hours to 1 week. It was discovered that the animals exposed repeatedly to the same level suffered no more pathological damage than did animals exposed only once to the same vapor concentrations and dosages. At higher concentration levels, the resulting pathological damage was less in the animals repeatedly exposed than in the animals exposed only once. Repeated exposure to fluorine at the same concentrations caused less pathological damage, apparently from some tolerance buildup. A test was devised to determine if previous exposure to low concentrations of fluorine would change the susceptibilities of rats and mice to fluorine. Groups of rats and mice were exposed to low levels of fluorine intermittently over varying periods of time. Then these treated animals and a control group of untreated animals were exposed to higher concentrations of fluorine. At sublethal concentrations the treated animals showed less pathological change than the control group. At lethal concentrations, the treated animals withstood the toxic effects better, and more survived than in the control group. This tolerance buildup was not substantial, but it did exist. It can be said with certainty that after repeated exposure to fluorine, test animals suffer no worse pathological effects than animals that have never been exposed before. Fluorine does not accumulate in the soft tissue; only a slight accumulation occurs in the bone tissue. The lack of any significant cumulative

effects is an indication of the rapid removal of fluorine from the body.

C.2. EFFECTS ON HUMANS

Keplinger also conducted some short-term exposure tests for irritation on student volunteers. The fluorine vapor concentrations were carefully monitored. The fluorine-contaminated air was administered through a mask-like apparatus that covered each volunteer's eyes and nose. The students held their faces against the masks, and if the irritation became too severe they could immediately remove their faces. The mouth was left uncovered, so that the volunteers could breathe the ambient air. This was an additional safety precaution, to help insure that the test subjects would not be harmed. The maximum exposure was to a concentration of 100 ppm of fluorine for 1 minute. At all the concentration levels used, the odor of fluorine was very prominent.

First, Keplinger ran a series of tests where volunteers were exposed just once to a specific concentration of fluorine. When student volunteers were exposed to 10 ppm fluorine for as long as 15 minutes, no irritation to the eyes or nose was reported. The doped air could be inhaled without causing any irritation to the respiratory tract. When the concentration level was raised to 23 ppm and exposure maintained for 5 minutes, a slight irritation to the eyes was noted. The air was inhaled intermittently over the 5-minute period without respiratory difficulty. At fluorine concentrations of 50 ppm continued for 3 minutes, the eyes were irritated, and slight irritation of the nose was reported by test subjects. The following concentrations were continued for 1 minute. At 67 ppm fluorine, the nose and eyes were very irritated; however, it was not unbearable. At 78 ppm, the eyes and nose were again very irritated, but the test subjects indicated that it was not as irritating as cigarette smoke blown in the eyes. After exposure, the face was slightly irritated. When the air was inhaled, coughing occurred. Concentrations of 100 ppm were very irritating to the eyes and nose. After exposure, the eyes continued to smart, and subjects reported that it felt like a film covered the eyes. The skin was irritated after exposure. When exposed to 100 ppm of F_2 for 30 seconds, the eyes and nose were irritated within a few seconds, but inadvertently the after-effects were not reported.

A second series of tests were run to determine the effects of repeated intermittent exposure to low concentrations of fluorine. Subjects were exposed to 10 ppm fluorine for 5 minutes, every 15 minutes over a 2-hour period. The only effect reported was a slight smarting of the eyes. Another run was conducted with a vapor concentration of 10 ppm fluorine being maintained for 3 minutes. Exposure was repeated every 15 minutes and continued for 3 hours. Both the eyes and skin were irritated. Some subjects reported that it felt like a film was covering their eyes.

C.3. CONCLUSIONS

The Keplinger tests indicate that the eyes are the most sensitive index of the subjective irritation caused by fluorine gas. (JPL has found the nose to be more sensitive.) The subjects agreed that a concentration of 100 ppm was extremely uncomfortable and that they would evacuate the area immediately if such concentrations were present. However, at this concentration all the volunteers thought that they would be capable of self-rescue and, if necessary, could enter a room without breathing apparatus to rescue an injured person. Based on his experiments, Keplinger postulated emergency exposure limits to fluorine of 60, 40, 30, and 25 ppm for 5, 15, 30, and 60 minutes, respectively, (shown by the upper curve in Figure 4-1 earlier in Section 4.3). While these levels would be irritating to personnel, they would cause no serious or permanent injury.

APPENDIX D

HOT AND COLD SPILLS

D.1. INTRODUCTION

When any dangerous substance is used, it is desirable to foresee the probable incidents that would accompany an accident. Fluorine is the most reactive chemical element, and further complications are added when it is used in the liquid state (Ref. D-1). First, a more concentrated source of fluorine exists (because of its higher density), and second, liquid fluorine is a cryogen, requiring special cold-storage equipment and handling. The corrosive and toxic nature of fluorine dictates that stringent safety procedures be followed while using liquid fluorine. To insure maximum safety for personnel, facilities, surrounding populations, and the environment, it is necessary that we be able to predict the behavior of a release of a large quantity of liquid fluorine. What will happen when a large quantity of a cryogenic liquid of extreme reactivity is spilled? What can be done to control or suppress a liquid fluorine spill? After fluorine is introduced to the environment, what will be the ground-level concentrations and dosage fields that result? The first step is to determine what the behavior of the spill will be. A typical cryogenic cloud may result, or the fluorine may start to react with materials at the spill site, igniting a fluorine-fed combustion. At what rates will the cryogenic liquid fluorine boil off or burn? How and where will the cloud plume travel? This appendix gives a qualitative description of what to expect in the event of a large liquid fluorine release.

Compatibility tests, spill neutralization tests, films of vehicle conflagrations, and the observation of spills at various centers that use liquid fluorine have given a clear indication of how liquid fluorine will behave when spilled. Information of what fluorine reacts with and on the characteristics of hot and cold spills is available in Refs. 3-4 and D-2.

Regardless of the cause of a liquid fluorine release, it will be one of two types: a hot or a cold release. Hot releases include all spills where a sufficient heat of reaction occurs, thereby lifting the reaction products well above the ground. Reference 2-6 contains an excellent analysis of hot and cold spills, which is summarized in the following paragraphs.

D.2. HOT SPILL DESCRIPTION

Motion pictures of fluorine and FLOX spilled upon JP-4 or charcoal and rocket conflagrations involving other propellant combinations reveal that following the initial reaction, a fireball forms and rises vertically into the air. As the fireball rises, the base of the fireball necks down to form a stem. A strong scavenging effect occurs along and near the ground. Debris and reactants near the ground are pulled up into the cloud and rapid, near vertical, cloud rise occurs.

In an Atlas failure using LOX and JP-1, the average wind speeds resulting from the scavenging effect were estimated to be 23 m/s (75 ft/s). The initial wind velocities at the base of the stem were thought to be as high as 90 m/s (300 ft/s) after initial cloud rise. The smoke color (of the ground fire) was seen to change from the characteristic white of an oxygen-rich to the black of an atmospheric-fed combustion. This indicates that practically all of the oxidizer had been consumed or swept upward into the top portion of the cloud column. In a large liquid fluorine spill that results in a conflagration, similar characteristics would be expected. The scavenging effect would lift the oxidizer high into the air, creating an elevated pollution source. This would reduce downwind ground-level pollution considerably. Any residual fluorine would react with water vapor in the air. The warm hydrogen fluoride would rise and diffuse rapidly into the atmosphere. The NASA-sponsored spill and diffusion studies cited above support these predictions.

A recent concern has been whether reaction-product clouds will penetrate or pierce temperature inversions. Temperature inversions, which may extend vertically for a hundred meters or more, are characterized by an increase of temperature with an increase in height. A warm, rising cloud would be trapped beneath the inversion layer, greatly increasing downwind ground-level exposure. Inversion penetration is more important when low-lying temperature inversions are present. The approximate energy required to penetrate inversions was estimated to be $5 \times 10^9 \text{ J}$ ($5 \times 10^6 \text{ Btu's}$), or about the energy released when 1,350 kg (3000 lb) of 30 percent (LF₂) FLOX reacts with charcoal of JP-4 with an efficiency of 30 percent. In this experiment low inversions from 240 to 400 m (800 to 1300 ft above the ground) were easily penetrated by reaction clouds, which rose to about 300 to 600 m (1000 to 2000 ft). A conflagration or hot spill involving liquid fluorine would probably proceed with greater efficiency than the above tests, which used 30 percent FLOX; as a consequence, more energy would be released. The resultant reactant cloud would pierce most low-lying inversions.

D.3. COLD SPILL

Liquid fluorine spilled onto materials with which it does not easily react, such as concrete or structural steel, creates a typical cryogenic cold spill. The cryogenic liquid will flash and boil off at high initial rates when it hits surrounding floors. The length of time required for boil-off will depend on how the spill is confined and if puddling occurs. If an appreciable wind exists and the spill is both shallow and dispersed, a flash boil-off is likely. When puddling occurs, the surfaces containing the cryogenic liquid will be chilled to a very low temperature and after the initial flash boil-off will continue at a reduced rate. The overall downwind dosage of atmospheric pollutants is not affected by the degree of puddling; however, if some containment of the spill occurs, the maximum downwind concentrations may be less than for an uncontained cold spill. The gaseous products (primarily gaseous fluorine; some hydrogen fluoride will form as water vapor reacts with fluorine) from the boil-off stay close to the ground. Under similar meteorological conditions, the atmospheric diffusion of pollutants is much slower for cold releases than hot releases.

Due to the slower diffusion process, downwind ground-level pollutant concentrations and dosages are higher for cold spills than hot spills involving the same amount of liquid fluorine. These observations are confirmed by several NASA and Air Force Studies (Refs. 3-4, B-4, and D-3 through D-5).

D.4. SMALL SPILLS

On occasion, liquid fluorine has spilled onto concrete aprons surrounding test sites, when fill hoses were disconnected. Residual liquid would slosh from the pipes, causing a small cryogenic cold spill. The liquid flash boils, and the cloud dissipates in a short period of time. These occurrences have been observed at many facilities that regularly handle liquid fluorine. Rickey (Ref. 3-4), in tests at Edwards Air Force Base, observed the effects of a 472 kg (1040 lb) liquid fluorine spill in a stainless steel pan. This spill was a warm spill. The fluorine reacted with a small amount of water in the tray, and fifteen seconds later the tray caught fire. However, very little heat was liberated, and this spill had many characteristics of a cold spill. The boil-off continued for over ten minutes, and downwind fluorine concentrations were greater than those recorded in an earlier induced hot spill that consumed 1-1/2 times as much liquid fluorine.

The ignition of the stainless steel tray clearly indicates the extreme reactivity of liquid fluorine. The fluorine initially reacted with the water, and the heat liberated in this reaction was enough to raise the temperature in the tray to the kindling point of stainless steel. A smoldering fluorine fire then consumed approximately 0.3 m² (3 ft²) of the stainless steel tray. If only a small quantity of fluorine had been spilled, the initial reaction with the water would have occurred, but there would not have been enough fluorine left to sustain the steel-fluorine combustion.

D.5 LARGE SPILLS

When large quantities of liquid fluorine are spilled around a launch facility, combustion will probably occur. The fluorine will initially react hypergolically with something that is not compatible with liquid fluorine, liberating enough heat to raise the immediate temperature to the kindling points of the fluorine-compatible metals. The metals will start to burn, and a conflagration resulting in serious damage to the vehicle and facility will occur. A fireball is likely to result, and the cloud plume will travel vertically upward.

In all of the above situations it is assumed no attempt is made to control or reduce the quantity released. The quantity spilled can be minimized in almost all failure modes by the proper design of the system piping and the utilization of a link-wire safety circuit. It is strongly recommended that maximum effort in design and procedural techniques be exercised to minimize the quantities of fluorine released.

D.6. SUMMARY

When a spill reacts chemically, normally enough heat is generated to cause a rising cloud, which is dispersed by the winds. A non-reactive spill leaves fluorine and HF at the ground level. A small reactive spill may react with its container but not generate enough heat to disperse it. Large spills can wipe out the facility unless controlled with emergency shutoff circuits.

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APPENDIX E
SPILL SUPPRESSION

E.1. BACKGROUND

NASA and the Air Force have been very interested in controlling liquid fluorine spills, and most of the work in this area was done early, when fluorine was first seriously considered as a propellant oxidizer. In 1959 an investigation was conducted that studied the effectiveness of water spray and sodium carbonate as suppressants (Ref. 3-4). Other suppressant studies are included in References 2-6, 4-4, B-3, and E-1 through E-3.

Operating procedures detailing the proper handling of liquid fluorine and improved system design have been developed, minimizing the risk of a large spill. However, the cryogenic and hypergolic properties of liquid fluorine and its toxic nature mandate the formulation and testing of emergency procedures to combat and suppress accidental liquid fluorine spills. Once spilled, liquid fluorine cannot simply be gathered in catch basins and reclaimed. The extreme reactivity of fluorine precludes this. As mentioned previously, there are two modes of liquid fluorine release, hot and cold. If large quantities of liquid fluorine are spilled, a cryogenic cold spill cannot be tolerated because of the extensive ground-level pollution that results. In all probability the spill would be a hot one, with the fluorine fire feeding upon the facility and vehicle in the spill area. The suppression of liquid fluorine spills has a dual purpose. Both ground-level pollution levels and facility damage are minimized. This is achieved by supplying an alternate reactant, in excess quantities, at the spill site, with which fluorine will react smoothly. A hot reaction occurs, liberating enough heat to carry the product cloud high into the atmosphere, thus speeding the disbursement of pollutants.

Ideally, the reaction between the reactant and fluorine will yield inert, nontoxic products. The reaction should be a smooth-burning one. Explosive, uneven combustion results in splattering, blowing some liquid fluorine away from the initial spill site and the suppressant. High heats of reaction are desirable because the released thermal energy and convection currents carry the product pollutants high into the atmosphere, creating an elevated pollution source, reducing ground-level pollution. Finally, the reactant must be relatively easy to deliver and apply on the spill.

E.2. SUPPRESSANT TESTS WITH VARIOUS MATERIALS

H. Schmidt has studied the reaction characteristics of charcoal and liquid fluorine at the Lewis Research Center (Refs. E-2 through E-5). Charcoal and liquid fluorine react hypergolically. Burning is very smooth, and a great deal of heat is released. The product cloud travels almost vertically upward and rapidly disperses into the atmosphere. The reaction product, tetrafluoromethane (carbon tetrafluoride), is both relatively

nontoxic and inert. Charcoal is, however, impractical as a spill reactant because it cannot be easily applied to the spill. It has been suggested that charcoal be placed around liquid fluorine handling areas and in trenches below pipes carrying liquid fluorine at ground handling stations. Charcoal has been used for the disposal of liquid fluorine at Lewis, and large charcoal reactors have been designed and tested by Schmidt. It is suggested that when a situation arises where a spill becomes probable, say the pressure in a loaded propellant tank becomes too high and cannot be brought down, these reactors could be used as emergency disposal units for liquid fluorine. The reactors would permit the dumping of liquid fluorine in emergency situations, but a very large unit would be required to get enough surface for reaction. As a spill suppressant, though, charcoal is not the recommended choice.

Sodium carbonate (Na_2CO_3 /Soda Ash) has been tested as a spill reactant by both NASA and the Air Force and is more efficient than charcoal. Rickey, during the Haystack Buttes tests, used 5,400 kg (6 tons) of sodium carbonate to neutralize 735 kg (1620 lbm) of liquid fluorine (Ref. 3-4). About 1,800 kg (2 tons) of additional sodium carbonate were in the tray from a previous test. During the time between tests, the residual carbonate became wet and hydrated due to rainfall and humidity. This residue was shovelled to the side but was not removed from the tray. The liquid fluorine was discharged into the pan, followed 20 seconds later by the release of the fresh sodium carbonate. The fluorine reacted violently with the hydrated carbonate from the previous test. When the fluorine and fresh carbonate combined, a great deal of heat was generated, and many small explosions were heard. The entire fluorine disbursement took about 3 minutes.

NASA conducted tests designed to determine if these reactions resulted in capture of fluorine by the deluge agent. Tests were conducted in a 2 x 2 m (6 ft x 6 ft) structure covered by 0.6 cm (1/4 in.) asbestos board. The structure was not gas tight, nor was it strong enough to withstand large pressure pulses; however, it did prevent the gases from blowing away. The tests with both gaseous and liquid fluorine indicated that approximately 30 percent of the fluorine was captured by the sodium carbonate.

Both tests showed that sodium carbonate was an effective reactant, but the removal of the glass-like fusion of fluorides and carbonate was extremely laborious, involving many man-hours. This reactant would make quite a mess at a test facility, and furthermore, it is difficult to deliver sodium carbonate to the site of the spill. Finally, sodium carbonate is slightly hygroscopic, absorbing moisture from humid air. The resulting hydrate reacts explosively with liquid fluorine.

E.3. WATER SUPPRESSANT TESTS

Water fog is considered to be the best neutralizing reactant for liquid fluorine spills. For clarity, the term neutralize, as used here, means to combine with until there is no further exothermic reaction. Fine droplets of water are sprayed onto the spill. Upon mixing with

the liquid fluorine, a smooth, hypergolic combustion occurs. In some studies, liquid fluorine was observed to react violently when spilled onto standing water. The smoothness of the liquid fluorine-water fog reaction is due, in part, to the increased surface area created by breaking up the water stream into fine particles. Since the reaction is smooth, all the fluorine remains near the spill site and reacts with the fog or is pulled up into the rising cloud columns by the scavenging effect. Since the reaction is highly exothermic, the gaseous toxic product, hydrogen fluoride, is carried almost vertically aloft, and the cloud column rapidly diffuses into the atmosphere.

In 1959 Rickey (Ref. 3-4) used 1,225 kg (2700 lbm) of water to neutralize 728 kg (1605 lbm) of liquid fluorine. Cloud dissipation was rapid, and the motion of the reaction cloud was nearly vertical from the spill site. It took approximately 2 minutes and 30 seconds for the fluorine spill to be neutralized. Test animals placed 46 m (150 ft) from the spill site did not show any signs of fluorine intoxication. This is another indication of the rapid upward dispersal of the reaction cloud. The NASA test measuring the amount of fluorine captured by the deluge agent estimated that water fog captured from 30 to 40 percent of the fluorine spilled. The open conditions that exist at launch sites would be likely to decrease this percentage. The plans for water fog neutralization systems should include catch basins to collect the runoff water, which will be contaminated with highly toxic hydrofluoric acid. This water can then be treated with $\text{Ca}(\text{OH})_2$ or other alkaline substances. The $\text{Ca}(\text{OH})_2$ would neutralize the acid as well as precipitate out the fluoride as insoluble CaF_2 .

Water fog deluge systems are presently considered the best suppressant technique for large liquid fluorine spills. The fog readily reacts with fluorine, forming the less toxic HF. The rapid reaction with water spray minimizes the damage to surrounding materials. The toxic gaseous products are reduced because of the entrapment in the liquid state and are carried rapidly aloft, minimizing ground-level pollution. Maximum neutralization of any fluorine spill is absolutely necessary, and water spray is the simplest method of doing the job.

More recent experience with neutralizing fluorine, consisting of planned releases by JPL at their Edwards Test Station, takes the water fog deluge one step further. A deluge scrubber system utilizing a 2% NaOH solution reacts with all planned releases of liquid and gaseous fluorine as well as engine combustion products. The NaOH solution's reaction rate with fluorine is significantly higher than that of water alone, and proper system design can assure 99.9% neutralization. The solution is all drained back to a large catch-scale basin, which is the supply source for the pump-fed deluge scrubber system. The fluorine is entrapped in the solution as NaF. Subsequently, it is precipitated out by the addition of $\text{Ca}(\text{OH})_2$. It is conceivable that similar area-wide deluge systems could be designed and installed to improve this neutralization efficiency for larger spills, but this would certainly entail more effort and expense than the straight water deluge. The trade-off is between the expense and the degree of neutralization required to insure personnel safety.

E.4. SUMMARY

Various spill suppressants were tested. Charcoal reactors would have to be large. Sodium carbonate leaves a residue hard to cleanup. Water sprays are superior and with the 2% NaOH solution used at ETS achieves the highest degree of neutralization.

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APPENDIX F

ATMOSPHERIC DIFFUSION STUDIES

F.1. INTRODUCTION

If an accidental release or spill were to occur while liquid fluorine was being used, the product cloud would consist primarily of hydrogen fluoride gas and a small amount of fluorine gas. Both of these products are toxic, and it is important to know how these gases diffuse into the atmosphere. Most investigations dealing with atmospheric pollutants have placed their emphasis on the time variation of the air pollution caused by the increasing amount of foreign materials being introduced into the air from such sources as automobiles, factories, and open fires. The air pollution problem facing NASA is the atmospheric diffusion of toxic fuel exhaust products. The release of liquid fluorine around the KSC facilities (Fig. B-1), as the result of accidents such as damage to transportation equipment, fire in a chemical-storage facility, or the rupture of a propellant tank, could create a situation where pollutants are released in an uncontrolled manner at an unpredictable time. Even under such circumstances, it should be possible to predict with fair accuracy the variety of probable conditions of an accident and hence to predict the corresponding exposure parameters. NASA has sponsored many diffusion programs that estimate concentration and dosage fields which would result from varying meteorological conditions and release modes. These models are completely general and can simulate fields for any airborne pollutant.

F.2. DIFFUSION MODELING

Formulation of a reliable diffusion model is a complicated and mathematically tedious process. First, the meteorological factors that influence diffusion and the conceivable modes of fluorine release must be identified and mathematically approximated. Variable parameters must be chosen so that various release modes and weather conditions may be simulated. A detailed study of meteorological conditions must be conducted to obtain input parameters appropriate for the area in which the diffusion processes are to be applied. A similar study must analyze the various release modes in order to determine the proper source parameters.

A model for the dispersion of toxic pollutant products must provide an accurate description of the atmospheric transport, dispersal, and decay of all nonsettling airborne toxic materials. The model must give satisfactory quantitative estimates of the concentration or dosage fields of toxic materials from a source characterized by a known strength and geometry. The model should also note the downwind ground-level distances at which concentrations and dosages exceed established threshold limits. Satisfactory quantitative estimates of the surface deposition of toxic materials resulting from gravitational settling, precipitation, and other removal mechanisms must be calculated. The diffusion models constructed to date have been generalized models applicable to different pollutants, source types and strengths, and varying weather conditions.

Some of the studies sponsored by NASA or the Air Force, detailing weather conditions in the KSC area and describing computerized diffusion models are References 4-8, B-3, B-4, and F-1 through F-6. These reports were built upon the foundation laid by previous models such as the Ocean Breeze and Dry Gulch Diffusion program.

Diffusion work is still developing, and many different approaches are used, but they still draw heavily from past work. Some of the earlier papers are References F-7 through F-13, and some of the more current literature on diffusion clouds is given in References F-14 through F-18, where the contaminant of most concern is hydrochloric acid from solid propellant rockets.

GCA (Refs. F-2, F-3) has developed generalized concentration and dosage models that are, in principle, applicable to all source types, to all environmental regimes, and to both microscale and mesoscale atmospheric processes. These generalized models were developed during programs sponsored by the Army (Refs. F-7, F-8) and the Pacific Missile Range (Ref. F-9). The focus of these models was on the transport and dispersal of pollutants between the ground and a height of 1 kilometer, but these concentration and dosage models were thought perfectly suitable for this project. The basic format of these generalized equations is based on the Gaussian plume model described by Pasquill (Ref. F-10, p. 190). Additional terms are included to account for the effects of mesoscale factors such as depth of surface mixing in the layers, wind shear in mixing layer, and elements that control vertical and lateral diffusion. The equations are also adjustable for source dimension and time of duration of emission.

Thayer at the Geomet Incorporation (Ref. F-4) formulated a diffusion model using similar concentration and dosage equations. However, this model is concerned with the mixing that occurs in the layer from 5 to 30 km above the ground. This program can be interfaced with the 0 to 5 km program designed by GCA.

These diffusion models are computer programs requiring basic input parameters. These can be divided into two categories: source inputs and meteorological inputs. The basic source information necessary to calculate concentrations and dosage fields is the amount of toxic material released, the rate at which it is released, the dimensions in space of the cloud after reaching equilibrium, and the physical and chemical properties of the materials in the stabilized cloud.

Large toxic propellant releases involving liquid fluorine would probably all be hot. An appreciable cold-fluorine spill would be reactive with the surroundings and likely become a hot spill. Research conducted on buoyant clouds, the type that results from a hot release, has been based on either small-scale or large-scale clouds like those generated by industrial smoke stacks or atomic explosions, respectively. An understanding of the growth and development of buoyant clouds would help in defining source parameters necessary for diffusion models. The best background information on instantaneous cloud sources is probably that of Morton, Taylor, and Turner (Ref. F-11). This work was modified by Braggs and was used to define sources in the GCA diffusion model.

In 1970 the Geomet Corporation undertook a theoretical and empirical study of the buoyant clouds that result from the exhaust plume of rocket-engine test firings. They constructed a physical-numerical model simulating rocket engine-exhaust cloud rise and growth. Geomet empirically analyzed films of static rocket engine test firings supplied by Marshall Space Flight Center. They then constructed a theoretical model that simulates many of the significant physical processes involved in the rise and growth of exhaust clouds. These included: (1) The maximum height to which the cloud ascends before it becomes environmentally stable, (2) The height of the cloud as a function of time after its formation, (3) The rise rate or vertical velocity of the cloud as a function of height or time after formation, (4) The temperature of the cloud as a function of height or time after formation, and (5) The growth rate of the cloud. The model formulations are general, applying to all types of buoyant clouds and various atmospheric conditions.

F.3. METEOROLOGICAL MODELLING

Cloud growth, development, and dissipation occur in three separate phases. First is the jet phase, where the exhaust cloud moves through the resisting air and is subjected to turbulence induced by its own motion. The second phase occurs when the jet-induced motion decreases in intensity and atmospheric turbulence becomes dominant. The mixing of exhaust gas with ambient air at this point proceeds at a rate determined by atmospheric properties. The maximum height to which the cloud rises before it becomes environmentally stable is reached during this phase. These two phases are the ones of interest in the exhaust cloud growth model. The third phase begins after the cloud has lost its effective independent motion and buoyancy; pure atmospheric diffusion now begins. A sound theoretical model on buoyant cloud growth and development is of use in diffusion cells because it helps to define necessary source parameters such as the dimensions in space of the cloud after reaching equilibrium.

The generalized equations for concentration and dosages also require meteorological inputs. These input parameters are principally determined from a detailed knowledge of the wind, temperature, and humidity fields within the reference air volume. Meteorological data at KSC have been extensively analyzed by GCA and others. Hill (Ref. F-12) reviewed the sea breeze circulation and described the characteristics of sea breeze fronts. Endlich *et al.* (Ref. F-13) used Jimisphere soundings to analyze features of vertical wind profiles in the layer of air extending from 200 m to 15 km above the ground. Smaller scale studies between ground level and 150 m have been done by several researchers. GCA analyzed flight data and daily readings from the 150 m KSC meteorological tower for a 2-year period. From this great quantity of data, average daily wind profiles and temperature gradients were determined for various seasons.

A multilayer atmospheric construction is used to describe the air mass around KSC. The atmosphere is often comprised of several layers of very distinct wind, temperature, and humidity fields. Large horizontal spatial variations in these regimes also occur in a single layer of the reference volume, primarily as a result of land-water interfaces. Vertical stratification is handled by applying the generalized concentration and

dosage models to individual layers in which the meteorological structure is reasonably homogeneous. Layer boundaries are placed arbitrarily at the points of major discontinuities in the vertical profile of wind, temperature, and humidity. For simplicity, it is assumed that no flux of materials occurs between layers as a result of turbulent mixing. However, provisions are made for the flux of materials across layer boundaries as a result of gravitational settling and precipitation scavenging. Step changes in the structure of a layer at some horizontal distance downwind are accommodated by stopping the transport and diffusion processes in the layer affected by the change in structure, calculating a set of initial source and meteorological model inputs, and then re-starting the transport process with new input.

The diffusion models are very general and require a great deal of sophisticated mathematics. They are not limited in applicability to KSC. However, before these diffusion models can be utilized at other locales, extensive meteorological studies must be carried out in the area in order to determine boundary layers and other meteorological inputs. The present programs can be used to estimate concentration and dosage fields for any toxic propellant, and both chemical and physical property parameters are built into them. The complexity of diffusion problems is very great, and the best models to date probably give only order of magnitude resolution estimates. Continued effort would probably lead to refinements in theory, particularly in the mesoscale interaction with bordering weather systems.

F.4. RECENT INVESTIGATIONS

Recent diffusion studies have focused on the dispersal of hydrochloric acid (HCl) from solid-propellant rocket launches. References F-14, F-15 are analytical predictions for Shuttle launches, which will use solid propellant rocket boosters. Measurements of HCl from earlier Titan 3 launches are correlated with theory in References F-16 through F-18, where various techniques are used, including ground measurements, photographs, rain-like water-droplet absorption, and aircraft measurements.

The FLOX/Atlas program estimated that 25,000 kg (55,000 lbm) of liquid fluorine in a 30 percent FLOX mixture would be needed to lift the Atlas booster. Estimates were made of the atmospheric concentrations of fluorides that would result from a vehicle conflagration involving the total 25,000 kg (55,000 lbm) of liquid fluorine. At a distance of 4.6 km (15,000 ft) the maximum fluorine concentrations range from 5.3 ppm in unstable air conditions to 180 ppm during very stable meteorological conditions. For a neutralized cold spill of 2,700 kg (6,000 lbm) of liquid fluorine, the maximum fluorine concentrations range from 0.2 to 6.2 ppm for unstable to very stable meteorological conditions, respectively. The pollutant concentrations resulting from a liquid fluorine mishap during the Shuttle program would be even less, since a maximum of about 1,350 kg (3000 lbm) of liquid fluorine would be carried by the payloads. Spill neutralization tests have indicated that the dispersal of the toxic cloud resulting from a 725 kg (1600 lbm) hot liquid fluorine spill is rapid. Maximum atmospheric fluorine concentrations were not high enough to cause fluorine intoxication of rats located only 46 m (150 ft) downwind from the spill site. These tests indicate that 1,350 kg (3000 lbm) of

liquid fluorine can dissipate with relative ease and that the public will not be exposed to fluoride concentrations exceeding established threshold values. The exposure can be further reduced by expanding the neutralization techniques but at an additional cost of operational time and money.

In Shuttle operations the development of a leak in the propellant system of the payload after launch must also be considered. One simple remedy for this situation would be to dump the liquid fluorine overboard into the upper atmosphere (Refs. 3-19 and 4-13). Recent concern has been expressed over the chemistry of pollutants in the upper atmosphere, particularly with ozone. At these altitudes the more energetic ultraviolet end of the spectrum has not been screened out. Consequently, many photochemical reactions not normally encountered take place. However, because of the low concentrations involved in a fluorine dump, the predicted effect on reducing ozone in the stratosphere is extremely small, and no adverse environmental impacts are predicted for the ionosphere should a dump occur there (Ref. 4-13).

F.5. CONCLUSION

The current design philosophy is to build a hermetically sealed container, which cannot leak under any of the environments anticipated, including launch loads, thermal environment, and a possible abort crash-landing load. Thus a dump no longer is a requirement.

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APPENDIX G

PROCEDURES FOR JPL EDWARDS TEST STATION "C" STAND

G.1. NORMAL OPERATIONS

Normal operations at the ETS "C" Stand are designed to permit firm scheduling of activities with a 100% confidence that people shall not be exposed to concentrations greater than the TLV/MAC (Threshold Limit Value/Maximum Allowable Concentrations for an eight-hour work day) of the toxic elements released from the engine exhaust or the venting of pressurants, as well as with a 99.8% confidence that personnel shall not be exposed to any toxic concentrations. This is insured by the use of a NaOH scrubber and/or charcoal burn barrels as neutralizing mediums. The predominant toxicant generated and to be neutralized is gaseous (HF) hydrogen fluoride. If all released toxicants could be directed into one or the other of the operational neutralizing mediums, there would be no test-control considerations needed with respect to wind conditions. This would not be practical nor economical for all potential fluorine system element failure modes. However, this technique, using a fume-hood, will be on as many test setups as practical to allow firm scheduling of the fluorine-type tests.

A second method of toxic release treatment, a water fog spray, is available to quickly reduce the atmospheric toxic concentration levels. However, this involves the additional handling and cleanup due to the resultant liquid HF. This technique results in all of the released fluorine being quickly and locally converted into HF vapor or liquid. The liquid pollutant would on necessity have to be kept from the groundwater table and directed into the NaOH pool for neutralization. Therefore, drainage and collection provisions must be provided as a part of this technique. This method is in service at "C" Stand, but the type of fog-spray nozzles, as well as the nozzle locations, is being reanalyzed for possible improvements in efficiency. The transformation of fluorine to gaseous HF also occurs naturally in atmospheric air due to humidity but over some more lengthy time interval and consequently over greater distances.

In any planned test or operation where the movement of fluorine is involved, the NaOH scrubber will be operating, and a preplanned audio page will precede any fluorine operation.

Tests or operations with fluorine at "C" Stand will be conducted under the following weather conditions:

At any time when satisfying any of the items below:

- (1) Wind - During regular station working hours, including any scheduled overtime

0.4 m/s (1 mph) or greater (definable wind)

From any direction where all nonrelated personnel can be cleared from the downwind area within the ETS facility, and

Breathing air available in quantity in the control center to permit movement of personnel to a safe area.

- (2) Wind - During all hours other than regular scheduled working hours

Any wind condition including zero velocity

Insure¹ toxic concentrations in any unrelated and occupied area \leq 3 ppm, and

Breathing air available in quantity in the control center to permit movement of personnel to a safe area.

- (3) Temperature with < 0.4 m/s (1 mph) wind (including zero velocity)

Insolation of -0.6°C (-1°F) or greater (meaning a larger negative number). This temperature is defined as the difference between a temperature measured at 16 m (54 ft) above ground level and at 2 m (6 ft) above ground level and expresses the thermal rise characteristics of the near-ground air

Insure¹ toxic concentrations in any unrelated and occupied area \leq 3 ppm, and

Breathing air available in quantity in the control center to permit movement of personnel to a safe area.

G.2. EMERGENCY OPERATIONS

There are possible situations which do not come under the definition of normal operations that must be considered. These are a consequence of certain facility or test-element failures which could result in a free release of liquid or gaseous fluorine and should be considered as unusual or emergency situations. It is emphasized that the controlling factor for these emergency situations is that no person will be subjected to toxic concentrations greater than the HF, 10 minute EEL (Emergency Exposure Limit) = 20 ppm.

¹Concurrence by the ETS Section Safety Representative is required for this condition.

Note: Any personnel detecting a strong fluorine odor should immediately move crosswind and to an area away from the source point, "C" Stand, as quickly as possible. They should first report the detection to the PBX operator immediately after leaving the area, secondly go to first aid, and thirdly report to their supervisors. "C" Stand personnel will immediately contact cognizant safety personnel, and further information will be transmitted to the PBX operator so that a preplanned audio page can be made.

G.2.1. Emergency Procedures for Regular Working Hours:

- (1) Discovery of a large propellant leak during a period of inactivity (Liquid spill or gross gas discharge will activate water deluge systems on fluorine propellant tanks if these areas are involved.):

If possible, the following two steps should be performed concurrently by two people:

Move all personnel in the immediate area to a crosswind and/or upwind location as fast as possible. If someone in a concentration of propellant vapors needs assistance, use a Scott Pack, and

Actuate the "Station Emergency Alarm" by dialing 115 and give the following page information:
"There is a propellant spill at C-Stand. All personnel evacuate to an area upwind of C-Stand. The wind is from the _____ @ _____ m/s (mph).

Notify the cognizant technical person of the situation; he will direct further action.

Neither emergency, safety, nor maintenance personnel will enter the stand area unless directed to do so by the cognizant technical person in charge of the emergency operations. If it becomes necessary for other personnel to enter the stand area, they will act only as directed by the cognizant technical person in charge.

Personnel who have been exposed to chemicals will be treated in accordance with the attached first-aid procedures as quickly as possible.

- (2) Discovery of a small propellant leak during period of inactivity (Fitting seepage, etc.):

Perform steps under G.2.1.(1) above. The judgment of the exposed person and the first-aid man will determine the extent of first-aid treatment.

- (3) Discovery of a propellant leak during propellant flow operations:

Emergency control circuits and link-wire alarm systems are automatically functional for the fluorine systems. Approved emergency procedures are immediately available for use by the cognizant person in charge in the event of an emergency.

G.2.2. Emergency Procedures for Other than Normal Working Hours:

- (1) If an emergency situation is apparent, perform the following:

Move all personnel upwind and away from any toxic vapors

Contact cognizant technical personnel, and

In no instance will anyone attempt to extinguish a fire or determine the cause of fumes until cognizant technical personnel are present to direct the operation.