NASA SP-3037

HANDLING AND USE OF FLUORINE AND FLUORINE-OXYGEN MIXTURES IN ROCKET SYSTEMS

SCHMIDT

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FLUORINE AND FLUORINE-OXYGEN MIXTURES IN ROCKET SYSTEMS

by Harold W. Schmidt
with assistance of Jack T. Harper

Lewis Research Center
Cleveland, Ohio

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FOREWORD

No other chemical propellant has excited more enthusiasm, more fear, more controversy, and less use than fluorine. Wildly cycling interest has spanned 20 years. There are people who have worked long with it and believe in its potential. There are those who decry the advantages available, and there are others who oscillate with the waves of enthusiasm for its use.

But fluorine has not changed. Its promise, behavior, and danger have remained consistent while engineers have come to understand it. Its promise has been repeatedly confirmed by high performance in rocket engine testing. Its behavior is all that can be expected from a source of high energy. Its danger is not of the unexpected and unexplained kind characterized by instability but is predictable and can itself be combated by fluorine's own characteristics.

Engineering understanding is the subject of this volume with the purpose to enlighten through the exposure of experience. Enlightenment may yet lead to the use of fluorine in rockets. The role of fluorine has still to reach fulfillment.

HOWARD W. DOUGLASS
Chief, FLOX Project Office

PREFACE

The NASA Lewis Research Center has conducted considerable research on fluorine for rocket application. This work, and the work of many others, has contributed technology sufficient to permit development of full-scale propulsion systems for fluorine and to establish ground-handling techniques for the safe use of fluorine.

The accumulated technology necessary for the practical application of fluorine as a rocket propellant is presented in this report. Physical and chemical characteristics peculiar to fluorine are considered in relation to specific areas in design and development of rocket systems and in testing and launch operations. The information given herein should provide the designer, the engineer, or the scientist with information peculiar to the characteristics of fluorine and fluorine-oxygen mixtures (FLOX) to enable him to work with these fluids intelligently and safely. An effort has been made to present practical information for facility and systems design, assembly, and operation that is directly applicable to specific fluorine or FLOX programs.

The use of fluorine demands engineering perfection. Primarily, it demands the highest standards in system design, maintenance, cleanliness, and operational techniques. These standards have been met consistently and without great difficulty in numerous experimental facilities where sustained test operations were performed. The experience thus gained has provided familiarity with the characteristics of fluorine; this in turn has bred the confidence that fluorine can be used as a rocket propellant, either alone or as an additive, within present technical capability.

However, although the technological base has been established to permit the use of fluorine in rockets, the problems of application in practice (i.e., for operational rocket launching) have not been fully explored. These problems are largely related to human factors, whether a large work force can be made to adhere to the necessary stringent operational practices and to the procedural discipline over the long time periods and throughout the complex tasks of launch operations.

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Chapter 1. Introduction

A major objective in the achievement of propulsion capability for future space missions is to provide capability for heavier payloads, higher mission velocities, and greater operational flexibility. Considering these requirements for improved propulsion, the propellants to be used should provide high specific impulse and high density, they should have smooth ignition characteristics and permit reliable multiple starting capability perhaps by virtue of being hypergolic, and they should offer combustion stability over wide ranges of pressure and propellant mixture ratios.

It is generally accepted that fluorine offers the highest performance of all stable chemical rocket oxidizers. The unusually high density of fluorine, coupled with the favorable propellant mixture ratios inherent in the stoichiometry of its combustion, decreases structural volume requirements and improves vehicle mass ratio.

The smooth hypergolic ignition obtained when using fluorine eliminates complex starting systems and offers simple, reliable multiple-start capability. A wide range of throttleability is probable for propulsion systems using fluorine. These characteristics offer a very useful operational flexibility with an inherent potential for improved reliability.

Although the advantages of fluorine have long been recognized, fluorine handling has remained controversial. The potential problems in handling fluorine tend to discourage its consideration for rocket systems.

The problems of handling fluorine have been misunderstood and exaggerated largely from some of the early attempts to use it as a propellant. Failures in early experiments resulted in a common belief that only a few selected materials could be used with fluorine because of its reactivity. Most experiences with fluorine system failures at the Lewis Research Center indicated that chemical ignition initiated between the fluorine and its containing system was the cause. Since the area in which ignition occurred was usually destroyed, the exact cause of failure was often obscured. However, after considerable experimental research, materials compatibility test programs, and a long history of successful facility operating experience, it has been shown that these early failures were caused by contamination. Primarily, contamination results from the use of improper system preparation and operating procedures. Secondary causes include improper choice of materials and/or system components and improper fabrication and assembly practices.

U. S. Air Force and NASA research and development programs have produced regeneratively cooled prototypes of flight-weight hydrogen-fluorine and hydrazine-fluorine rocket engines and supporting systems that show potential for high reliability. Rockets that use fluorine as the oxidizer have been designed, developed, and successfully demonstrated in captive tests up to the point of operational evaluation and development. These successes were based on a sound background of applied know-how in fluorine handling, systems design, and systems operation. NASA tests with fluorine-oxygen mixtures (FLOX, expressed as percent fluorine by weight in the mixture) indicate that current rocket systems can be adapted to use FLOX with low fluorine content without major system modification.

1.1 HISTORICAL BACKGROUND

Fluorine technology began in 1886 when Henri Moissan successfully produced fluorine by electrolyzing anhydrous hydrogen fluoride obtained by distillation from molten potassium acid fluoride (KHF_2). Present methods for producing fluorine are fundamentally the same, since no chemical reaction has been clearly shown to produce free fluorine, and all the processes now in use include the electrolysis of a liquid mixture of potassium fluoride and hydrogen fluoride. Much progress has been made in volume production of elemental fluorine, and within recent years fluorine has passed from being a laboratory curiosity to an item of industrial production and an object of investigation for rocket propulsion (ref. 1).

Prior to World War II, fluorine generation in laboratory quantities was difficult. Now fluorine is being produced on a large scale at a reasonable cost (ref. 1). During World War II, fluorine was produced on an industrial scale both in the United States and in Germany (ref. 2). In neither country were fundamentally new processes developed, but numerous difficult technical problems were resolved to obtain continuous, nearly trouble-free operation of the fluorine-producing cells. Work done in the United States for the Manhattan District yielded the basic knowledge to establish a fluorine technology. Since World War II private industry has made large contributions particularly in the areas of fluorine production and in industrial applications. Most major developments of fluorine rocket technology have been carried out under government-sponsored NASA and U. S. Air Force programs, however.

1.2 FLUORINE STUDIES AT LEWIS RESEARCH CENTER

Work to apply fluorine to rocketry at Lewis began with theoretical studies in 1948. Promising theoretical evaluation of fluorine with fuels such as JP-4 fuel and hydrogen was followed by firings of 100-pound-thrust engines in 1949. A major step in fluorine logistics was reached in October 1949 with the first delivery of fluorine in the liquid phase (prior to this time all shipments were made in the gaseous phase in 6-lb quantities at 400 psig). In the years 1951 to 1954, a number of studies were conducted culminating in the firing of low-thrust engines that used fluorine-diborane, fluorine-hydrazine, and fluorine-ammonia propellants. In January 1954, FLOX–JP-4 fuel firing established 10-percent FLOX as the minimum for *reliable* hypergolicity with JP-4 (this minimum depends on the fuel and ranges to about 30 percent for hydrogen). In 1955, FLOX–JP-4 fuel firings were made at much higher thrust levels (1000, 5500, and 10 000 lb). Later tests (1958 and 1959) with fluorine-oxidized engines involved thrust levels of 20 000 pounds, and the latest operations have included the firing of a FLOX-oxidized Atlas sustainer engine (standard thrust of about 57 000 lb with liquid oxygen–RP-1 propellants), and the successful operation of a modified RL-10 engine using hydrogen and fluorine to provide a nominal 15 000-pound thrust.

A Lewis facility (fig. 1–1) was designed specifically for high-energy propellants and equipped to accommodate substantially larger rockets

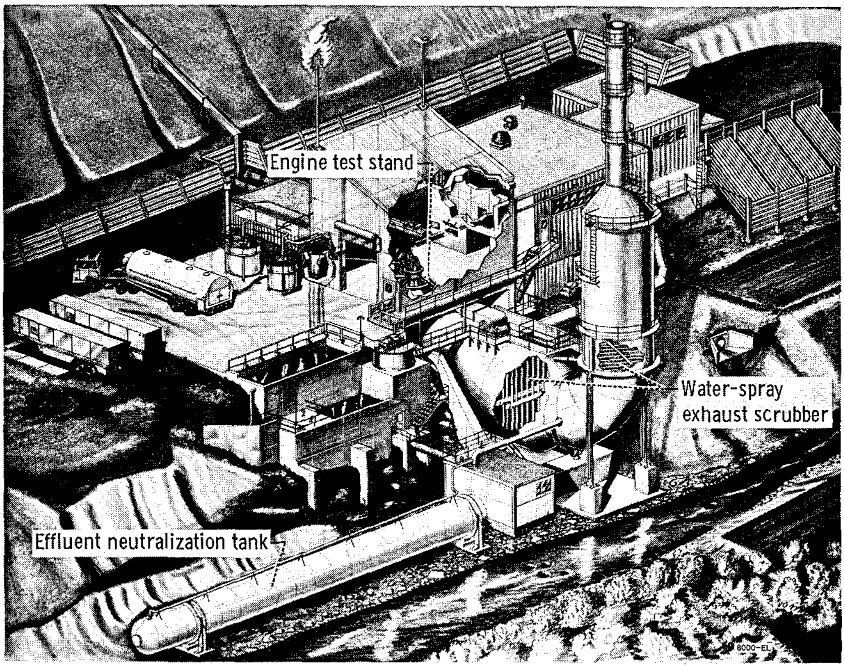

FIGURE 1–1.—Rocket engine research facility at Lewis.

(up to 50 000-lb thrust) than those previously tested. Since the facility is located close to a populated area, it includes a water-spray scrubber to cool the exhaust, to remove hydrogen fluoride from exhaust products, and to act as a muffler to reduce noise levels during operation. Disposal water from this facility is stored in a catch tank and treated to inert the hydrogen fluoride content. It is then later disposed of in a remotely located safe dumping area. An engine test stand is also located at the Lewis Plum Brook facility at Sandusky, Ohio (fig. 1–2). This test stand includes propellant tanks mounted above the rocket engine to simulate actual propellant feed systems.

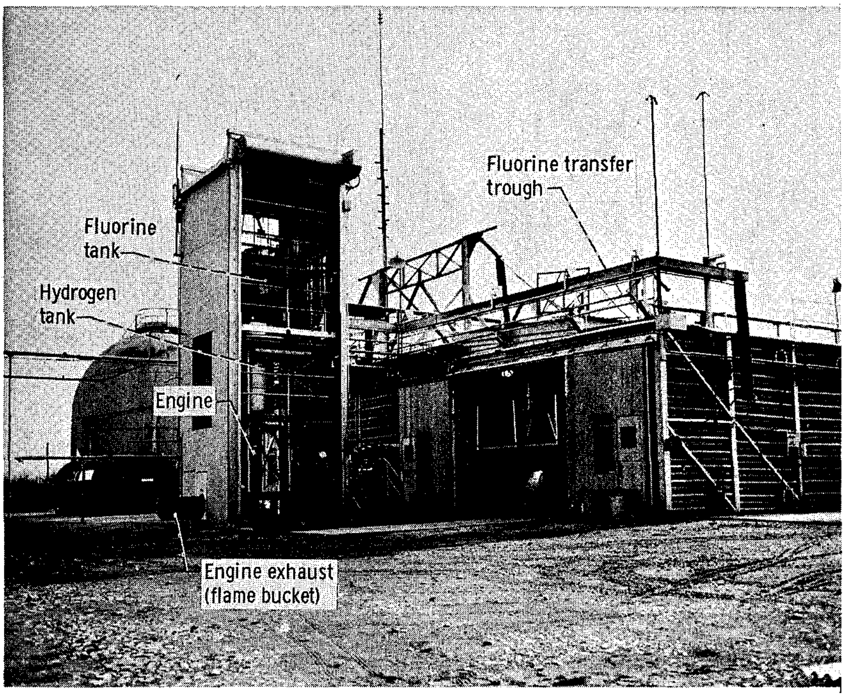

FIGURE 1–2.—Rocket test facility at Plum Brook.

The materials evaluation program at Lewis was begun in 1957. Included were compatibility studies to determine effects of pressure and flow velocity (of both fluorine and FLOX) on reactivity with metals and nonmetals. In addition, development and evaluation of design concepts were performed for quick disconnects, valves, and components for in-line installation in fluorine systems. The most recent work in this area has involved testing of standard rocket system components modified for use in FLOX concentrations with testing performed under actual operating conditions. Much of this work was conducted at two Plum Brook test areas, a turbopump and seal test facility, and a high-pressure high-flow test facility (fig. 1–3), which includes an associated area used for fluorine and FLOX spill tests described in chapter 3.

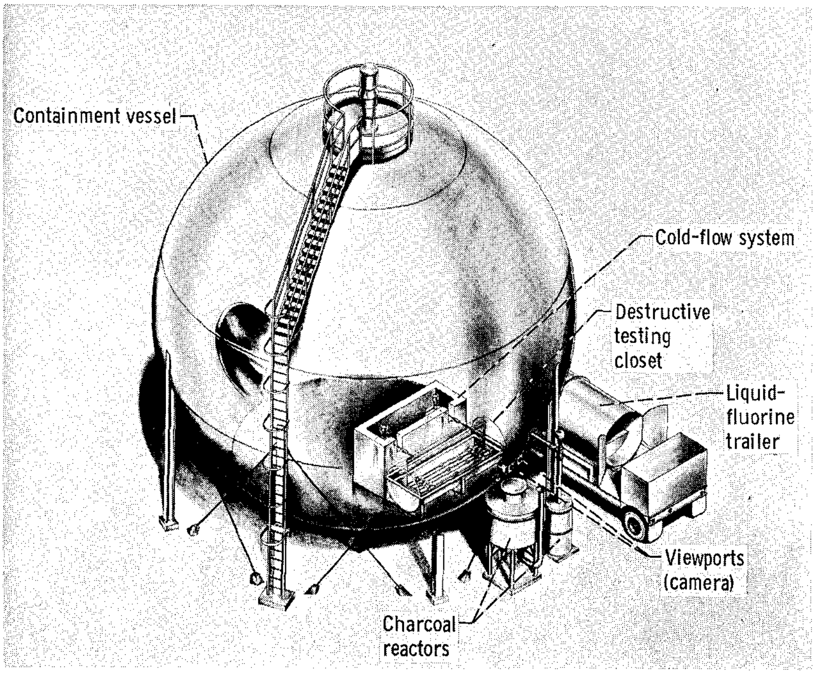

FIGURE 1–3.—High-pressure-flow test facility at Plum Brook.

Various disposal techniques were explored that involved the use of water, sodium carbonate, and charcoal as disposal agents for fluorine. A significant conclusion from these studies is that charcoal is an effective agent for reacting fluorine to an inert product. This use of charcoal was first reported in July 1957, and was followed by a report on design of charcoal reactors in January 1959. Tests to define effectiveness of water and other agents for inerting fluorine spills were also conducted in 1959.

Exploratory spill tests were made in 1964 by using small quantities (5 to 10 lb) of fluorine and FLOX on selected common materials to determine reaction characteristics. At the same time, diffusion studies were performed to predict patterns of reaction cloud diffusion. Results from these two preliminary studies were then used as a basis for a large-scale FLOX spill and diffusion study program during 1965 to establish test and launch operations criteria for fluorine oxidized vehicles. Inversion penetration, atmospheric hydrolysis of fluorine to hydrogen fluoride, and other characteristics of large-spill diffusion patterns were investigated (ref. 3). This study culminated in large spills of FLOX (3000 lb) on charcoal and JP-4 fuel.

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2. Simons, J. H.: Scientific and Utilitarian Value of Fluorine Chemistry. Ind. Eng. Chem., vol. 39, no. 3, Mar. 1947, pp. 238–241.
3. Thayer, J. R.; Hood, J. H.; Smith, T. B.; Beesmer, K. M.; and Miller, R. L.: Atmospheric Diffusion of Fluorine from Spills of Fluorine-Oxygen Mixtures. Rept. No. GD/C-DDB 66-001 (NASA CR-54926), General Dynamics Convair Division, Apr. 1966.

Chapter 2. Properties of Fluorine and Fluorine-Oxygen (FLOX) Mixtures

Most rocket fuels or oxidizing agents are highly reactive, possess hazardous properties, and require special and careful handling. Fluorine is unique as an oxidizer only because (1) it is one of the most reactive oxidizing agents, (2) it is toxic, and (3) its reaction with hydrogen-containing fuels produces a toxic by-product, hydrogen fluoride (HF). This chapter includes selected information on the physical and chemical properties of fluorine and various concentrations of FLOX (FLOX concentrations are expressed herein as percent liquid fluorine, by weight, in liquid-oxygen–liquid-fluorine mixtures). Conversion factors are included in the appendix. Additional information on fluorine and FLOX properties is presented in chapter 3, "Compatibility of Materials."

2.1 THERMODYNAMIC, CHEMICAL, AND PHYSICAL PROPERTIES OF ELEMENTAL FLUORINE

Appearance

Gaseous fluorine is yellow brown over a wide range of temperaturees and pressures. The liquid (depending on quantity or depth) varies from yellow to amber or light brown. The solid form at 96.37° R is yellow, and as the temperature is reduced it undergoes a change in crystalline structure at 81.99° R to produce a white solid.

Odor

Fluorine has a characteristic halogen odor, but a difference of opinion exists on the initial sensation (sec. 9.2.1). In many circumstances some hydrogen fluoride will be present or formed in the nasal passage that causes an odor with a slight similarity to that of ozone. Tests indicate that fluorine can be detected by its odor at concentrations of less than 1 part per million (ppm) (sec. 9.2.1).

Stability

Fluorine itself is a stable chemical. In other words, shock, spark, heat, etc., will not cause decomposition. Because of its extremely reactive nature, however, containers of fluorine should not be subjected to shock or high temperatures because (1) shock could damage the container and cause failure and (2) sufficiently high temperature could initiate reaction between the fluorine and its container.

Selected values for the physical properties of fluorine, together with oxygen, nitrogen, and helium, are given in table 2-I. The oxygen information is included because oxygen is a component of FLOX. Nitrogen and helium are included because they are intimately associated with fluorine systems as pressurants and coolants.

The properties of fluorine are presented in figures 2–1 to 2–12 and associated tables 2-I to 2-XIII, as shown in the INDEX TO PROPERTIES. The tabular information has been edited to remove some obvious anomalies found when the data were cross-plotted. More complete information on a single property is given in the reference cited.

2.2 PROPERTIES OF FLUORINE-OXYGEN (FLOX) MIXTURES

The physical and thermodynamic properties of FLOX are included in figures 2–14 to 2–21, which are based on the assumption that fluorine and oxygen behave as ideal fluids and that they follow Raoult's law. The vapor-liquid equilibrium diagram is shown in figure 2–13, and the vapor pressures for oxygen, fluorine, and FLOX mixtures are shown in figure 2–14. Variations in density in FLOX mixtures are shown in figure 3–15.

Small-scale tests at Lewis indicated that liquid oxygen and fluorine were completely miscible in all proportions and tend to be self-mixing (ref. 1). In addition, three-point concentration samplings were made 2 weeks after mixing 30-percent FLOX in a large tank, which confirmed the conclusions drawn from the small-scale miscibility tests. Since self-mixing occurs slowly under zero-heat-leak conditions, some mixing process, such as helium bubbling, is recommended in practice to assure immediate and thorough mixing, particularly in large storage systems.

2.3 INDEX TO PROPERTIES

	TABLE	FIGURE
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Dielectric constant	2-XII	2–11
Equilibrium constant of dissociation, $F_2 \rightleftarrows 2F$	2-XIII	2–12
FLOX (fluorine-oxygen mixtures):		
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TABLE 2-I.—SELECTED PHYSICAL AND THERMODYNAMIC PROPERTIES OF FLUORINE, OXYGEN, NITROGEN, AND HELIUM

Property	Fluorine [a]	Oxygen [b]	Nitrogen [c]	Helium [c]
Molecular weight	38.00	32.00	28.01	4.00
Normal boiling point:				
°R	153.036	162.302	139.18	7.668
°K	85.02	90.168	77.32	4.26
Density of liquid at normal boiling point, lb/cu ft	93.96	71.27	50.46	7.798
Density of vapor at normal boiling point, lb/cu ft	0.3519	0.2766	0.28	1.06
Heat of vaporization at normal boiling point, Btu/lb	71.514	91.6273	85.70	9.10
Entropy of vaporization, Btu/(lb)(°R)	0.48363	0.56454	0.614	1.15
Critical temperature:				
°R	259.128	277.848	227.27	9.37
°K	143.96	154.36	126.26	5.21
Critical pressure, atm	55.00	49.718	33.50	2.305
Critical density, lb/cu ft	29.437	26.840	19.60	4.13
Critical compressibility factor	0.375	0.292	0.29	0.3265
Specific heat of liquid (constant pressure and normal boiling point), Btu/(lb)(°R)	0.36697	0.40543	0.4856	1.150
Specific heat of gas (constant pressure and normal boiling point), Btu/(lb)(°R)	0.18305	0.218	0.264	1.241
Specific heat of gas (constant pressure), Btu/(lb)(°R)	0.19784 at 70° F	0.2193 at 70° F	0.249 at 80° F	1.248 at 70° F

[a] Refer to appropriate table and figure in this section for fluorine properties.

[b] Properties selected from refs. 2 to 5.

[c] Properties for nitrogen and helium selected from refs. 2 and 6 to 11.

TABLE 2-I.—SELECTED PHYSICAL AND THERMODYNAMIC PROPERTIES OF FLUORINE, OXYGEN, NITROGEN, AND HELIUM—Continued

Property	Fluorine [a]	Oxygen [b]	Nitrogen [c]	Helium [c]
Specific heat of gas (constant volume), Btu/(lb)(°R)	0.14565 at 70° F	0.1566 at 70° F	0.178 at 80° F	0.777 at 70° F
Ratio of heat capacities, C_p/C_v	1.3583	1.400	1.400	1.660
Thermal conductivity of liquid at normal boiling point, Btu/(hr)(ft)(°R)	0.0915	0.08525	0.0803	0.0016
Thermal conductivity of vapor at normal boiling point, Btu/(hr)(ft)(°R)	0.00415	0.00450	0.00546 at 180° R	0.00470
Critical thermal conductivity, Btu/(hr)(ft)(°R)	0.0231	0.025181	0.0225	0.0063
Absolute viscosity of liquid at normal boiling point, lb mass/(sec)(ft)	1.65×10^{-4}	1.28×10^{-4}	1.055×10^{-4}	2.0×10^{-6}
Absolute viscosity of gas at normal boiling point, lb mass/(sec)(ft)	3.725×10^{-8}	5.22×10^{-6}	3.72×10^{-6}	8.6×10^{-7}
Critical absolute viscosity, lb mass/(sec)(ft)	1.2337×10^{-5}	1.358×10^{-5}	1.72×10^{-5}	9.8×10^{-7}
Index of refraction of liquid at normal boiling point	1.200 (probably 5890 Å)	1.22503 at 5893 Å	1.2019 at 4358 Å	1.0246 at 5462 Å
Index of refraction of gas at 32° F and 1.0 atm	1.000214 at 5890 Å	1.00027 at 5893 Å	1.000294 at 4358 Å	1.000035
Dielectric constant of liquid at normal boiling point	1.51	1.46	1.43	1.0474
Dielectric constant of gas	1.43 at 85.02° K	1.000523 at 273.16° K	1.00058 at 273.16° K	1.000070 at 273.16° K

[a] Refer to appropriate table and figure in this section for fluorine properties.

[b] Properties selected from refs. 2 to 5.

[c] Properties for nitrogen and helium selected from refs. 2 and 6 to 11.

[d] Computed by using the equation $\eta = 5.023T^{0.647}$, where η is expressed in micropoises and T in °K (ref. 11).

TABLE 2-I.—SELECTED PHYSICAL AND THERMODYNAMIC PROPERTIES OF FLUORINE, OXYGEN, NITROGEN, AND HELIUM—Concluded

Property	Fluorine [a]	Oxygen [b]	Nitrogen [c]	Helium [c]
Normal melting or freezing point (liquid to solid I):				
°R	96.372	97.8336	113.70	4.49
°K	53.540	54.352	63.165	2.495
Triple point temperature, °K	53.54	54.352	63.16	----------
Triple point pressure, atm	2.184×10^{-3}	1.448×10^{-3}	0.1238	0.05
Triple point density, lb/cu ft:				
Solid	119.81	85.65	54.89	----------
Liquid	107.064	81.58	54.50	----------
Heat of fusion (liquid to solid I), Btu/lb	5.778	5.979	11.08	1.5
Entropy of fusion, Btu/(lb)(°F)	5.9913×10^{-2}	6.111×10^{-2}	0.173	----------
Transition temperature, °R:				
Solid I to solid II	81.99	78.796	63.98	----------
Solid II to solid III (O_2 only)	----------	42.058	----------	----------
Heat of transition, Btu/lb:				
Solid I to solid II	8.237	9.990	3.520	----------
Solid II to solid III	----------	1.261	----------	----------
Entropy of transition, Btu/(lb)(°R):				
Solid I to solid II	0.1005	0.12769	0.055	----------
Solid II to solid III	----------	.029458	----------	----------

[a] Refer to appropriate table and figure in this section for fluorine properties.

[b] Properties selected from refs. 2 to 5.

[c] Properties for nitrogen and helium selected from refs. 2 and 6 to 11.

TABLE 2-II.—DENSITY OF LIQUID AND GASEOUS FLUORINE

Temperature		Pressure, psia	Density		Reference
°R	°K		lb/cu ft	g/cu cm	
Liquid					
118.40	65.78	------	102.26	1.638	12
129.17	71.76	------	99.51	1.594	
134.87	74.93	------	98.51	1.578	
141.46	78.59	------	96.77	1.550	
146.10	81.72	------	95.64	1.532	
146.11	81.73	------	95.39	1.528	
151.81	84.34	------	94.52	1.514	
[a] 153.09	[a] 85.05	------	93.96	1.505	
156.44	86.91	------	93.49	1.496	
158.87	88.26	------	92.46	1.481	
159.30	88.50	------	92.65	1.484	
162.14	90.08	------	91.90	1.472	
164.79	91.55	------	91.02	1.458	
165.15	91.75	------	91.24	1.460	
170.51	94.73	------	89.52	1.434	
175.61	97.56	------	88.15	1.412	
180.38	100.21	------	86.84	1.391	
184.95	102.75	------	85.53	1.370	
Gas (saturated vapor)					
153.43	85.24	14.696	0.352	0.005636	13
162	90	23.80	.570	.009124	
171	95	40.31	.895	.01434	
180	100	62.55	1.355	.02171	
189	105	84.69	1.973	.03161	
198	110	122.06	2.824	.04524	
207	115	186.54	3.934	.06302	
216	120	252.76	5.391	.08636	
225	125	234.00	7.297	.11690	
234	130	419.21	9.801	.15700	
243	135	508.35	13.328	.21350	
252	140	676.44	19.134	.30650	
259.20	144	808.28	29.441	.47160	

[a] Normal boiling point from ref. 2. For selected boiling point, see table 2-I.

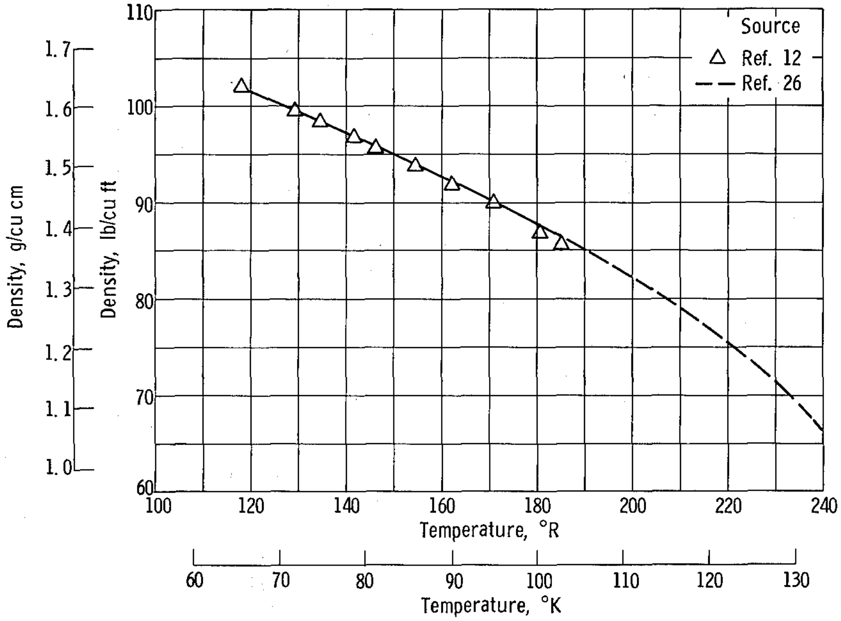


FIGURE 2-1.—Density of liquid fluorine.

TABLE 2-III.—VAPOR PRESSURE OF LIQUID FLUORINE

Temperature		Vapor pressure		Reference
°R	°K	psia	mm Hg	
96.41	53.56	0.032	1.67	14
98.98	54.99	.052	2.73	14
103.61	57.56	.115	5.94	14
107.82	59.90	.195	10.10	15
108.90	60.50	.249	12.89	14
114.28	63.49	.501	25.93	14
114.50	63.61	.509	26.30	15
117.00	65.00	.686	35.50	15
119.74	66.52	.930	48.12	14
120.69	67.05	1.000	51.70	16
123.66	68.70	1.261	65.20	15
125.23	69.57	1.630	84.30	14
125.98	69.99	1.780	92.05	15
130.61	72.56	2.701	139.67	14
131.13	72.85	2.772	143.35	15
135.02	75.01	4.043	209.10	15
137.70	76.50	4.999	258.50	16
138.91	77.17	5.422	280.40	14
139.52	77.51	5.598	289.50	15
142.83	79.35	7.377	381.50	15
143.96	79.98	7.780	402.35	15
144.05	80.03	7.981	412.75	14
147.69	82.05	9.997	517.00	16
149.51	83.06	11.681	604.12	14
150.17	83.43	11.758	608.10	15
152.24	84.58	13.980	722.98	14
[a]153.05	85.03	14.696	760.00	6
153.49	85.27	15.210	786.60	16
155.18	86.21	16.343	845.20	15
155.88	86.60	17.539	907.07	14
157.54	87.52	19.389	1 002.72	14
158.69	88.16	20.000	1 034.29	16
160.92	89.40	23.589	1 219.89	14
167.18	92.88	30	1 551.44	16
178.69	99.27	50	2 585.74	↓
186.70	103.72	70	3 620.03	
193.70	107.61	90	4 653.20	
196.18	108.99	100	5 171.47	
215.69	119.83	200	10 342.90	
228.19	126.77	300	15 514.40	
236.68	131.49	400	20 685.88	
243.68	135.38	500	25 857.40	
249.70	138.72	600	31 020.82	
254.68	141.49	700	36 200.30	
258.70	143.72	800	41 371.76	

[a] Normal boiling point from ref. 6. For selected boiling point, see table 2-I.

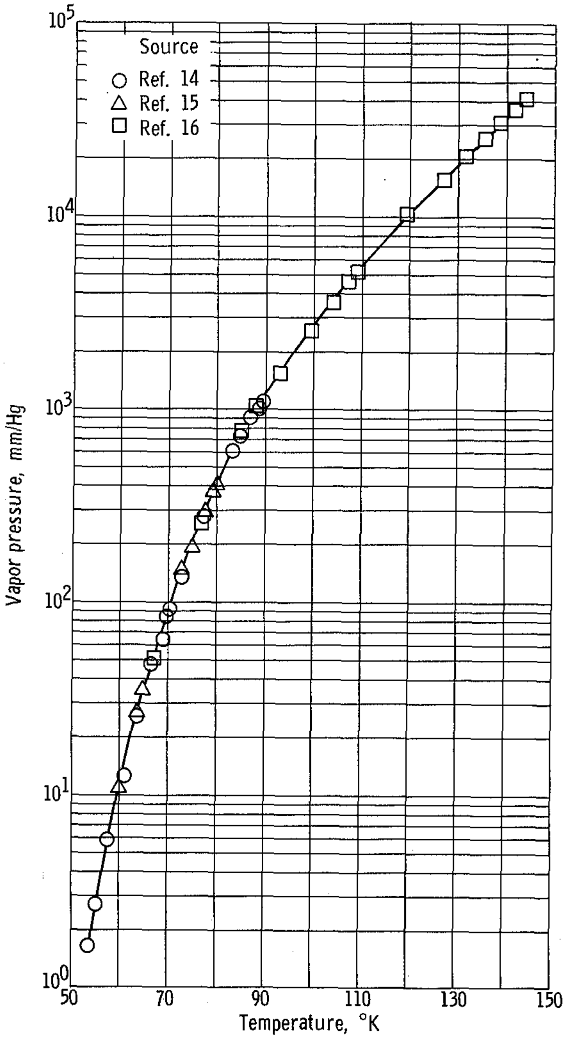


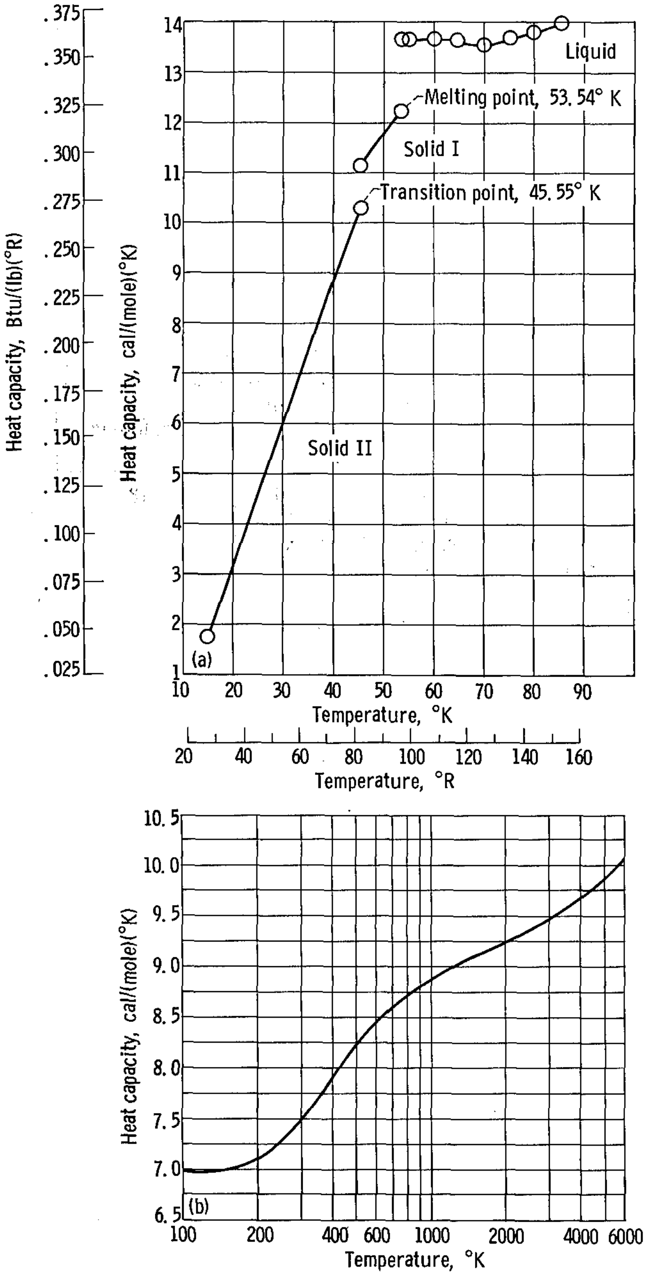
FIGURE 2-2.—Vapor pressure of liquid fluorine.

TABLE 2-IV.—HEAT CAPACITY OF FLUORINE

Temperature		Heat capacity		Reference
°R	°K	Btu/(lb)(°R)	cal/(mole)(°K)	
		Solid II		
27	15	0.0459	1.745	17
36	20	.0817	3.104	
45	25	.1213	4.609	
54	30	.1587	6.031	
63	35	.1954	7.427	
72	40	.2310	8.778	
81	45	.2668	10.142	
81.99	45.55	.2707	10.290	
		Solid I		
81.99	45.55	0.2925	11.120	17
90	50	.3102	11.792	17
96.37	53.54	.3213	12.210	17
		Liquid		
96.37	53.54	0.3604	13.700	17
99	55	.3603	13.698	
108	60	.3599	13.680	
117	65	.3579	13.607	
126	70	.3566	13.558	
135	75	.3589	13.642	
144	80	.3628	13.793	
153.04	85.02	.3669	13.948	
		Gas		
153.04	85.02	0.1830	6.9576	5
162	90	.1830	6.9578	
171	95	.1830	6.9582	
180	100	.1831	6.9587	
360	200	.1867	7.0970	
536.69	298.15	.1969	7.4869	
540	300	.1972	7.4949	
720	400	.2077	7.8941	
900	500	.2157	8.1985	
1 080	600	.2214	8.4184	
1 260	700	.2257	8.5788	
1 440	800	.2288	8.6990	
1 620	900	.2313	8.7923	
1 800	1000	.2332	8.8670	
1 980	1100	.2349	8.9287	
2 160	1200	.2363	8.9811	
2 340	1300	.2374	9.0266	
2 520	1400	.2385	9.0669	
2 700	1500	.2395	9.1034	

TABLE 2-IV.—HEAT CAPACITY OF FLUORINE—Concluded

Temperature		Heat capacity		Reference
°R	°K	Btu/(lb)(°R)	cal/(mole)(°K)	
2 880	1600	.2403	9.1368	5
3 060	1700	.2412	9.1679	
3 240	1800	.2419	9.1971	
3 420	1900	.2427	9.2248	
3 600	2000	.2434	9.2512	
3 780	2100	.2440	9.2767	
3 960	2200	.2447	9.3013	
4 140	2300	.2453	9.3252	
4 320	2400	.2459	9.3485	
4 500	2500	.2465	9.3713	
4 680	2600	.2471	9.3937	
4 860	2700	.2477	9.4157	
5 040	2800	.2483	9.4374	
5 220	2900	.2488	9.4589	
5 400	3000	.2494	9.4800	
5 580	3100	.2499	9.5010	
5 760	3200	.2505	9.5218	
5 940	3300	.2510	9.5425	
6 120	3400	.2516	9.5630	
6 300	3500	.2521	9.5834	
6 480	3600	.2526	9.6036	
6 660	3700	.2532	9.6238	
6 840	3800	.2537	9.6438	
7 020	3900	.2542	9.6638	
7 200	4000	.2547	9.6837	
7 380	4100	.2553	9.7036	
7 560	4200	.2558	9.7234	
7 740	4300	.2563	9.7431	
7 920	4400	.2568	9.7628	
8 100	4500	.2573	9.7824	
8 280	4600	.2578	9.8020	
8 460	4700	.2584	9.8216	
8 640	4800	.2589	9.8411	
8 820	4900	.2594	9.8606	
9 000	5000	.2599	9.8800	
9 180	5100	.2604	9.8994	
9 360	5200	.2609	9.9188	
9 540	5300	.2614	9.9382	
9 720	5400	.2619	9.9576	
9 900	5500	.2624	9.9769	
10 080	5600	.2630	9.9962	
10 260	5700	.2635	10.0155	
10 440	5800	.2640	10.0348	
10 620	5900	.2645	10.0541	
10 800	6000	.2650	10.0733	



(a) Liquid and solid (ref. 17).

(b) Gas (ref. 5).

FIGURE 2-3.—Heat capacity of fluorine.

TABLE 2-V.—HEATS OF VAPORIZATION OF FLUORINE

Temperature		Heat of vaporization		Reference
°R	°K	Btu/lb	cal/g	
153.43	85.24	71.526	39.736	13
162	90	69.252	38.473	
171	95	66.694	37.052	
180	100	63.947	35.526	
189	105	61.105	33.947	
198	110	57.931	32.184	
207	115	54.473	30.263	
216	120	50.636	28.131	
225	125	46.326	25.736	
234	130	41.163	22.868	
243	135	34.721	19.289	
252	140	25.437	14.131	↓
259.20	144	6.39	3.55	2

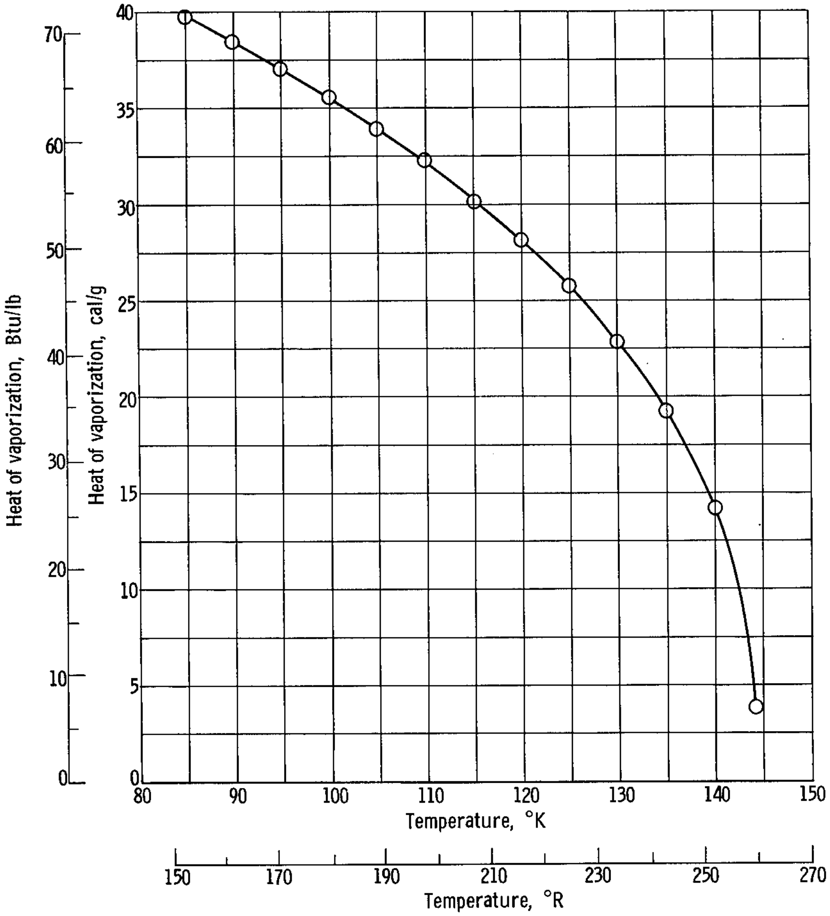


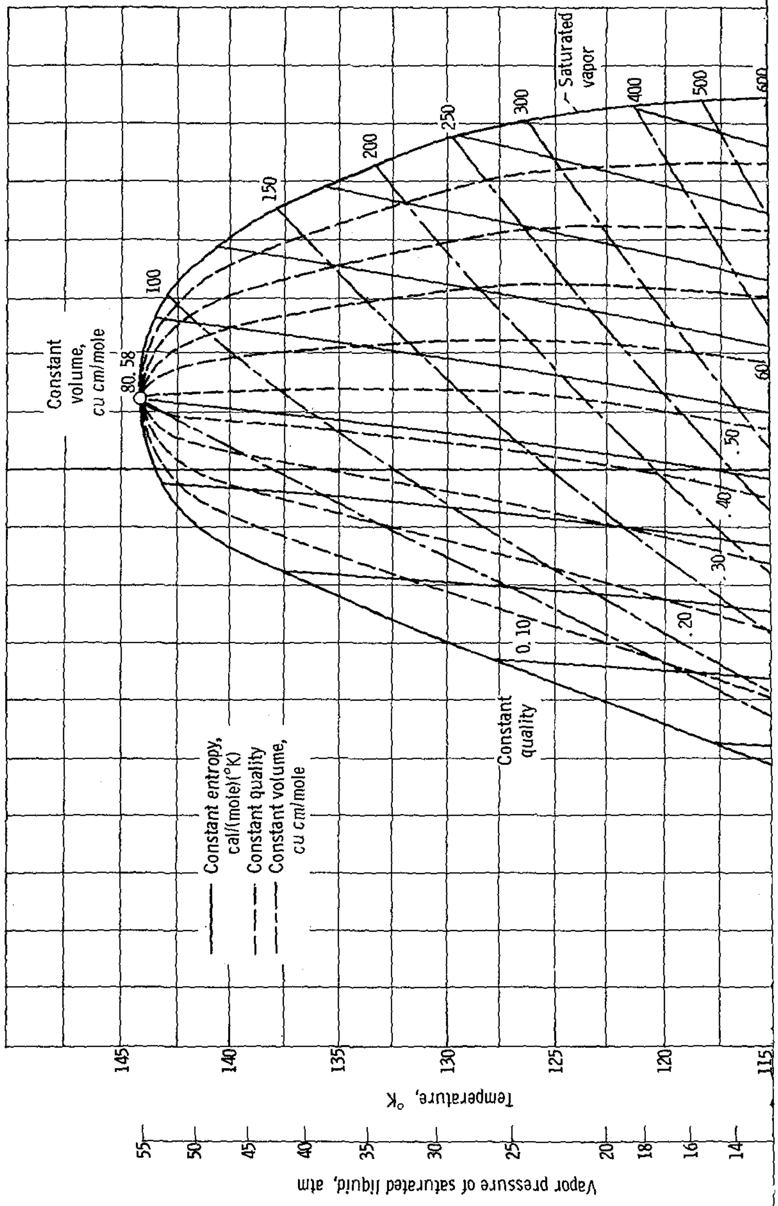
FIGURE 2-4.—Heats of vaporization of fluorine (ref. 13).

TABLE 2-VI.—ENTHALPY OF GASEOUS FLUORINE AT 1 ATMOSPHERE

Temperature		Enthalpy		Reference
°R	°K	Btu/lb	cal/mole	
153.04	85.02	27.975	590.59	5
162	90	29.616	625.24	
171	95	31.264	660.03	
180	100	32.912	694.82	
216	120	39.506	834.03	
252	140	46.108	973.42	
288	160	52.728	1 113.18	
324	180	59.380	1 253.60	
360	200	66.076	1 394.97	
396	220	72.830	1 537.56	
432	240	79.652	1 681.59	
468	260	86.550	1 827.21	
504	280	93.528	1 974.52	
536.69	298.15	99.931	2 109.7	
540	300	100.589	2 123.6	
720	400	137.067	2 893.7	
900	500	175.216	3 699.1	
1 080	600	214.602	4 530.6	
1 260	700	254.874	5 380.8	
1 440	800	295.809	6 245.0	
1 620	900	337.241	7 119.7	
1 800	1000	379.071	8 002.8	
1 980	1100	421.223	8 892.7	
2 160	1200	463.645	9 788.3	
2 340	1300	506.295	10 688.7	
2 520	1400	549.148	11 593.4	
2 700	1500	592.186	12 502.0	
2 880	1600	635.385	13 414.0	
3 060	1700	678.736	14 329.2	
3 240	1800	722.233	15 247.5	
3 420	1900	765.863	16 168.6	
3 600	2000	809.621	17 092.4	
3 780	2100	853.502	18 018.8	
3 960	2200	897.265	18 942.7	
4 140	2300	941.619	19 879.1	
4 320	2400	985.846	20 812.8	

TABLE 2-VI.—ENTHALPY OF GASEOUS FLUORINE AT 1 ATMOSPHERE—Concluded

Temperature		Enthalpy		Reference
°R	°K	Btu/lb	cal/mole	
4 500	2500	1030.177	21 748.7	5
4 680	2600	1074.622	22 687.0	
4 860	2700	1119.165	23 627.5	
5 040	2800	1163.819	24 570.1	
5 220	2900	1208.565	25 514.9	
5 400	3000	1253.429	26 461.9	
5 580	3100	1298.385	27 411.0	
5 760	3200	1343.436	28 362.1	
5 940	3300	1388.587	29 315.3	
6 120	3400	1433.837	30 270.6	
6 300	3500	1479.181	31 227.9	
6 480	3600	1524.625	32 187.3	
6 660	3700	1570.160	33 148.6	
6 840	3800	1615.793	34 112.0	
7 020	3900	1661.522	35 077.4	
7 200	4000	1707.344	36 044.8	
7 380	4100	1753.258	37 014.1	
7 560	4200	1799.271	37 985.5	
7 740	4300	1845.373	38 958.8	
7 920	4400	1891.570	39 934.1	
8 100	4500	1937.833	40 911.4	
8 280	4600	1984.245	41 890.6	
8 460	4700	2030.721	42 871.8	
8 640	4800	2077.288	43 854.9	
8 820	4900	2123.950	44 840.0	
9 000	5000	2170.701	45 827.0	
9 180	5100	2217.548	46 816.0	
9 360	5200	2264.484	47 806.9	
9 540	5300	2311.510	48 799.7	
9 720	5400	2358.631	49 794.5	
9 900	5500	2405.847	50 791.3	
10 080	5600	2453.148	51 789.9	
10 260	5700	2500.543	52 790.5	
10 440	5800	2548.029	53 793.0	
10 620	5900	2595.610	54 797.5	
10 800	6000	2643.275	55 803.8	


Constant volume, cu cm/mole
80.58
100
150
200
250
300
Saturated vapor
400
500
600
.60
.50
.40
.30
.20
0.10
Constant quality
Constant entropy, cal/(mole)(°K)
Constant quality
Constant volume, cu cm/mole
145
140
135
130
125
120
115
Temperature, °K
55
50
45
40
35
30
25
20
18
16
14
Vapor pressure of saturated liquid, atm

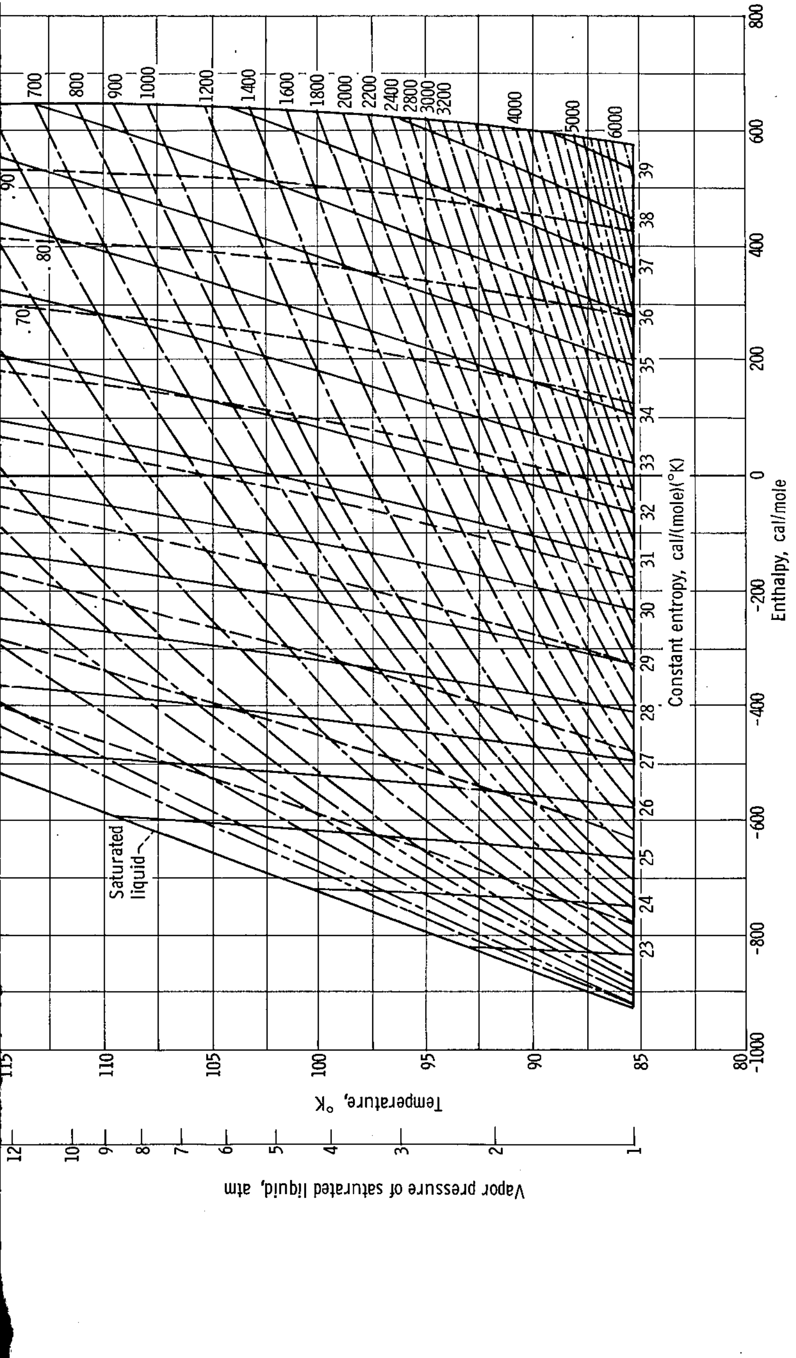


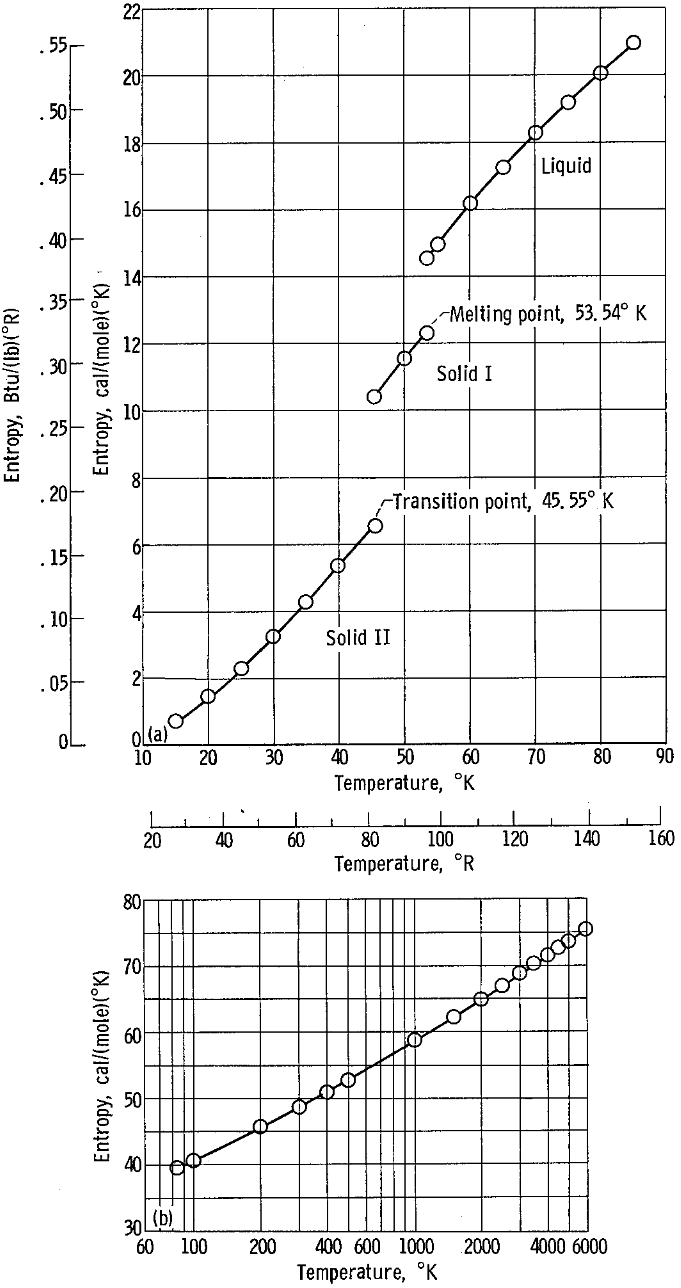
FIGURE 2-5.—Temperature-enthalpy diagram for fluorine (ref. 13).

TABLE 2-VII.—ENTROPY OF SOLID, LIQUID, AND GASEOUS FLUORINE

Temperature		Entropy		Reference
°R	°K	Btu/(lb)(°R)	cal/(mole)(°K)	
Solid II				
27	15	0.0195	0.741	14
36	20	.0375	1.422	
45	25	.0600	2.276	
54	30	.0854	3.245	
63	35	.1126	4.281	
72	40	.1411	5.363	
81	45	.1703	6.475	
81.99	45.55	.1736	6.599	
Solid I				
81.99	45.55	0.2740	10.417	14
90	50	.3021	11.486	
96.37	53.54	.3238	12.308	
Liquid				
96.37	53.54	0.3837	14.586	14
99	55	.3934	14.955	
108	60	.4247	16.146	
117	65	.4535	17.239	
126	70	.4799	18.245	
135	75	.5046	19.182	
144	80	.5279	20.067	
153	85	.5500	20.907	
153.036	85.02	.5500	20.909	
153.036	(Vapor)	1.0334	39.287	
Gas				
153.04	85.02	1.0408	39.5665	5
162	90	1.0512	39.9625	
171	95	1.0611	40.3387	
180	100	1.0879	41.3590	
360	200	1.1980	45.5437	
536.69	298.15	1.2744	48.4460	
540	300	1.2756	48.4924	
720	400	1.3338	50.7051	
900	500	1.3810	52.5011	
1 080	600	1.4209	54.0164	
1 260	700	1.4554	55.3268	
1 440	800	1.4857	56.4805	
1 620	900	1.5128	57.5107	
1 800	1000	1.5373	58.4411	
1 980	1100	1.5600	59.2892	
2 160	1200	1.5801	60.0684	
2 340	1300	1.5990	60.7891	

TABLE 2-VII.—ENTROPY OF SOLID, LIQUID, AND GASEOUS FLUORINE—Concluded

Temperature		Entropy		Reference
°R	°K	Btu/(lb)(°R)	cal/(mole)(°K)	
2 520	1400	1.6167	61.4595	5
2 700	1500	1.6332	62.0864	
2 880	1600	1.6487	62.6750	
3 060	1700	1.6632	63.2298	
3 240	1800	1.6771	63.7547	
3 420	1900	1.6902	64.2527	
3 600	2000	1.7026	64.7265	
3 780	2100	1.7145	65.1785	
3 960	2200	1.7259	65.6106	
4 140	2300	1.7368	66.0246	
4 320	2400	1.7472	66.4220	
4 500	2500	1.7573	66.8041	
4 680	2600	1.7669	67.1721	
4 860	2700	1.7763	67.5270	
5 040	2800	1.7853	67.8698	
5 220	2900	1.7940	68.2014	
5 400	3000	1.8025	68.5224	
5 580	3100	1.8107	68.8366	
5 760	3200	1.8186	69.1356	
5 940	3300	1.8263	69.4289	
6 120	3400	1.8338	68.7141	
6 300	3500	1.8411	69.9916	
6 480	3600	1.8482	70.2618	
6 660	3700	1.8552	70.5252	
6 840	3800	1.8619	70.7821	
7 020	3900	1.8685	71.0329	
7 200	4000	1.8749	71.2778	
7 380	4100	1.8812	71.5172	
7 560	4200	1.8874	71.7513	
7 740	4300	1.8934	71.9803	
7 920	4400	1.8993	72.2045	
8 100	4500	1.9051	72.4241	
8 280	4600	1.9108	72.6393	
8 460	4700	1.9163	72.8504	
8 640	4800	1.9218	73.0573	
8 820	4900	1.9271	73.2605	
9 000	5000	1.9323	73.4599	
9 180	5100	1.9375	73.6557	
9 360	5200	1.9423	73.8381	
9 540	5300	1.9475	74.0372	
9 720	5400	1.9524	74.2232	
9 900	5500	1.9572	74.4061	
10 080	5600	1.9620	74.5860	
10 260	5700	1.9666	74.7631	
10 440	5800	1.9712	74.9375	
10 620	5900	1.9757	75.1092	
10 800	6000	1.9802	75.2783	



(a) Solid and liquid (ref. 14).

(b) Gas (ref. 5).

FIGURE 2-6.—Entropy of fluorine.

TABLE 2-VIII.—FREE-ENERGY FUNCTION OF FLUORINE

Temperature		Free-energy function, $-(F - H_0)$[a]		Reference
°R	°K	Btu/lb	cal/mole	
Solid II				
27	15	0.155	3.270	14
36	20	.408	8.620	
45	25	.843	17.800	
54	30	1.496	31.590	
63	35	2.386	50.365	
72	40	3.526	74.440	
81	45	4.926	103.995	
81.99	45.55	5.096	107.589	
Solid I				
81.99	45.55	5.096	107.589	14
90	50	7.406	156.350	
96.37	53.54	9.404	198.526	
Liquid				
96.37	53.54	9.404	198.526	14
99	55	10.423	220.055	
108	60	14.108	297.840	
117	65	18.064	381.355	
126	70	22.268	470.120	
135	75	26.701	563.700	
144	80	31.349	661.840	
153	85	36.200	764.235	
153.04	85.02	36.212	764.500	
Vapor				
153.04	85.02	36.231	764.840	14
Gas				
153.04	85.02	131.37	2 773.4	5
144	90	140.75	2 971.4	
180	100	159.85	3 374.7	
216	120	199.02	4 201.7	
252	140	239.30	5 052.0	
288	160	280.53	5 922.4	
324	180	322.58	6 810.2	
360	200	365.38	7 713.8	
450	250	475.20	10 032.3	
536.69	298.15	584.25	12 334.5	

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[a] Free energy minus chemical energy at 0° K for liquid and solid phases and at the boiling point for gaseous phases.

TABLE 2-VIII.—FREE-ENERGY FUNCTION OF FLUORINE—Continued

Temperature		Free-energy function, $-(F - H_0)$[a]		Reference
°R	°K	Btu/lb	cal/mole	
540	300	588.50	12 424.2	5
720	400	823.64	17 388.4	
900	500	1 068.19	22 551.4	
1 080	600	1 320.56	27 879.3	
1 260	700	1 579.59	33 347.9	
1 440	800	1 844.14	38 939.4	
1 620	900	2 114.46	44 639.9	
1 800	1000	2 389.11	50 438.3	
1 980	1100	2 667.97	56 325.4	
2 160	1200	2 950.67	62 293.8	
2 340	1300	3 236.92	68 337.1	
2 520	1400	3 526.47	74 449.9	
2 700	1500	3 819.09	80 627.6	
2 880	1600	4 114.58	86 865.9	
3 060	1700	4 412.78	93 161.5	
3 240	1800	4 713.53	99 510.9	
3 420	1900	5 016.71	105 911.5	
3 600	2000	5 322.18	112 360.6	
3 780	2100	5 629.85	118 856.1	
3 960	2200	5 939.61	125 395.7	
4 140	2300	6 251.38	131 977.6	
4 320	2400	6 565.07	138 600.1	
4 500	2500	6 880.60	145 261.5	
4 680	2600	7 197.91	151 960.4	
4 860	2700	7 516.93	158 695.5	
5 040	2800	7 837.60	165 465.4	
5 220	2900	8 159.87	172 269.1	
5 400	3000	8 483.68	179 105.3	
5 580	3100	8 808.99	185 973.2	
5 760	3200	9 135.75	192 871.7	
5 940	3300	9 463.93	199 800.0	
6 120	3400	9 793.47	206 757.3	
6 300	3500	10 124.35	213 742.6	
6 480	3600	10 456.52	220 755.3	
6 660	3700	10 789.95	227 794.7	
6 840	3800	11 124.62	234 860.2	
7 020	3900	11 460.49	241 951.0	
7 200	4000	11 797.53	249 066.5	
7 380	4100	12 135.72	256 206.3	
7 560	4200	12 475.04	263 369.8	
7 740	4300	12 854.45	270 556.4	
7 920	4400	13 156.93	277 765.7	
8 100	4500	13 499.46	284 997.2	

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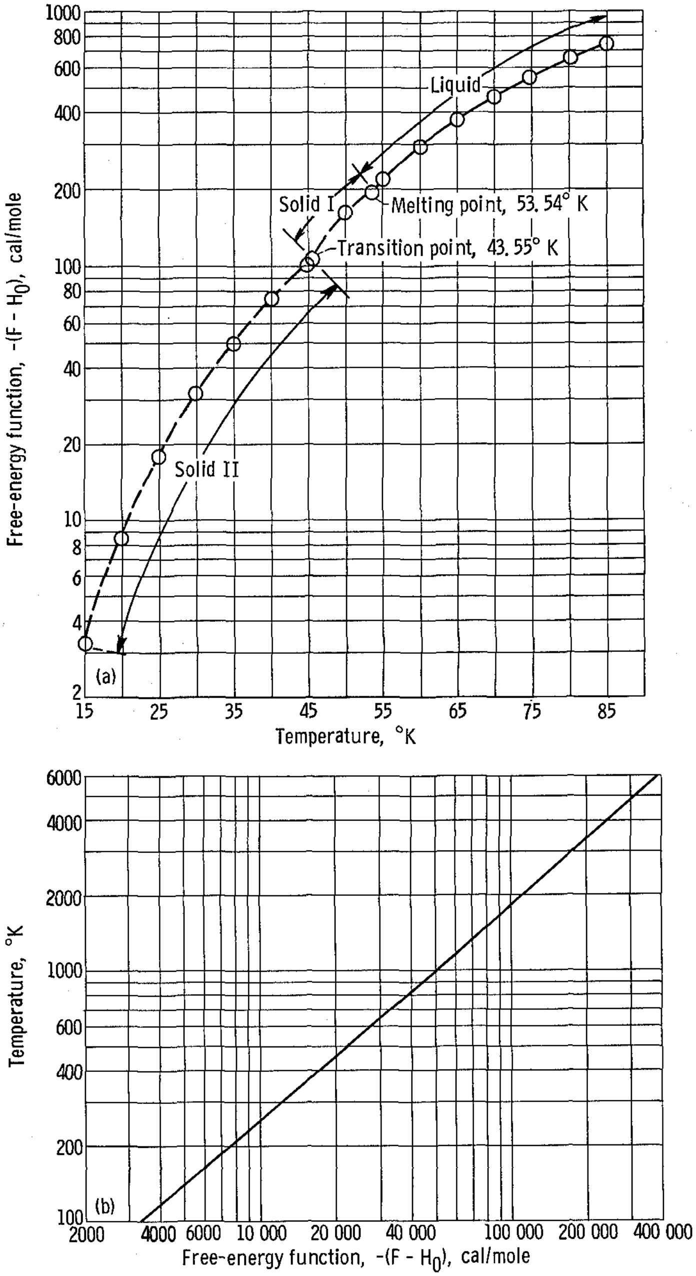
[a] Free energy minus chemical energy at 0° K for liquid and solid phases and at the boiling point for gaseous phases.

TABLE 2-VIII.—FREE-ENERGY FUNCTION OF FLUORINE—Concluded

Temperature		Free-energy function, $-(F - H_0)$[a]		Reference
°R	°K	Btu/lb	cal/mole	
8 280	4600	13 843.02	292 250.4	5
8 460	4700	14 187.60	299 524.9	
8 640	4800	14 533.16	306 820.3	
8 820	4900	14 879.69	314 136.2	
9 000	5000	15 227.18	321 472.3	
9 180	5100	15 575.60	328 828.1	
9 360	5200	15 924.94	336 203.3	
5 540	5300	16 275.19	343 597.6	
9 720	5400	16 626.32	351 010.7	
9 900	5500	16 978.33	358 442.1	
10 080	5600	17 331.20	365 891.8	
10 260	5700	17 684.91	373 359.3	
10 440	5800	18 039.45	380 844.3	
10 620	5900	18 394.82	388 346.7	
10 800	6000	18 750.99	395 866.1	↓

[a] Free energy minus chemical energy at 0° K for liquid and solid phases and at the boiling point for gaseous phases.



(a) Solid and liquid (ref. 14).

(b) Gas (ref. 5).

FIGURE 2-7.—Free-energy function of fluorine.

TABLE 2-IX.—VISCOSITY OF FLUORINE

(a) Liquid

Temperature		Viscosity		Reference
°R	°K	lb force/ (sec) (sq ft)	cP	
124.6	69.2	8.6526×10^{-6}	0.414	18
131.9	73.2	7.289	.349	
135.5	75.3	6.851	.328	
140.8	78.2	6.245	.299	
145.5	80.9	5.743	.275	
149.9	83.2	5.368	.257	

(b) Gas

Pressure, psia	Temperature		Viscosity		Reference
	°R	°K	lb force/ (sec) (sq ft)	cP	
14.657	156.2	86.8	1.1592×10^{-9}	0.555×10^{-4}	19
14.657	162.0	90.0	1.6020	.767	20
14.657	214.0	118.9	1.8275	.875	19
14.773	267.8	148.8	2.2551	1.080	19
14.773	302.2	167.9	2.5084	1.201	19
14.773	304.7	169.3	2.9742	1.424	20
14.754	346.1	192.3	2.8802	1.379	19
14.754	360.0	200.0	3.5089	1.680	20
14.754	383.6	213.1	3.1162	1.492	19
(a)	413.3	229.6	3.3647	1.611	19
(a)	448.0	248.9	3.6070	1.727	19
(a)	491.8	273.2	4.3714	2.093	19
(a)	520.4	289.1	4.8978	2.345	20
(a)	588.8	327.1	5.3197	2.547	20
(a)	768.1	426.7	6.4329	3.080	20
(a)	847.8	471.0	6.8715	3.290	20

[a] Approximately atmospheric pressure.

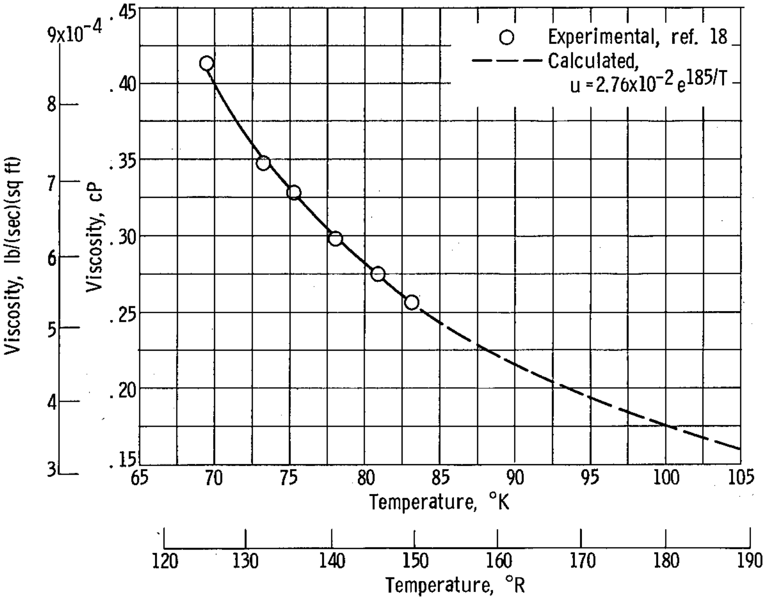


FIGURE 2-8.—Viscosity of liquid fluorine.

TABLE 2-X.—SURFACE TENSION OF LIQUID FLUORINE

Temperature		Surface tension		Reference
°R	°K	lb/ft	dynes/cm	
119.18	66.21	129.16×10^{-5}	18.85	21
124.56	69.20	122.65	17.90	18
126.47	70.26	121.28	17.70	21
127.13	70.68	119.23	17.40	21
128.16	71.20	119.23	17.40	18
129.69	72.05	116.62	17.02	21
131.76	73.20	114.43	16.70	18
132.03	73.35	115.53	16.86	21
135.16	75.09	112.99	16.49	21
135.34	75.19	111.55	16.28	21
135.54	75.30	111.01	16.20	18
137.52	76.40	108.95	15.90	18
138.87	77.15	107.79	15.73	21
140.76	78.20	105.52	15.40	18
143.82	79.90	101.48	14.81	21
145.80	81.00	100.04	14.60	18

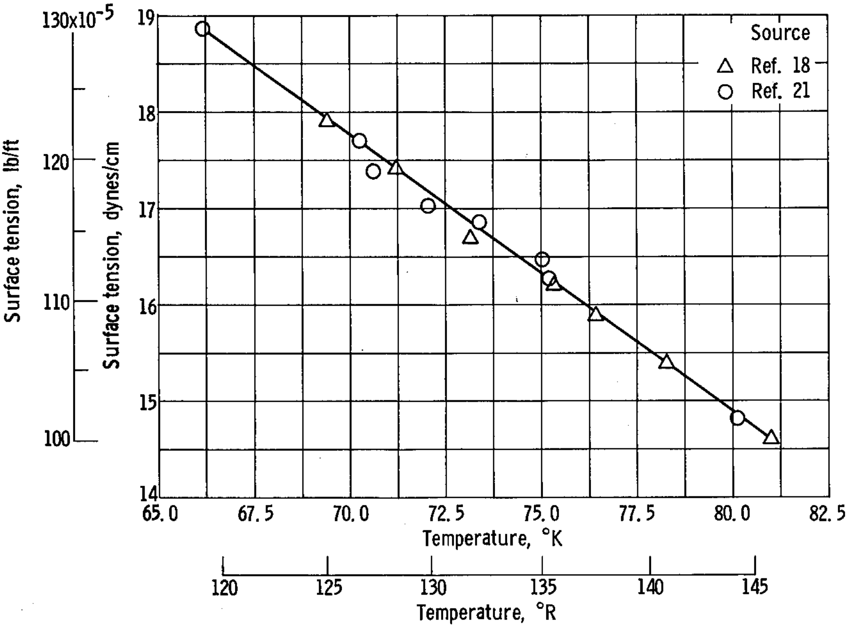


FIGURE 2–9. Surface tension of liquid fluorine.

TABLE 2-XI.—THERMAL CONDUCTIVITY OF FLUORINE

(a) Liquid fluorine

Temperature		Pressure		Thermal conductivity		Reference
°R	°K	psia	atm	Btu/(ft)(hr)(°R)	cal/(cm)(sec)(°K)	
146.7	81.5	37	3.52	8.83×10^{-2}	3.65×10^{-4}	22
147.1	81.7	87	6.92	8.95	3.70	
147.2	81.8	5	1.34	8.83	3.65	
147.2	81.8	187	13.72	9.00	3.72	
147.2	81.8	390	27.53	9.05	3.74	
153.0	85.0	37	3.52	8.56	3.54	
153.0	85.0	187	13.72	8.64	3.57	
166.0	92.2	20	2.36	7.89	3.26	
166.0	92.2	390	27.53	7.98	3.30	
169.7	94.3	187	13.72	7.62	3.15	
170.1	94.5	37	3.52	7.55	3.12	
188.1	104.5	87	6.92	6.85	2.83	
188.1	104.5	187	13.72	6.89	2.85	
188.1	104.5	328	23.31	6.99	2.89	
192.8	107.1	87	6.92	6.58	2.72	
206.1	114.5	187	13.72	5.95	2.46	
206.5	114.7	380	26.85	6.02	2.49	
208.6	115.9	306	21.82	5.95	2.46	
209.0	116.1	168	12.43	5.85	2.42	
221.4	123.0	250	18.01	5.32	2.20	
226.8	126.0	285	20.39	4.94	2.00	
230.4	128.0	340	24.13	4.69	1.94	

(b) Gaseous fluorine at 1 atmosphere

Temperature		Thermal conductivity		Reference
°R	°K	Btu/(ft)(hr)(°R)	cal/(cm)(sec)(°K)	
180	100	4.98×10^{-3}	0.0000206	23
270	150	7.76	.0000321	
360	200	10.55	.0000436	
450	250	13.16	.0000544	
493.2	273	14.32	.0000592	
540	300	15.55	.0000643	
630	350	17.80	.0000736	
720	400	19.91	.0000823	
810	450	21.99	.0000909	
900	500	24.02	.0000993	
990	550	26.08	.0001078	
1080	600	28.21	.0001166	
1170	650	30.26	.0001251	
1260	700	32.32	.0001336	
1350	750	34.30	.0001418	
1440	800	36.36	.0001503	

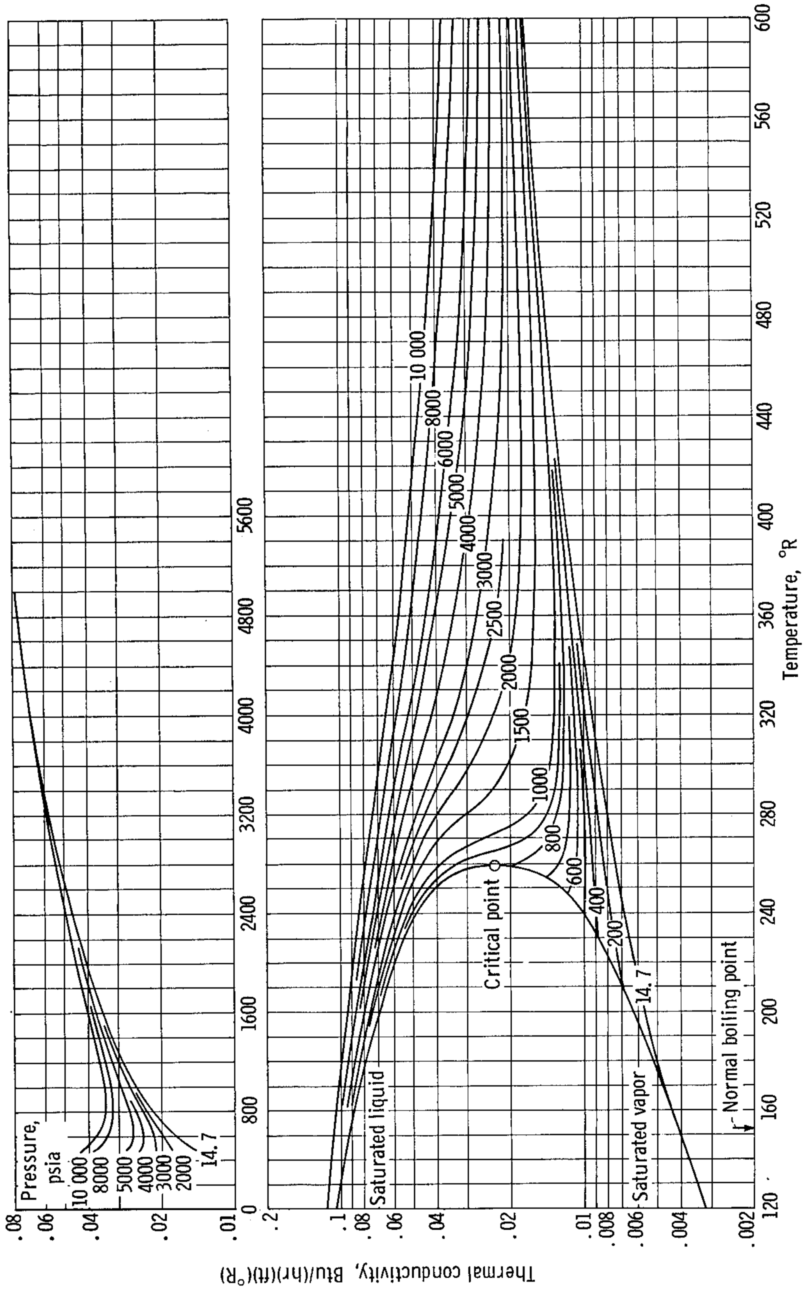


FIGURE 2-10.—Thermal conductivity of fluorine (ref. 23).

TABLE 2-XII.—DIELECTRIC CONSTANT OF LIQUID FLUORINE

Temperature		Dielectric constant	Reference
°R	°K		
103.32	57.40	1.567	24
108.92	60.51	1.561	
115.94	64.41	1.553	
123.07	68.38	1.546	
131.40	73.00	1.536	
135.02	75.01	1.533	
142.92	79.40	1.524	
149.78	83.21	1.517	

TABLE 2-XIII.—EQUILIBRIUM CONSTANT OF DISSOCIATION AS FUNCTION OF TEMPERATURE, $F_2 \rightleftarrows 2F$

Temperature		Equilibrium constant, K_p, atm	Reference
°R	°K		
536.6	298.1	2.74×10^{-48}	25
540	300	5.97×10^{-48}	
720	400	1.26×10^{-34}	
900	500	1.334×10^{-26}	
1080	600	3.11×10^{-21}	
1260	700	2.18×10^{-17}	
1440	800	1.69×10^{-14}	
1620	900	3.04×10^{-12}	
1800	1000	1.95×10^{-10}	
2700	1500	5.41×10^{-5}	
3600	2000	2.99×10^{-2}	
4500	2500	2.36×10^{-2}	
5400	3000	17.4×10^{-2}	
6300	3500	109×10^{-2}	
7200	4000	432×10^{-2}	
9000	5000	3019×10^{-2}	

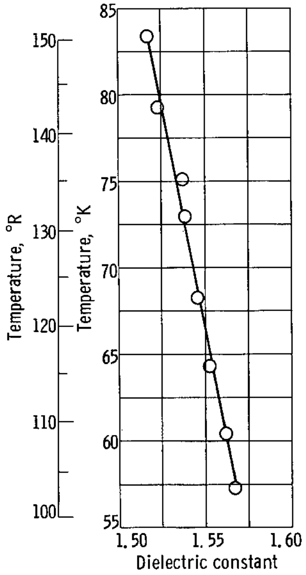


FIGURE 2-11.—Dielectric constant of liquid fluorine (ref. 24).

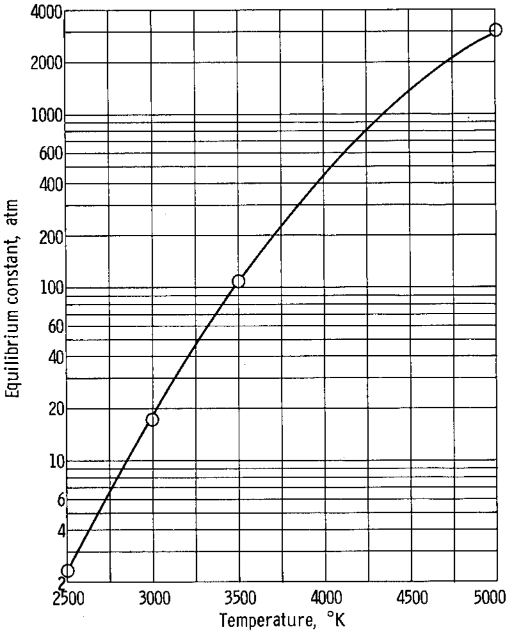


FIGURE 2-12.—Equilibrium constant of dissociation of molecular fluorine $F_2 \rightleftarrows 2F$ (ref. 25).

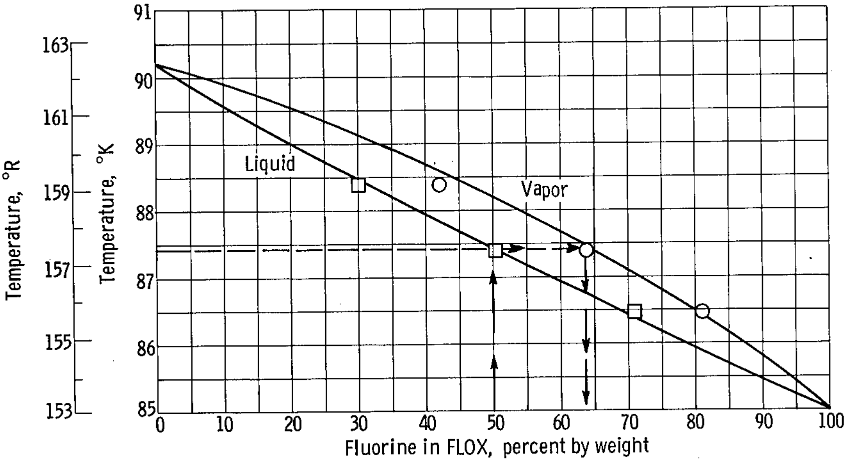


FIGURE 2-13.—Boiling point composition diagram for FLOX mixtures. A 50-percent FLOX mixture boils at approximately 87.42° K; the fluorine content of boiloff gas is approximately 63.7 percent. Oxygen vapor pressure is from reference 5, fluorine vapor pressure is from reference 14, and curves were calculated from Raoult's law.

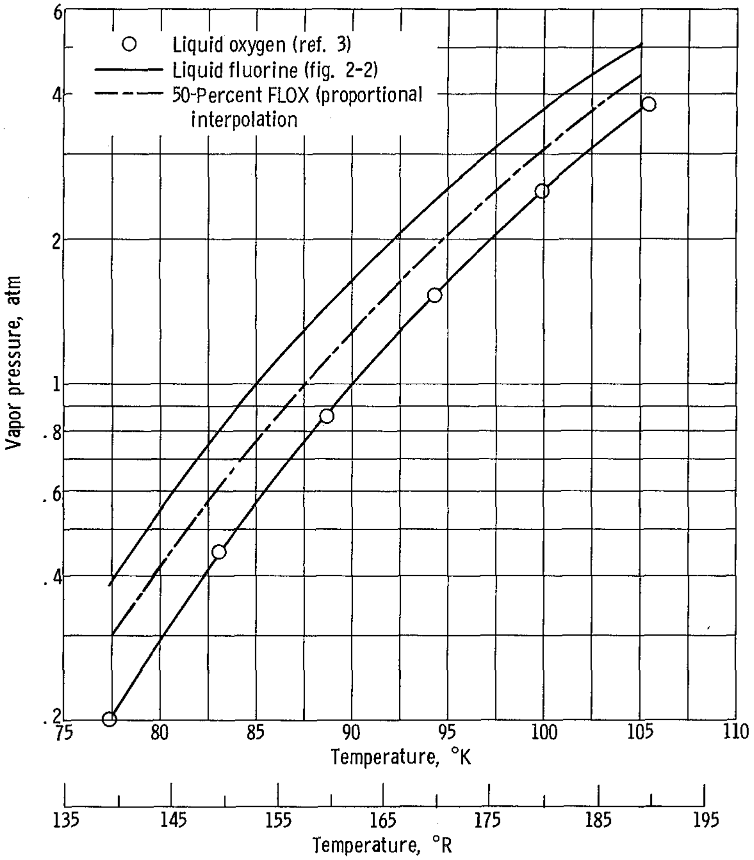


FIGURE 2–14.—Vapor pressure of liquid-fluorine–liquid-oxygen mixtures.

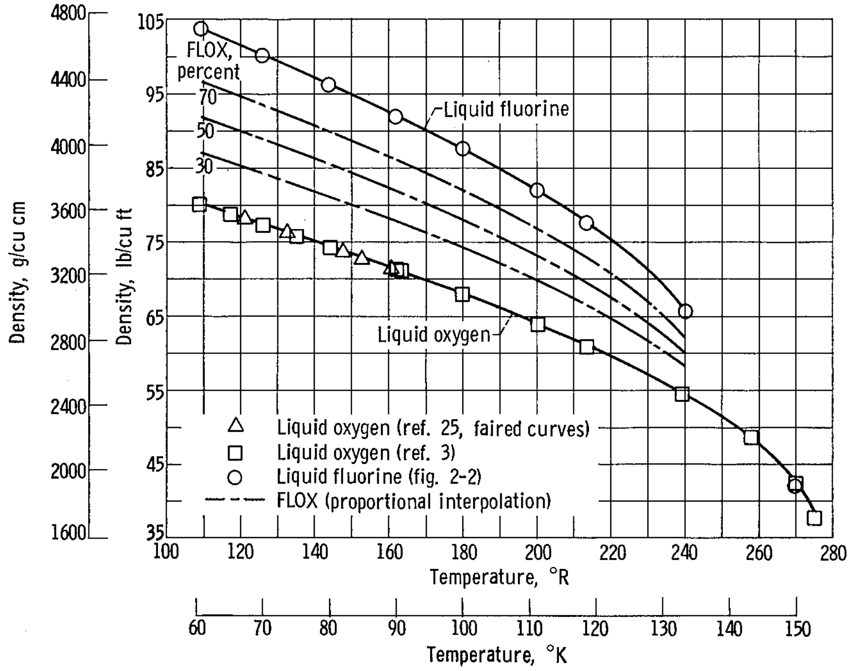


FIGURE 2-15.—Density of liquid-fluorine–liquid-oxygen mixtures.

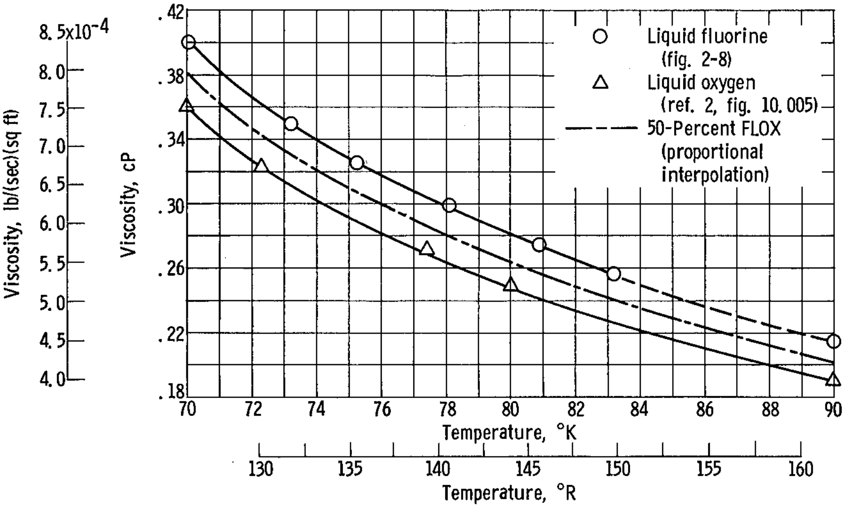


FIGURE 2-16.—Viscosity of liquid-fluorine–liquid-oxygen mixtures.

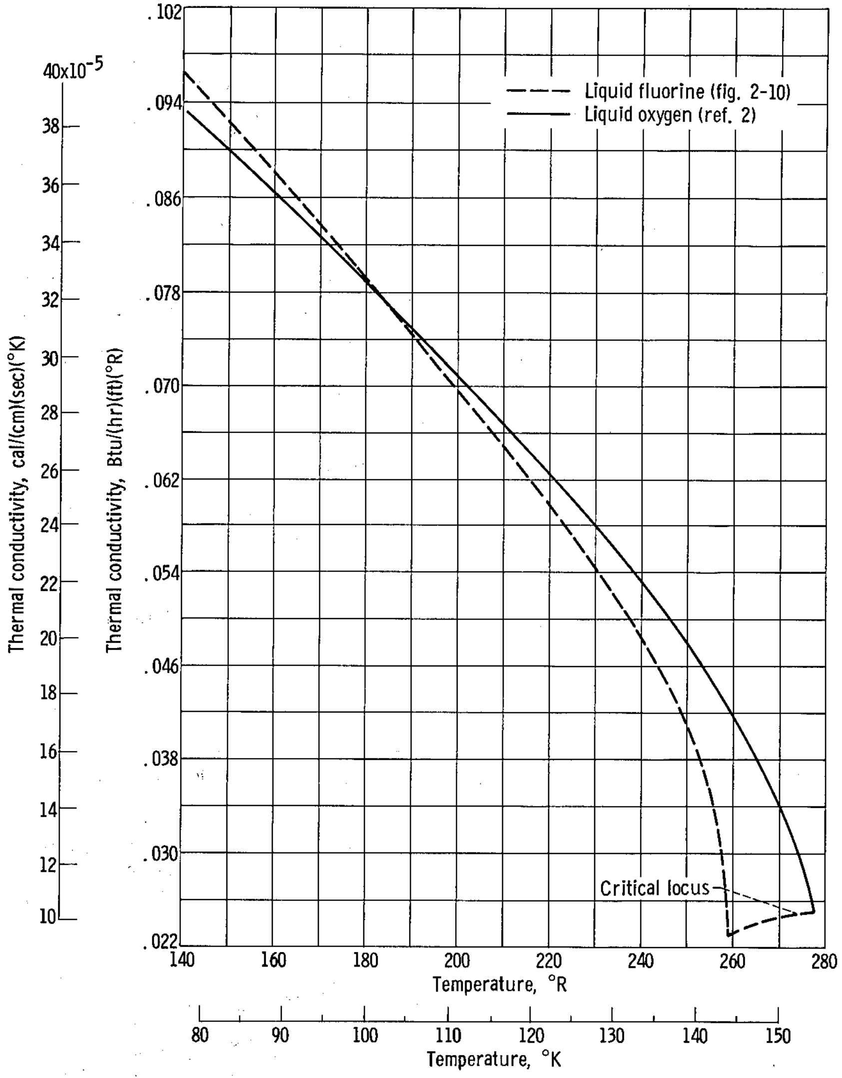


FIGURE 2-17.—Thermal conductivity of liquid fluorine and liquid oxygen.

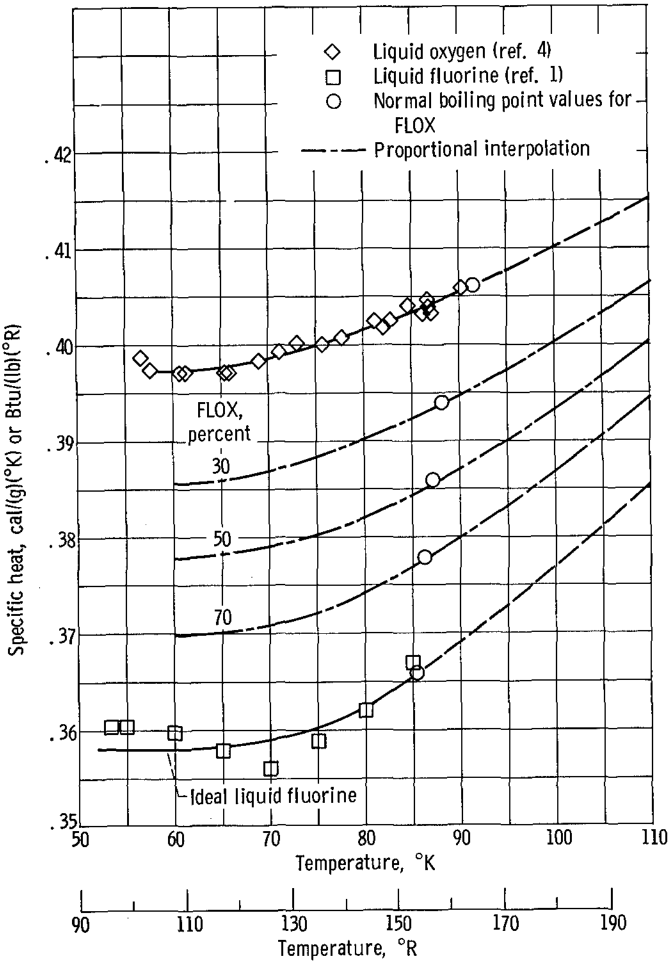


FIGURE 2-18.—Specific heat of liquid-fluorine-liquid-oxygen mixtures.

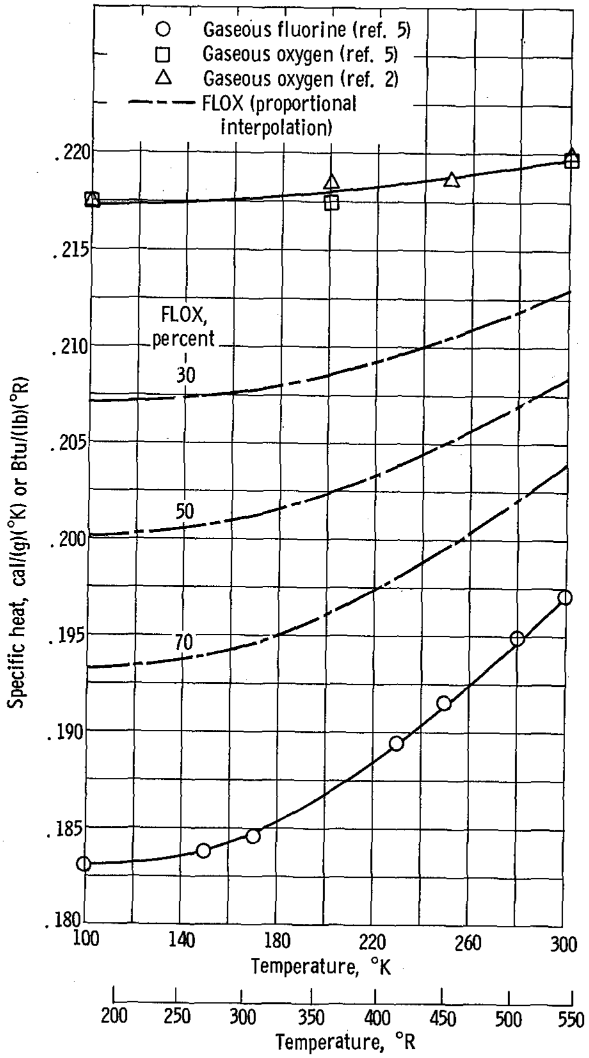


FIGURE 2–19.—Specific heat of gaseous-fluorine–gaseous-oxygen mixtures at 1 atmosphere from 100° to 300° K.

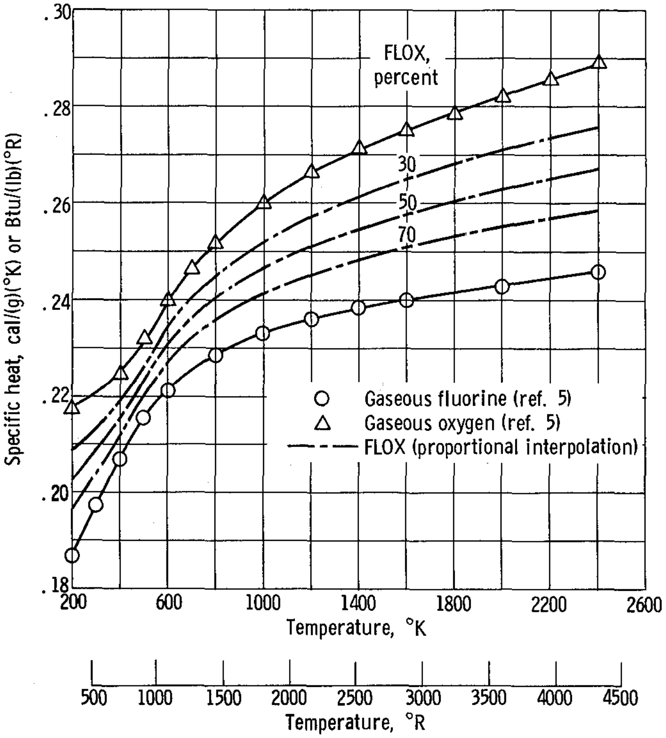


Figure 2-20.—Specific heat of gaseous-fluorine–gaseous-oxygen mixtures at 1 atmosphere.

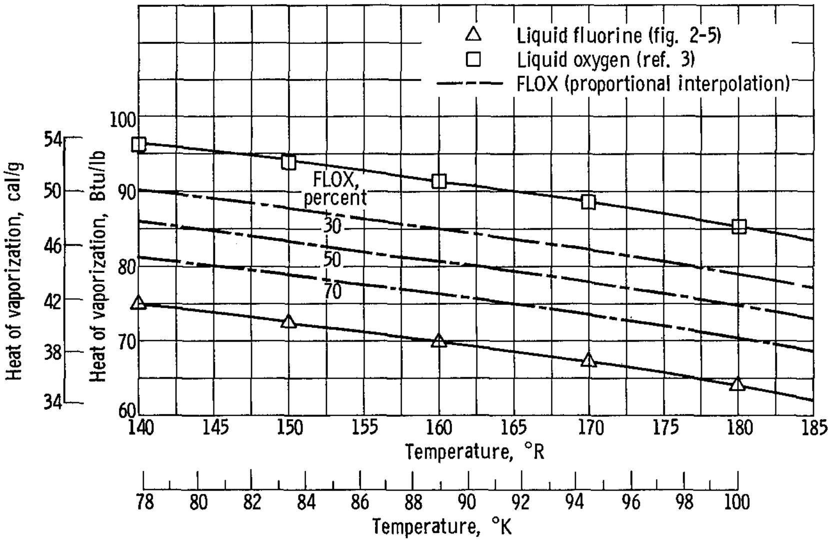


Figure 2-21.—Heat of vaporization of liquid-fluorine–liquid-oxygen mixtures.

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Chapter 3. Compatibility of Materials

In the early stages of fluorine technology development, a number of failures occurred that were characterized by a chemical ignition between the fluorine and its containment system. Since the zone where ignition occurred was usually consumed in the reaction, the exact cause of failure was often obscured. Evidence indicated that either the incompatibility of materials or contamination was the cause.

To define compatibilities of materials (metals and nonmetals), a series of investigations was conducted at Lewis with both fluorine and FLOX. Test results indicated that, with proper design and selection of materials, reliable systems can be built. Successful operation can then be assured by scrupulously maintaining the system free of contamination.

Most common metals of construction are compatible for use in a fluorine environment. Metals can burn with fluorine (or oxygen) only if the reaction is initiated by inducing combustion at the reaction zone by reaction of a secondary material (contaminant) or by localized addition of energy, such as friction, impact, or heating to ignition temperature. The choice of metals for use in fluorine systems is primarily based on property requirements for a given application, such as strength and shock resistance at cryogenic temperatures, welding and brazing or soldering characteristics, and thermal conductivity. Considerations peculiar to the fluorine environment would include exposure to friction (film characteristics), the ignition temperature of the metal in fluorine, and resistance to hot and cold hydrogen fluoride.

Many inorganic nonmetals can be used in limited applications with fluorine, including fused metal oxides and fluorides (cermets), Pyrex, and all fully fluorinated compounds. Partially fluorinated materials must be considered as a special case. Most notable of these are polytetrafluoroethylene (TFE) and polychlorotrifluoroethylene (PCFE) because of their resistance to reaction with fluorine and FLOX. These polymers have been used successfully for gaskets and seals in limited applications.

3.1 CHARACTERISTICS OF FLUORINE AND FLOX

3.1.1 Chemical

Fluorine is one of the most powerful oxidizing agents known and can react with practically all organic and inorganic substances. The few exceptions include the inert gases (under normal conditions of contact), fluorinated compounds in their highest state of oxidation, and a few fluorinated polymers. Even these polymers may burn in fluorine atmospheres if reaction is initiated. The reaction characteristics of FLOX are similar to those of fluorine, except that, at lower concentrations, FLOX mixtures tend to become less hypergolic as the percent fluorine in the mixture is decreased.

The activation energy required to initiate combustion with fluorine is generally much lower than that required for any other oxidant. Fluorine molecules in a fluorine system are always at a state of energy (with respect to a possible reactant) that is closer to their activation energy than other oxidizers in comparable systems. In fact, many materials react spontaneously on exposure to fluorine even at very low temperatures. In concentrations as low as 5 to 10 percent, FLOX ignites spontaneously with many materials and reacts with charcoal at concentrations of less than 1 percent fluorine (ref. 1).

Whether or not a substance will burn spontaneously on exposure to fluorine or FLOX depends on the conditions of exposure. The most important parameters affecting these conditions are

(1) Initial temperature and pressure of the system

(2) Thermal conductivity of the substance, if the reacting material is a solid

(3) Particle size (or surface area exposed, with respect to the mass of substance)

(4) Degree of dynamic or static exposure

(5) Concentration of fluorine in a mixture such as FLOX

3.1.1.1 *Temperature effects.*—Partially oxidized material may be fully oxidized by exposure to an oxidizing atmosphere at a suitable temperature; this is particularly true with fluorine (ref. 2). Fluorine has the highest oxidation potential of all the elements, and ordinary oxides may be considered to be in a state less than maximum oxidation since fluorine can replace the oxygen atoms with sufficient heat release to maintain combustion. Even firebrick (Al_2O_3-SiO_2) will burn in fluorine as was demonstrated at Lewis. A fluorine-hydrogen torch was used to heat the firebrick to a high temperature. The hydrogen was then shut off, and the brick began to burn vigorously with the fluorine.

The reaction of fluorocarbon polymers with fluorine is another example of reaction to a higher state of oxidation. Polytetrafluoroethylene $(CF_2\text{-}CF_2)_x$, for example, is a fluorocarbon chain polymer, but fluorine is capable of breaking the carbon-carbon bond and reacting the carbon to a higher degree of saturation, forming carbon tetrafluoride (CF_4). Reaction may be initiated by reaching the ignition temperature or by providing activation energy mechanically by impact, friction, high flow velocities, or by reaction with a contaminant.

3.1.1.2 *Pressure effects.*—A pressure increase can also promote reaction initiation with fluorine (ref. 3). A group of nonmetallic materials was tested under static conditions for compatibility with both liquid and gaseous fluorine at atmospheric pressure and 1500 pounds per square inch gage (ref. 4). In most of the tests in which no reaction occurred at atmospheric pressure, reaction was initiated by a pressure increase. These tests are discussed in section 3.3.1.

3.1.1.3 *Thermal conductivity.*—Materials with a high thermal conductivity resist ignition with fluorine more readily than materials with low conductivity. Combustion with fluorine will not occur if the heat of reaction can be dissipated from the point of ignition fast enough to maintain the temperature below the ignition point of the material involved (ref. 5). In an actual case, a brass flowmeter was installed in a stainless-steel, liquid-fluorine flow line (fig. 3–1). Ignition occurred at the flange connection between the two metals and resulted in destructive combustion of the flange materials as well as a considerable length of the stainless-steel line. At the surface of contact between the two metals, the steel material was reacted completely away, leaving the end of the brass fitting unaffected.

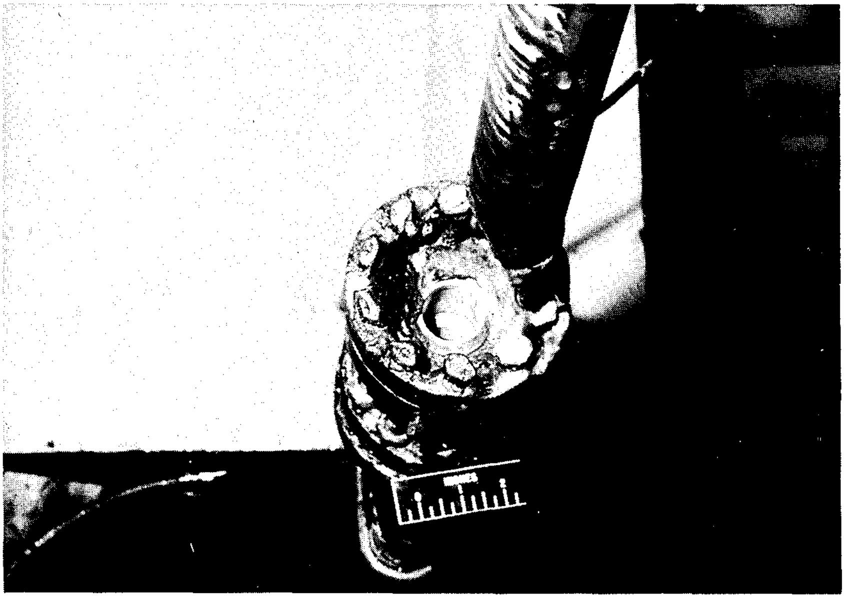


FIGURE 3–1.—Results of fluorine burnout between stainless-steel flange and brass fitting (ref. 2).

3.1.1.4 *Surface-area effects.*—Fluorine will react with the surface of nearly all solid materials. If the material is not spontaneously combustible (like most metals), surface reaction simply forms a fluoride film on or in the surface. If, however, the surface area exposed to fluorine is very large in proportion to its mass (e.g., fine-mesh screen or finely divided material such as powdered metal or spun glass) the heat of surface reaction may initiate combustion and the material becomes spontaneously reactive because the rate of heat dissipation is reduced.

3.1.1.5 *Dynamic and static effects.*—Tests at Lewis have shown that most materials are less resistant to reaction when exposed to a fluorine or FLOX environment under kinetic (flow) conditions than under static conditions. These tests show that

(1) Flow conditions contribute to the activation energy required to initiate reaction (i.e., reactivity increases with increase in rate of flow).

(2) Activation energy and/or flow conditions required to initiate reaction with FLOX is/are greater than that required for fluorine.

3.1.2 **Reactions**

3.1.2.1 *Reaction with water.*—Tests at Lewis (unpublished data) have shown that two types of reaction can occur with water: a slow noncombustive reaction and a fast combustion reaction. The occurrence of combustive reaction in these tests was determined to be a function of the water droplet size and the fluorine concentration. Water *vapor* will react combustively with fluorine and with FLOX as a function of the FLOX concentration. (FLOX concentration is expressed as the percent fluorine by weight in the mixture.)

Fluorine can be bubbled through water without combustion; however, at room temperature, the vapor above the liquid will sometimes ignite and burn with the fluorine. As ice, water shows no apparent reactivity with gaseous fluorine; however, an explosive reaction occurs when ice is exposed to liquid fluorine (or when liquid fluorine is dropped into water). This reaction is usually preceded by a variable and unpredictable induction period, which is affected by pressure and flow conditions.

The results of a fluorine-ice reaction are shown graphically in figure 3–2. The section of tubing shown was part of a fluorine flow system that, was evacuated while partly immersed in liquid nitrogen. When an unknown leak permitted air to get into the system, atmospheric moisture apparently condensed and froze in the tubing at the liquid-nitrogen level. The resulting explosion occurred when liquid fluorine contacted the ice during tank pressurization. *Water, in the form of moisture in the atmosphere or contained in pressurant or purge gases which were inadvertently introduced into a cryogenic fluorine or FLOX system, has been a major cause of fluorine system failures (see sec. 5.2.6.1).*

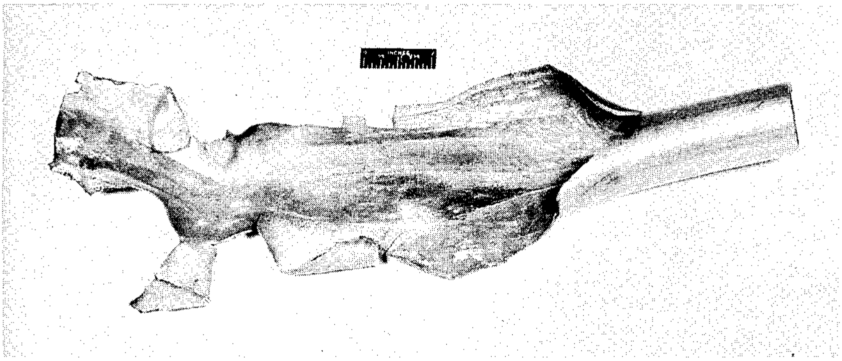


FIGURE 3-2.—Result of contamination in Monel propellant line carrying liquid fluorine (ref. 2).

Spill tests have demonstrated that 30-percent FLOX will not usually react combustively with water (refer to section 3.4). However, that some reaction does occur is shown by the decrease in pH (increase in acidity) in the water during these spill tests. Lewis tests involved dumping FLOX into a pan of water and into a showerhead spray. Unpublished data from Rocketdyne Inc. indicated that similar results occurred when FLOX was dumped into a water fog; a combustive reaction did not occur in either case. It is concluded that some FLOX concentration higher than 30 percent would be required to obtain reliable ignition with a water spray. In general, the reactivity of fluorine at any given concentration is a function of particle size, being more pronounced with fine water sprays or fogs than with coarse sprays. When the water present is in vapor form (e.g., humid air), the reactivity is a function of fluorine-moisture concentration, temperature, and rate of mixing or diffusion.

3.1.2.2 *Reaction with carbon.*—The reaction of fluorine with carbon has been the subject of considerable investigation. Experience at Lewis has shown that the characteristics of reaction-ignition obtained with carbon are determined largely by its state of crystallinity (ref. 6). In addition, the reactivity of carbon is dependent on its state of subdivision (particle size) and the temperature. Graphitic or crystallized carbon tends to react explosively with fluorine after an indeterminate induction period in a manner similar to that of ice; amorphous carbon and charcoal are highly hypergolic with fluorine and react smoothly at all conditions, even at very low fluorine concentrations (refer to section 3.3.3.6 and ref. 6).

The higher activation energy of crystalline carbon, as opposed to amorphous carbon, is probably a result of the carbon-carbon bond, which forms an orderly hexagonal pattern with a lamellar structure. If reaction is initiated, however, it is self-sustaining and produces the same reaction products as amorphous carbon does.

The reaction between fluorine and amorphous carbon is a most important and useful chemical reaction in the handling of fluorine or FLOX, since it provides a feasible method for reacting fluorine to a chemically inert and relatively nontoxic gas that can be vented to the atmosphere. Fluorine and carbon react to produce primarily carbon tetrafluoride (CF_4) with trace amounts of other fluorocarbons (e.g., C_2F_6).

The nontoxicity of fluorocarbons has been established in some limited experiments, and reference 7 states that "The fluorocarbons are probably the most non-toxic organic compounds possible. . . ." Reference 8 gives carbon tetrafluoride a toxicity rating of moderate (temporary effects, not severe enough to threaten life or cause permanent physical impairment). The source data for this rating are not given, and it may be that the indicated toxicity might take into account heating of the fluorocarbon above its decomposition temperature. Polytetrafluoroethylene $(C_2F_4)_n$ begins to dissociate at about 842° F (ref. 9) and these fluorocarbons have been in wide use as cooking utensil coatings without reported ill effects to users.

A recent experiment at the von Kármán Center of Aerojet-General Corporation (unpublished data) involved piping the effluent from a fluorine-charcoal reactor into a cage of laboratory rats. No ill effects to the animals were observed. In earlier studies (ref. 10), 2,2-difluoropropane (which is a less stable fluorocarbon than carbon tetrafluoride) was used as a substitute for nitrogen in the breathing atmosphere for guinea pigs. In these tests, no ill effects were observed either. Thus it seems reasonable to assume that, under the normal conditions of exposure that might be expected at a rocket facility, the carbon tetrafluoride effluent from a charcoal disposal system would be relatively nontoxic.

3.2 COMPATIBILITY OF METALS WITH FLUORINE AND FLOX

Many studies have been performed to determine the compatibility of various metals with fluorine and FLOX. There is considerable variation in the reaction of fluorine with the surface of metals reported in these studies, which was probably a result of the difference in experimental conditions employed, and particularly in the purity of fluorine used and the amount of hydrogen fluoride or other contamination present. Fluorine will form hydrogen fluoride when brought into contact with any hydrogen-bearing compound, including atmospheric moisture. In fact, the *primary* contaminant that must be carefully guarded against in fluorine systems is moisture. Thus, in maintaining fluorine and FLOX purity, it is vitally important to exclude all atmospheric contamination from fluorine or FLOX systems.

The following paragraphs summarize the results of various studies on the effect of fluorine or FLOX on the surface of metal materials.

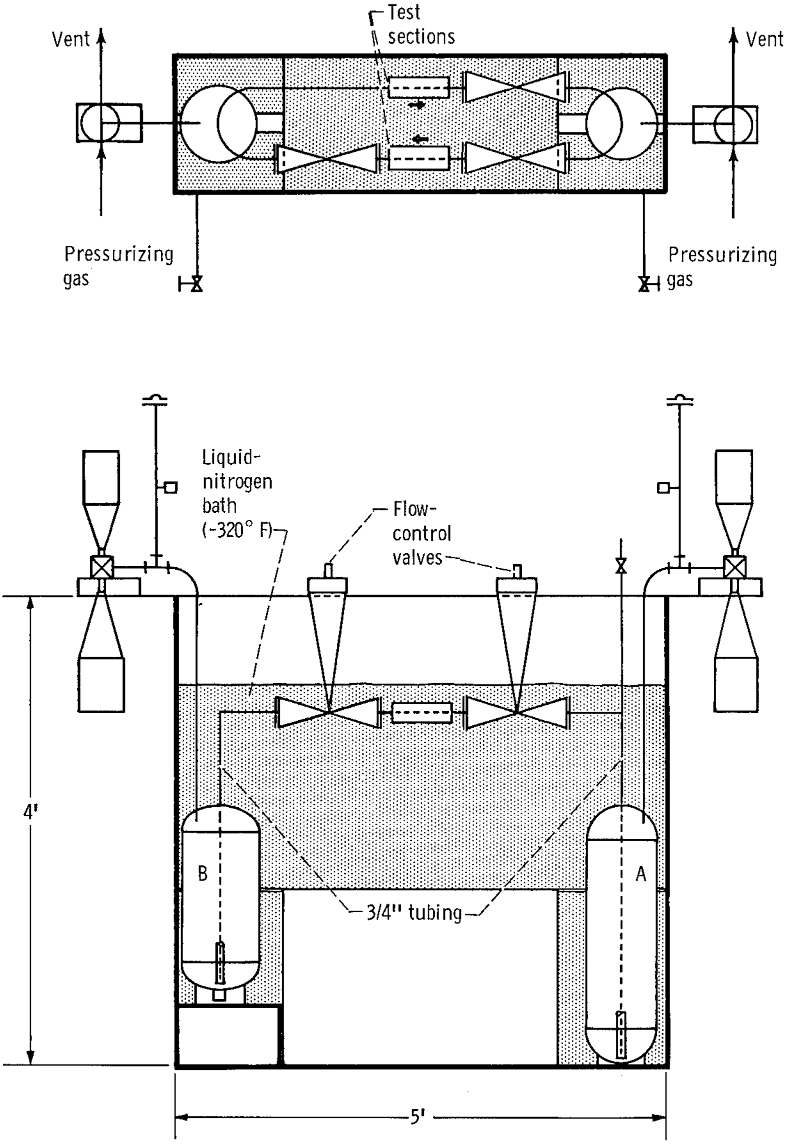
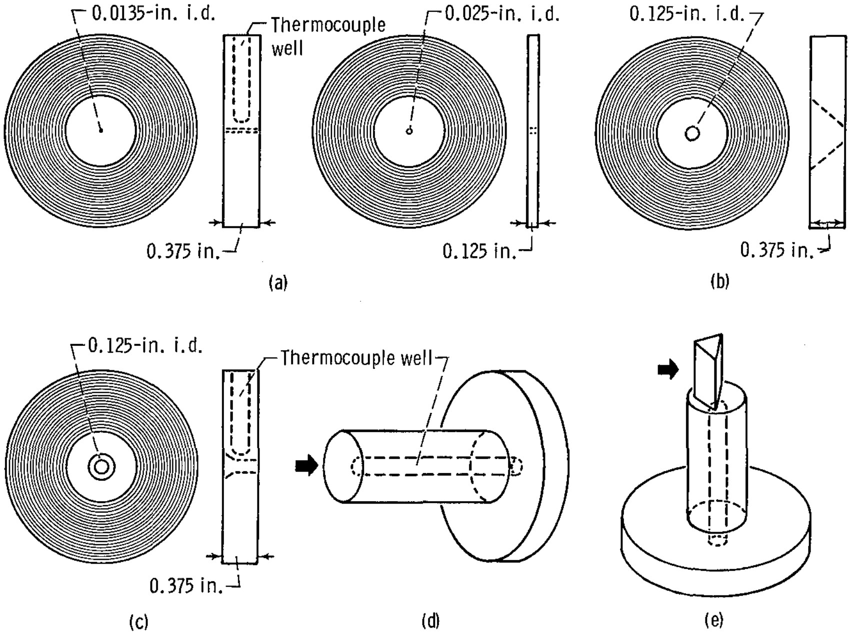


FIGURE 3-3.—High-pressure fluorine-flow apparatus.

3.2.1 High-Pressure High-Velocity Fluorine Flow Tests

In a series of tests (ref. 3) conducted at Lewis, specimens of several metals in various configurations were exposed to liquid fluorine under controlled conditions of flow and pressure in the test apparatus shown schematically in figure 3–3. The fluorine flow system consisted of two stainless-steel tanks (A and B) mounted in a liquid-nitrogen container. A pair of 3/4-inch stainless-steel flow lines with appropriate control valves were installed between the tanks so that fluorine could be cycled at high pressure from one tank to the other through alternate paths.

In these tests, metals generally considered suitable for fluorine flow systems were tested for compatibility under exposure to carefully controlled flow conditions. Rigid control was maintained to ensure cleanliness both of the system and of the specimens using the general cleaning and passivation procedures described in chapter 6. Specimens of nickel, stainless steel, aluminum, and brass were fabricated in three basic configurations (fig. 3–4) representative of conditions commonly found in flow systems. These configurations included orifices for produc-



(a) Leak-simulator orifices. (b) Sharp-edged orifice.

(c) Rounded-approach orifice. (d) Impact specimen. (e) Triangular wedge.

FIGURE 3–4.—Test specimen configurations for high-pressure high-flow-velocity tests.

ing high velocities and simulating leaks, flat-faced plugs for impact tests, and triangular wedges for turbulence effects and exposure of sharp edges and corners to fluorine flow.

These specimens were exposed to a range of flow velocities and pressures. The following results were obtained:

(1) Flow velocities of up to 400 feet per second at a temperature of −320° F and pressures up to 1500 pounds per square inch gage caused no measurable physical erosion, and no chemical attack occurred with nickel, stainless-steel, aluminum, or brass specimens.

(2) All configurations tested were found acceptable for fluorine systems under the conditions imposed.

(3) Sudden release of high-pressure liquid fluorine in metal tubes containing gaseous fluorine without liquid-nitrogen jacketing (ambient temperature) had no effect on the system.

In addition, turbulence, fluid friction, and impact effects resulting from high-pressure high-velocity liquid-fluorine flow through clean tubing or past irregularly shaped or sharp-edged objects will not initiate fluorine system failures. The successful operations achieved in this series of compatibility tests were attributed to the care taken in the assembly, cleaning, and operating techniques used before exposing the system to severe dynamic fluorine service (ref. 3).

3.2.2 Chemical Effects on Metals Exposed to Fluorine

3.2.2.1 *Corrosion studies.*—When metals are exposed to fluorine, one of two chemical effects can be expected to occur, film formation or corrosion. In the presence of pure fluorine, metals form a fluoride film in the surface, with film formation occurring almost entirely in the first few hours of exposure. Fluoride films, like the oxide films that form on aluminum in air, are so closely bonded to the metal surface that they are considered "in" rather than "on" the surface of the metal.

Corrosion of metals occurs when moisture is present in any quantity. The moisture reacts with fluorine and fluorides to form hydrogen fluoride and fluoride complexes; this in turn destroys the metal fluoride film, and corrosion will occur from exposure to hydrogen fluoride. Since the film immediately re-forms, a cycle is set up whereby the base metal is reacted away. The process continues until the hydrofluoric acid is exhausted or the base metal is destroyed.

The fact that corrosion can occur in fluorine systems is the reason for extreme stress herein on cleanliness and on selection of procedures to keep fluorine or FLOX systems free of moisture contamination.

LONG-TERM EXPOSURE: Several test programs have been run to determine "corrosion" of metals exposed to fluorine environments. Some early tests showed excessive rates of apparent corrosion in metals exposed to fluorine, though this high rate was later attributed to the presence of contaminants in the fluorine. The most important result from more recent studies (ref. 11) is that most metals show little or no sign of corrosion following prolonged exposure to contaminant-free liquid fluorine. (However, most metals are attacked severely by hydrogen fluoride, particularly in the presence of free moisture, ref. 12.) Corrosion problems involved in handling fluorine of FLOX will be relatively insignificant if hydrogen fluoride is excluded from the system and the fluorine or FLOX is kept in a high state of purity. Table 3-I lists results of U. S. Air Force tests in which test specimens of various metals were immersed in liquid fluorine for 1 year.

TABLE 3-I.—CORROSION [a] OF METAL SPECIMENS IMMERSED IN LIQUID FLUORINE FOR 1 YEAR (REF. 11)

[Area of specimen, 4.20 sq in.]

Metal	Sample	Sample weight		Weight difference after cleaning, g
		Before exposure, g	After exposure, g	
Stainless steel 304	1	18.6849	18.6873	0.0009
	2	18.5512	18.5540	—.0026
	3	18.7305	18.7298	—.0002
	4	18.6154	18.6210	.0009
	5	18.5245	18.5325	.0022
Stainless steel 410	6	17.8507	17.8298	—0.0483
	7	18.1199	18.0981	—.0427
	8	17.8918	17.8766	—.0342
	9	17.9080	17.8005	—.0223
	10	18.0191	18.0123	—.0207
Monel 15–7	11	17.9713	17.9760	0.0008
	12	17.9272	17.9371	—.0006
	13	18.1022	18.1104	.0022
	14	17.9481	17.9553	.0029
	15	17.9088	17.9144	.0001
Copper	16	19.5659	19.5715	—0.0027
	17	19.7531	19.7639	.0005
	18	19.6306	19.6379	—.0008
	19	19.7691	19.7752	.0006
	20	19.6955	19.7001	—.0017
Aluminum 1100	21	6.3930	6.3616	—0.0488
	22	6.4349	6.4106	—.0422
	23	6.3277	6.3046	—.0399
	24	6.3876	6.3688	—.0315
	25	6.3828	6.3675	—.0314

[a] Based on weight difference after cleaning.

TABLE 3-I.—CORROSION [a] OF METAL SPECIMENS IMMERSED IN LIQUID FLUORINE FOR 1 YEAR (REF. 11)—Concluded

[Area of specimen, 4.20 sq in.]

Metal	Sample	Sample weight		Weight difference after cleaning, g
		Before exposure, g	After exposure, g	
Aluminum 6061	26	6.0088	5.9928	—0.0315
	27	5.9816	5.9697	—.0295
	28	6.0216	6.0163	.0432
	29	5.9744	5.9578	—.0333
	30	5.9193	5.8984	—.0333
Nickel	31	20.4919	20.4952	—0.0035
	32	20.4087	20.4149	—.0006
	33	20.6207	20.6281	.0014
	34	20.5791	20.5999	.0032
	35	20.6101	20.6206	.0038
Monel	36	20.5294	20.5366	—0.0010
	37	20.4504	20.4604	—.0004
	38	20.4651	20.4715	—.0035
	39	20.6064	20.6157	—.0021
	40	20.6896	20.6916	—.0036
Titanium A-110 AT	41	10.4057	10.3207	—0.0900
	42	10.3669	10.2730	—.1008
	43	10.4500	10.3724	—.0847
	44	10.3437	10.2718	—.0795
	45	10.2572	10.1847	—.0795
Titanium C-120 AV	46	10.3558	10.2710	—0.0897
	47	10.3333	10.2516	—.0877
	48	10.3732	10.3085	—.0730
	49	10.4072	10.3659	—.0654
	50	10.3463	10.3091	—.0516
Magnesium AZ-31	51	3.9513	3.9416	—0.0460
	52	3.9398	3.9696	—.0175
	53	3.9748	3.9706	—.0485
	54	3.9345	3.9097	—.0501
	55	3.9334	3.9261	—.0431
Magnesium HM-31	56	3.9925	3.9491	—0.0307
	57	4.0097	3.9558	—.0892
	58	4.0078	3.9671	—.0843
	59	4.0017	3.9215	—.1022
	60	3.9625	3.9942	—.0973

[a] Based on weight difference after cleaning.

Studies at Lewis (ref. 13) involved exposure of test specimens (tubes) of 3S-O and 52S-O aluminum, 347 and 321 stainless steels, A-nickel, and low-leaded brass alternately to liquid and gaseous fluorine for periods up to $3\frac{1}{2}$ months. Results of these tests were confirmed by the recent tests described in reference 11. For conditions that involved very clean systems and high purity in the fluorine used, the amount of specimen weight change was relatively slight and for most purposes could be con-

TABLE 3-II.—CORROSION DATA (REF. 13)

Metal	Weight, g		Weight change, g	Internal area, sq in.	Time, hr
	Before exposure	After exposure			
Aluminum 3S-O	18.9033	18.9033	0	7.20	[a]1055
	18.6296	18.6322	.0026	7.12	1055
	16.4636	16.4744	.0108	5.83	[b]2730
	16.3856	16.3962	.0106	5.83	2730
	18.8299	18.8313	.0014	7.20	2730
	18.6457	18.6563	.0106	7.20	2730
Aluminum 52S-O	28.6731	28.6750	0.0019	8.36	1055
	27.8926	27.9019	.0093	8.21	1055
	27.7912	27.8075	.0163	8.06	2730
	27.9204	27.9041	—.0163	8.06	2730
	28.1495	28.1594	.0099	8.36	2730
	26.5484	26.5579	.0095	7.77	2730
Stainless steel AISI 347	42.2858	42.2870	0.0012	7.29	1055
	41.8131	41.8132	.0001	7.12	1055
	35.4984	35.5015	.0031	5.83	2730
	35.6087	35.6121	.0034	5.91	2730
	42.1893	42.1932	.0039	7.12	2730
	42.6253	42.6275	.0022	7.20	2730
Stainless steel AISI 321	27.3230	27.3249	0.0019	7.20	1055
	26.9847	26.9865	.0018	7.03	1055
	23.4952	23.4980	.0028	5.91	2730
	23.5475	23.5523	.0048	5.83	2730
	27.2577	27.2587	.0010	7.12	2730
	27.7913	27.7934	.0021	7.20	2730
A-nickel	43.5582	43.5587	0.0005	7.20	1055
	43.6383	43.6387	.0004	7.20	1055
	36.3945	36.4005	.0060	5.74	2730
	41.4378	43.4404	.0026	7.12	2730
	38.8173	38.8203	.0030	6.34	2730
Low-leaded brass	57.7751	57.7800	0.0049	6.58	1055
	59.2956	59.2993	.0037	6.82	1055
	48.5486	48.5662	.0176	5.39	2730
	48.4982	48.5133	.0151	5.39	2730
	58.6092	58.6168	.0076	6.66	2730
	59.0067	59.0116	.0049	6.66	2730

[a] Exposed 783 hr to gas, 272 hr to liquid.

[b] Exposed 1714 hr to gas, 1016 hr to liquid.

sidered insignificant. Data from these tests (table 3-II) show a small weight gain for each specimen that includes the gain expected from normal fluoride film as well as any reaction products from hydrogen fluoride corrosion.

Metallurgical examination of the test specimens did not reveal any intergranular corrosion except for nickel. Very slight intergranular corrosion was observed; however, this was considered negligible for the time period involved. The physical appearance of the test specimens was

TABLE 3-III.—TEMPERATURE EFFECTS ON CORROSION OF METALS AND ALLOYS IN FLUORINE FOR 5-DAY EXPOSURE (REF. 14)

Material	Type	Average temperature, °F	Area, sq in.	Weight change, g
Aluminum -----	1100 H-14	79	2.082	0.0004
		79	2.088	.0002
		394	2.079	.0001
		394	2.069	.0001
		673	1.990	.1871
		673	1.998	.1976
		1009	2.021	.7470
		1009	1.989	.7308
	2024 T-3	79	2.020	0.0001
		79	2.019	0
		394	2.014	.0001
		394	2.016	.0003
		673	1.740	.0113
		673	1.733	.0171
		1020	1.725	.0028
		1020	1.740	.0033
	5154 H-34	79	1.608	0
		79	1.612	—.0003
		356	1.601	—.0004
		356	1.612	—.0003
	5154-O	640	1.989	0.0012
		640	2.007	.0012
		1017	1.991	.0031
		1017	1.999	.0030
Magnesium ----	M1A	79	2.002	0.0003
		79	2.002	.0001
		358	1.981	.0002
		358	2.002	.0001
		653	1.926	.0010
		653	1.968	.0011
		1006	1.972	.0128
		1006	1.954	.0121

reported (ref. 13) as follows:

(1) Both exposed and unexposed surfaces of nickel appeared identical.

(2) Both aluminum samples appeared considerably lighter in color but appeared unchanged otherwise.

TABLE 3-III.—TEMPERATURE EFFECTS ON CORROSION OF METALS AND ALLOYS IN FLUORINE FOR 5-DAY EXPOSURE (REF. 14)—Concluded

Material	Type	Average temperature, °F	Area, sq in.	Weight change, g
Magnesium ----	AZ81A-T6	79	2.735	0.0003
		79	2.806	0
		363	2.762	—.0002
		363	2.772	—.0002
		691	2.762	.0003
		691	2.737	.0005
		1000	2.780	.0060
		1000	2.783	.0039
	AZ91C-T6	79	2.558	—0.0002
		79	2.552	.0002
		406	2.640	0
		406	2.664	—.0002
		691	2.656	.0020
		691	2.629	.0015
		1002	2.642	.0012
		1002	2.644	.0026
Monel ---------		79	2.002	0.0005
		79	2.003	.0003
		396	1.996	.0004
		396	2.003	.0001
		684	2.009	.0027
		684	1.951	.0031
		1020	1.991	.0179
		1020	1.984	.0180
Nickel ---------	A	79	1.988	0
		79	1.997	0
		396	2.002	.0002
		396	2.004	0
		684	1.997	.0010
		684	2.007	.0008
		1026	1.982	.0350
		1026	1.984	.0349
Stainless steel --	304L	79	2.086	0
		79	2.093	.0001
		406	2.088	.0942
		406	2.094	.0891

(3) Iridescence that occurred in some areas of the stainless steels indicated the presence of fluoride films. This was most prevalent in 347-series steels; however, occurrence was not general in test specimens.

(4) A low-leaded brass was lightly covered with a reddish film that was not continuous, but generally covered the entire surface.

There was no visual difference reported between those portions of the test specimens exposed only to the gaseous phase and those exposed to both liquid and gas, nor was the gas-liquid demarcation line detectable on the specimens.

TEMPERATURE EFFECTS: Some data on the effects of temperature on surface reactivity obtained under U. S. Air Force contract (ref. 14) is presented in table 3-III. The weight change column in the table shows the general effect that can be expected from temperature increase. The data appear to fall within the scatter band that could be expected in the experimental process.

The effect of hydrogen fluoride (anhydrous hydrofluoric acid) in causing corrosion of various metals has been discussed in reference 15 and is presented in table 3-IV (from ref. 15). This reference states that, for Monel and nickel, the rates of corrosion for mixtures of water and hydrofluoric acid are of the same order.

3.2.2.2 *Fluoride film studies.*—According to reference 11, fluoride film formation on the surface of metals in fluorine occurs mostly in the first few minutes of exposure, after which time the reaction rate drops off sharply. Thus, this film acts to inhibit further attack of the base metal.

TABLE 3-IV.—CORROSION RATES OF HYDROGEN FLUORIDE WITH VARIOUS METALS (REF. 15)

Metal	Temperature, °C		
	500	550	600
	Penetration, in./month		
Stainless steel:			
430	0.005	0.030	0.038
304	----	----	.044
347	0.6	1.5	.58
309 Cb	.019	.14	.55
310	.04	.33	1.0
Nickel	.003	----	.003
Monel	.004	----	.006
Copper	.005	----	.004
Inconel	.005	----	----
Aluminum 2S (2 percent manganese)	.016	----	0.005
Magnesium	.042	----	.048

Figures 3–5 to 3–12 illustrate the typical film formation that can be expected when various metals are exposed to fluorine. The film thickness was measured in angstroms as a function of time. It should be remembered that the measurements taken during these studies included the normal fluoride film formation as well as any possible "corrosion" or formation of chemical complexes by hydrogen fluoride or trace amounts of other system contaminants.

Figures 3–5 to 3–9 generally show a film formation in the range of 2 to 14 angstroms during a period of 230 minutes (or about 4 hr) at temperatures from −113° to 183° F. Figure 3–10 shows an extension of the exposure time under similar conditions (86° F) up to 90 hours. As shown, slight increases in film thickness were measured (now in the range of 10 to 30 Å) but again a constant thickness is approached. Figures 3–11 and 3–12 repeat the exposure of selected metals at the maximum temperature (183° F) but show little significant effect.

Generally, the variations in film thickness with respect to the exposure variables were slight, though exposure time has the greatest effect. In

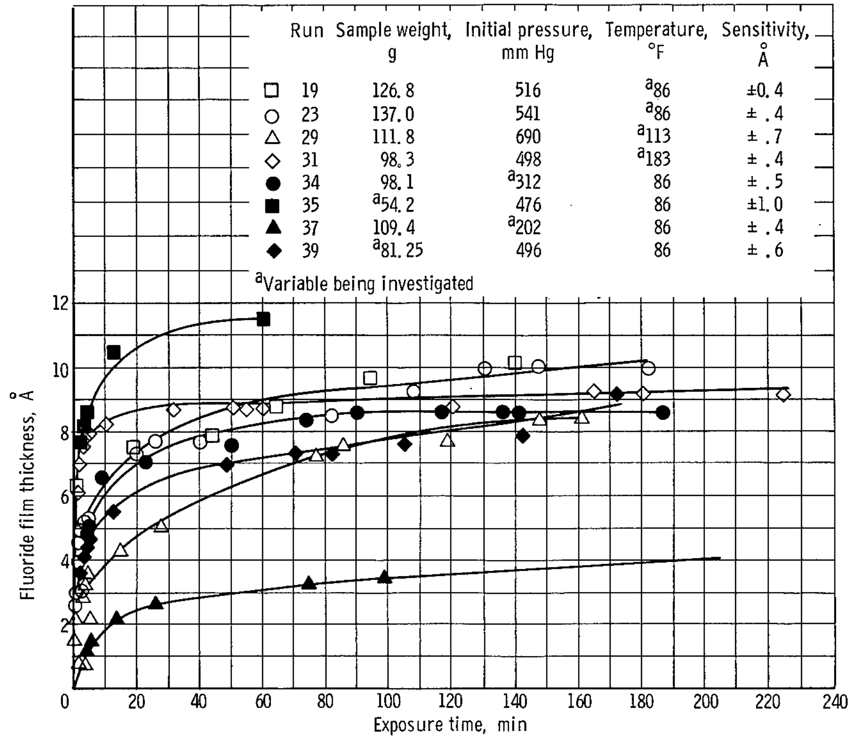


Figure 3–5.—Variation of fluoride film thickness on Monel powders to time of exposure to fluorine (ref. 11).

all cases, film thickness tended to become constant at less than 50 angstroms.

The characteristics of metallic surface films and surface reaction are as follows:

(1) Aluminum and aluminum alloys form a tenacious and protective oxide film when the bare metal is exposed to air or oxygen. A similar

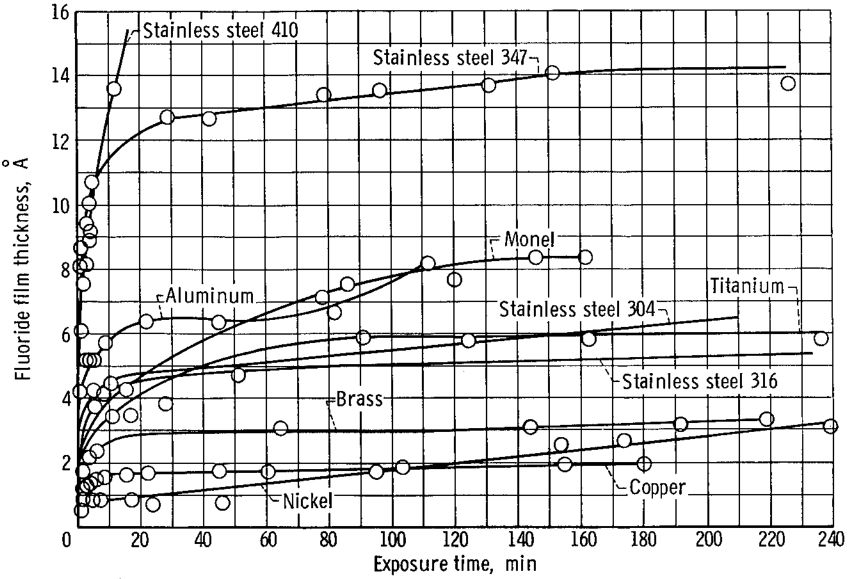


FIGURE 3-6.—Variation of film thickness on metal powders at —113° F with time of exposure to fluorine (ref. 11).

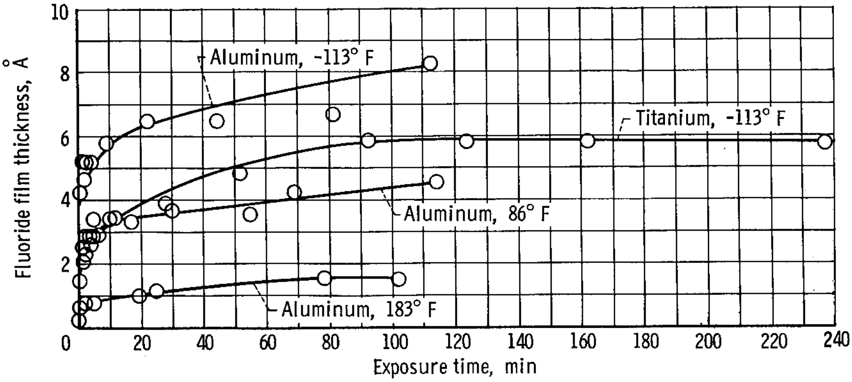


FIGURE 3-7.—Variation of film thickness on aluminum and titanium with time of exposure to fluorine (ref. 11).

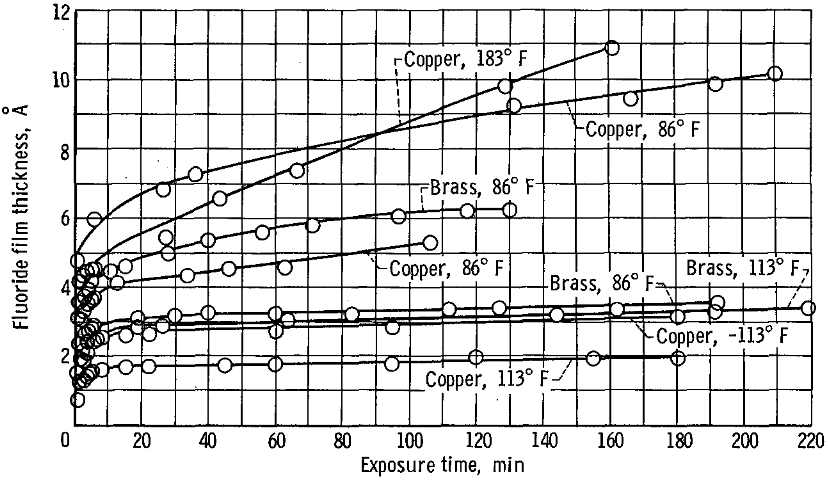


FIGURE 3-8.—Variation of fluoride film thickness on copper and brass powders at two different temperatures (ref. 11).

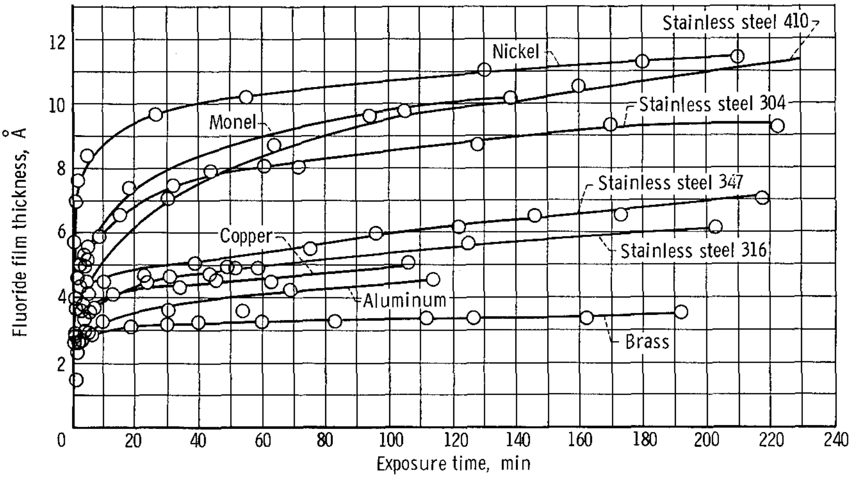


FIGURE 3-9.—Variation of film thickness on metal powders at 86° F with time of exposure to gaseous fluorine in initial period (ref. 11).

film (AlF_3) is formed on exposure to fluorine; if the oxide film is present, fluorine will replace this film. Although the replacement mechanism is not known, the most probable method is by diffusion through the oxide film to react with the bare metal, by replacement of the oxygen, or by both of these. The melting point of aluminum is below its ignition point with fluorine gas (ref. 16); fluoride formation on molten aluminum

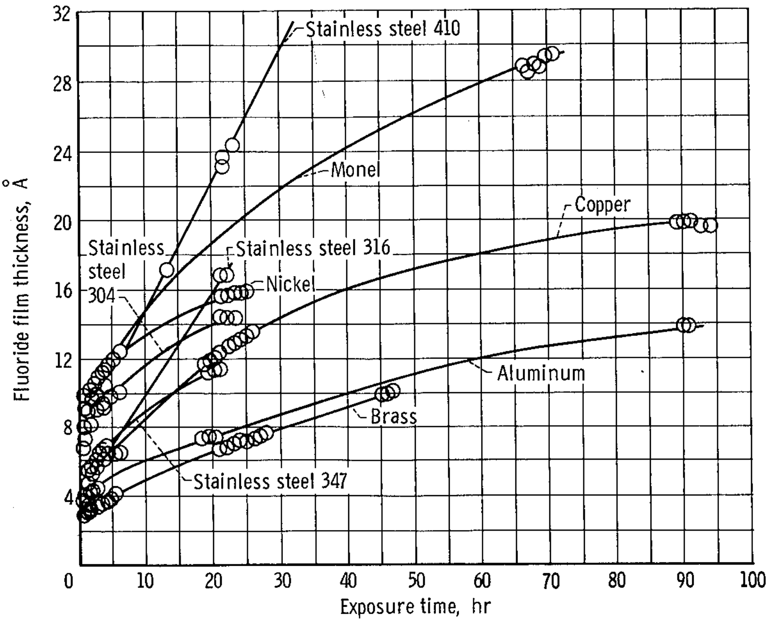


FIGURE 3-10.—Variation of film thickness on metal powders at 86° F with time of exposure to gaseous fluorine for total run (ref. 11).

would probably be similar to the oxide formation on mercury.

(2) Fluorine reacts with the surface of iron, iron alloys, and mild steels to form ferrous and ferric fluoride films at a higher rate and depth than with the more resistant metals. The films are less stable than those of more resistant metals, particularly when exposed to moisture (ref. 17). Susceptibility to corrosion from hydrogen fluoride is also greater.

(3) Stainless steels are more resistant to attack by hydrogen fluoride than mild steels and form stable fluoride films similar to those formed on Monel, though less stable at elevated temperatures. Stainless-steel welds have the same characteristics as the parent material.

(4) Nickel (A, D, and L) and Monel form films similar to those formed on aluminum, but are particularly stable for use at high temperatures (1200° F; refer to section 3.2.4). Welding does not reduce the corrosion resistance of nickel or Monel if fluxes either are not used or are completely removed. Inconel, Illium, Illium "R", and Duranickel are less resistant than either nickel or Monel at higher temperatures but are generally similar to stainless steels.

(5) Copper has a high resistance to fluorine attack. The copper alloys, red brass, and yellow brass are also highly resistant. Cupric

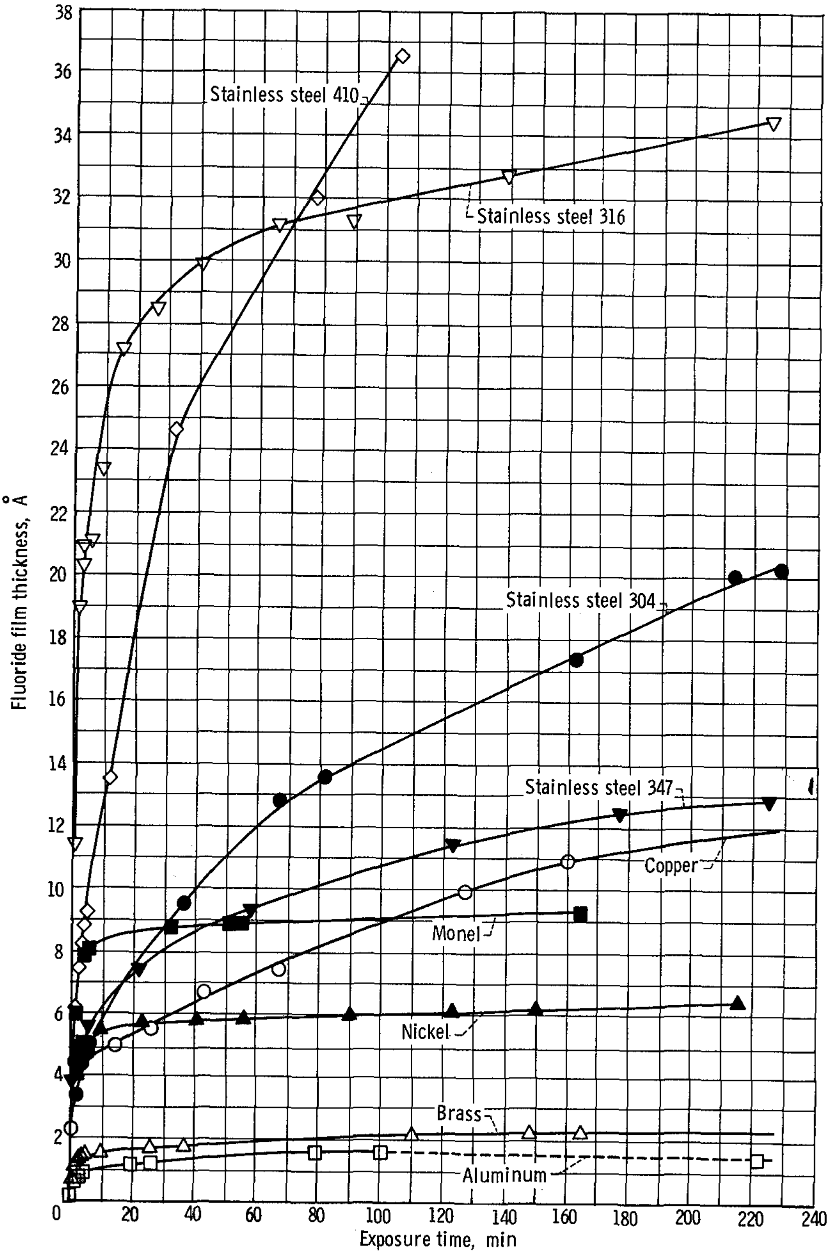


FIGURE 3-11.—Variation of film thickness on metal powders at 183° F with time of exposure to gaseous fluorine (ref. 11).

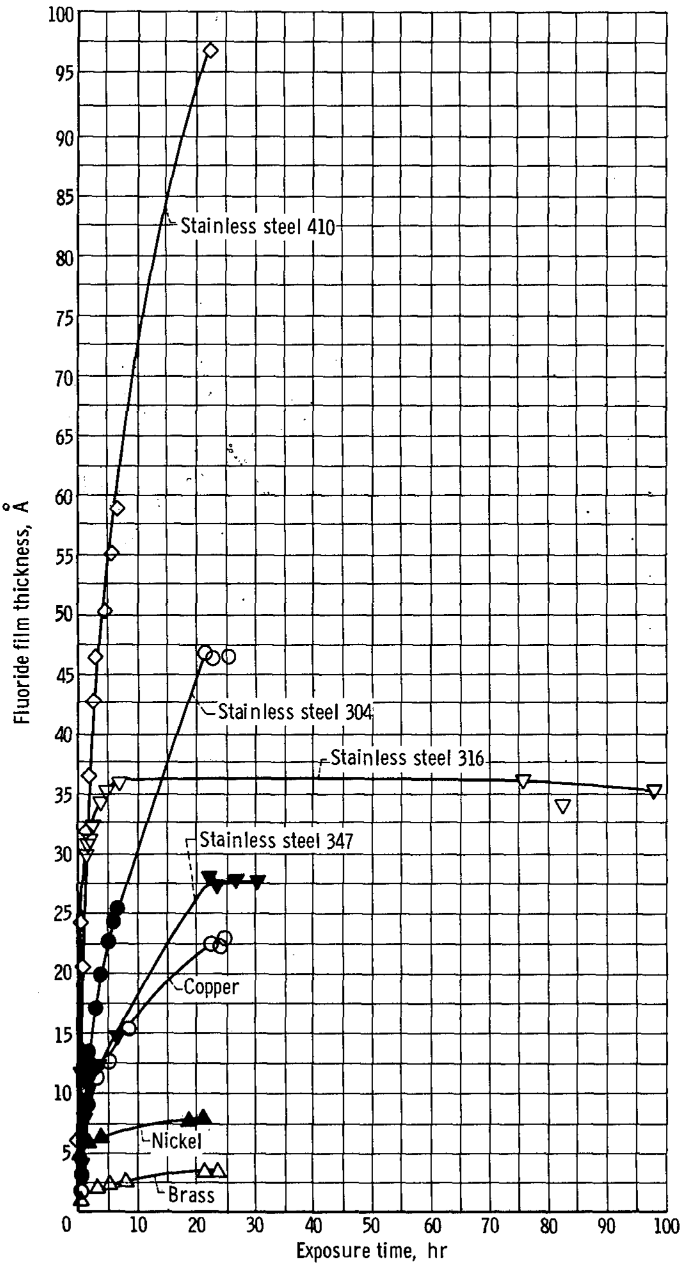


FIGURE 3-12.—Variation of film thickness on metal powders at 183° F with time of exposure to gaseous fluorine for total run (ref. 11).

fluoride film is very stable in the presence of dry fluorine or dry hydrogen fluoride, but hydrolyzes readily in moisture to form hydrofluoric acid, which attacks all copper alloys.

(6) Magnesium, like aluminum, is always coated with a tenacious oxide film. Fluoride film formation is similar to that on aluminum.

(7) Limited experience with titanium indicates poor resistance to hydrogen fluoride and film characteristics similar to stainless steels. In fracture tests with titanium in liquid fluorine (ref. 18), specimens did not ignite, and in other tests (ref. 19) the ignition of titanium was more severe in liquid oxygen than in liquid fluorine. However, gaseous fluorine will rapidly attack titanium at temperatures above 300° F (149° C), according to reference 11, and there have been cases reported where titanium was ignited at −113° F (−81° C), although these authors noted that *catalysis* was necessary and that the reaction was smothered by the fluoride film (refs. 11 and 17).

(8) Silver solder and Nicrobraze are recommended for most of the joining where welding is impractical or impossible. (Flux should *not* be used; refer to section 4.9.3.) Exact film characteristics of these materials have not been determined; however, these metals have been widely used and have provided highly reliable connections.

(9) Chromium forms four fluorides (ref. 20): (1) divalent, (2) trivalent, (3) tetravalent, and (4) pentavalent ((3) and (4) are volatile). When chromium is reacted with fluorine below 300° F (149° C) it forms a protective divalent fluoride similar to the film on nickel plate. Above 300° F, the fluoride is converted from a divalent to a volatile tetravalent fluoride form (ref. 20) and loses its protective ability. Chromium may be used below 300° F with no problems other than those associated with nickel plate.

(10) Beryllium behaves much the same as nickel in fluoride film formation (ref. 20). Tantalum should not be used at temperatures above 150° F (66° C). Because of its low ignition point, little research data are available on tantalum.

(11) Lead forms a nontenacious fluoride film. In passive exposure, however, it has been used successfully as seal or gasket material.

(12) Tin reacts in a manner similar to lead and has had some use for soft gaskets in cryogenic service (ref. 20).

(13) Rhodium, palladium, and platinum can be used in contact with fluorine at room temperature essentially without attack (ref. 20). These metals are used in some equipment because they are inert to hydrogen fluoride.

Some additional information on the effects of exposure temperatures on metal surfaces exposed to fluorine is given in table 3-V. The reason for the contradictory information on Monel is not known; however, this as well as other inconsistencies may be partly a result of the different

TABLE 3-V.—COMPATIBILITY OF MATERIALS IN FLUORINE

Material	Resistant at temperature (material unaffected), °F, of—	Attack at temperature, °F, of—			Combustion temperature, °F
		Slight	Moderate	Severe	
Iron	-----	-----	-----	-----	[a]1242
Carbon steel	[b]700	-----	-----	[b]930	-----
Stainless steel 302	-----	-----	-----	[b]400 to 500	[d]1258
Chromium plate	[c]302	-----	-----	-----	-----
Molybdenum	-----	-----	-----	-----	[a]401
Monel	-----	[d]1382	-----	[b]930 to 1100	[a]797
Tungsten	-----	-----	-----	-----	[a]580
Inconel	[b]750	[d]1022	-----	[d]1382	-----
Dow metal (G)	[b]930	-----	-----	[a]900	-----
Copper	-----	[b]930 to 1100	-----	[c]1290	[a]1277
Copper wool	-----	-----	-----	-----	[a]200–250
Aluminum (2S)	[b]850 [b]930	-----	[c]1110	-----	Above melting point
Nickel	[b]1100	-----	[c]1290 [d]1382	-----	[a]2097
Soda glass	[e]302	-----	-----	-----	-----
Borosilicate	[e]392	-----	-----	-----	-----
Silica	[e]482	-----	-----	-----	-----
Metallic oxides	-----	-----	-----	-----	[c]482

[a] Ref. 20 (for further information refer to section 3.2.4).

[b] Ref. 12.

[c] Ref. 27.

[d] Ref. 28.

[e] Ref. 29.

methods used by the various investigators in obtaining the data. The reaction of copper foil and gaseous fluorine was studied in an all-glass apparatus at pressures to about 200 millimeters of mercury and temperatures from 800° to 1200° F (refs. 21 and 22). The rate of reaction in film formation increased at elevated temperatures in this study; however, the apparent final film thickness (as measured by fluorine consumption) was less than at lower temperatures.

3.2.3 Effects of Fluorine Exposure on Mechanical Properties of Metals

3.2.3.1 *Tensile properties.*—Studies that involved comparison of the effects on test specimens from immersion in liquid nitrogen and liquid fluorine (ref. 11) indicated that the tensile properties of metals were not affected by exposure to the fluorine environment. The corrosion (ref. 11, p. 45) for most of the test specimens was less than 1 mil per year. Thus, the conclusions drawn earlier (section 3.2.2.1) regarding the corrosive effects of fluorine exposure were confirmed. (The 1 mil/yr "rate" assumes that this corrosion would continue, which is unlikely. Again, too, the fluoride film penetration may be what is indicated by ref. 11 as corrosion; this penetration, as indicated by the data, is negligible.)

Samples were tested after removal from liquid-fluorine and liquid-nitrogen baths following the 1-year soaking period. According to reference 11, the mechanical properties of 120 specimens were determined in a standard tensile testing machine. As shown by values given in table 3-VI, there were no significant differences in mechanical properties between samples immersed in liquid nitrogen or liquid fluorine. Long-term exposure to cryogenic (−320° F) temperatures appeared to improve tensile properties over the handbook values. Table 3-VI, from these studies, displays scatter within the limits that could be expected for the particular data. Recent studies at General Dynamics/Convair (unpublished data) have shown these earlier conclusions regarding tensile properties to be true.

3.2.3.2 *Stressed samples.*—In tests by the U. S. Air Force (ref. 19), specimens of the same metals listed in table 3-VII were stressed to just below their yield points and suspended in liquid fluorine for 2 weeks. None of the test specimens showed signs of stress-corrosion cracking under the test conditions and exposure time (ref. 19).

Tests were run at Lewis on stressed tensile specimens to study the effects of liquid-fluorine environment on the mechanical properties of several sheet alloys (ref. 18). The smooth and notch tensile strengths and the elongation properties of steel, nickel, aluminum, and titanium alloys were determined in a liquid-fluorine environment at −320° F. Mechanical properties data obtained in fluorine were compared with data on specimens of the same sheet and heat treatment tested in an

TABLE 3-VI.—AVERAGE TENSILE PROPERTIES OF 1-YEAR TEST SPECIMENS (REF. 11)

Metal	Treatment (liquid at −320° F)	Average yield stress, psi	Average ultimate stress, psi
Stainless steel 304	Nitrogen	60 620	93 960
	Fluorine	63 440	94 100
Stainless steel 410	Nitrogen	74 680	88 920
	Fluorine	73 700	89 380
Armco steel 15-7 Ph-Mo	Nitrogen	71 660	143 420
	Fluorine	70 700	141 900
Copper	Nitrogen	53 580	57 640
	Fluorine	54 080	58 660
Aluminum 1100	Nitrogen	21 480	23 120
	Fluorine	21 700	22 940
Aluminum 6061	Nitrogen	41 840	45 820
	Fluorine	41 480	46 360
Nickel	Nitrogen	89 960	96 900
	Fluorine	89 680	96 420
Monel	Nitrogen	58 020	93 740
	Fluorine	58 120	93 040
Titanium A110 AT	Nitrogen	125 400	151 600
	Fluorine	126 200	152 000
Titanium C120 AV	Nitrogen	124 000	153 200
	Fluorine	121 400	152 200
Magnesium AZ31	Nitrogen	35 500	41 600
	Fluorine	34 160	41 720
Magnesium HK-31	Nitrogen	49 000	49 960
	Fluorine	46 000	48 240

environment of liquid nitrogen (−320° F).

Short-term (2 hr) exposure of stressed tensile specimens to liquid fluorine (ref. 18) indicated possible slight deterioration of some mechanical properties when compared with similar tests in a nonreactive environment (liquid nitrogen) at the same temperature, as shown in table 3-VII. This indicated deterioration was believed to be a result of contaminants in the gaseous-fluorine supply. The data described in detail in table 3-VII show scatter within the limits that can be expected for the particular test. The results of the Lewis tests (ref. 18) are summarized as follows:

TABLE 3-VII.—TEST RESULTS OF MECHANICAL PROPERTIES AFTER 2-HOUR EXPOSURE IN LIQUID NITROGEN AND LIQUID FLUORINE AT —320° F (REF. 18)

Alloy	Liquid nitrogen			Liquid fluorine		
	Smooth tensile strength, psi	Elongation, percent	Notch tensile strength, psi	Smooth tensile strength, psi	Elongation, percent	Notch tensile strength, psi
Stainless steel AM 350	298×10^3	21.0	79×10^3	262×10^3	6.7	76×10^3
	293	22.5	104	252	7.0	101
	272	6.0	90	256	7.0	--------
	270	9.0	--------	242	8.5	--------
	293	21.0	--------	--------	----	--------
Av. ----	285×10^3	15.9	91×10^3	253×10^3	7.3	88.5×10^3
Stainless steel ASM 6434	276×10^3	6.8	52.2×10^3	271×10^3	2.0	--------
	298	----	65.2	270	2.1	--------
	290	4.0	--------	277	2.5	--------
	276	4.0	--------	274	3.0	--------
Av. ----	285×10^3	4.9	58.7×10^3	273×10^3	2.4	--------
Inconel X ----	192×10^3	10.7	--------	179×10^3	19.0	--------
	199	18.0	--------	195	21.0	--------
	189	13.5	--------	192	18.0	--------
Av. ----	193×10^3	14.1	--------	189×10^3	19.3	--------
Stainless steel AISI 301	340×10^3	1.5	219×10^3	349×10^3	1.0	216×10^3
	344	1.3	226	--------	----	--------
70 percent Cr						
Av. ----	342×10^3	1.4	223×10^3	--------	----	--------
Stainless steel AISI 304L	257×10^3	----	256×10^3	240×10^3	2.0	250×10^3
	253	1.5	254	251	2.0	--------
	264	1.5	--------	--------	----	--------
Av. ----	258×10^3	1.5	255×10^3	246×10^3	2.0	--------

(1) Exposure of several alloys to liquefied commercial fluorine gas produced a detrimental effect on the tensile strength of some alloys. A limited number of tests indicated that 2 hours of exposure lowered tensile strength from insignificant amounts to as much as 11 percent. The elongations showed similar trends.

(2) The sharp-notch strengths were not significantly affected.

(3) The presence of contaminants (probably mainly hydrogen fluoride) could have been the cause of the degradation, and different amounts of contaminants could account for the variations in mechanical properties observed.

(4) The surface appearance of specimens exposed to liquid fluorine

TABLE 3-VII.—TEST RESULTS OF MECHANICAL PROPERTIES AFTER 2-HOUR EXPOSURE IN LIQUID NITROGEN AND LIQUID FLUORINE AT —320° F (REF. 18)—Concluded

Alloy	Liquid nitrogen			Liquid fluorine		
	Smooth tensile strength, psi	Elongation, percent	Notch tensile strength, psi	Smooth tensile strength, psi	Elongation, percent	Notch tensile strength, psi
Aluminum	84.0×10^3	13.0	56.4×10^3	82.0×10^3	12.0	58.5×10^3
2014-T6 clad	86.0	14.0	60.7	83.3	12.0	59.7
	83.0	13.5	--------	79.5	11.0	--------
Av. ----	84.3×10^3	13.5	58.6×10^3	81.6×10^3	11.7	59.1×10^3
Aluminum	60.6×10^3	24.0	55.5×10^3	60.2×10^3	20.5	58.2×10^3
6061-T6 bare	61.3	22.5	58.7	56.0	16.5	55.5
	--------	----	54.7	62.0	17.5	--------
	--------	----	56.0	--------	----	--------
Av. ----	61.0×10^3	23.3	56.2×10^3	59.4×10^3	18.2	56.9×10^3
Aluminum	94.5×10^3	14.5	38.7×10^3	89.8×10^3	10.5	--------
7075-T6 clad	94.0	14.0	34.2	93.0	11.0	--------
	94.0	----	39.6	--------	----	--------
Av. ----	94.2×10^3	14.3	37.5×10^3	91.4×10^3	10.8	--------
Titanium alloy	207×10^3	6.0	183×10^3	183×10^3	6.5	181×10^3
Ti-6Al-4V	203	11.0	199	180	6.0	187
annealed	205	11.7	196	--------	----	--------
Av. ----	205×10^3	9.6	193×10^3	182×10^3	6.3	184×10^3
Titanium alloy	226×10^3	17.0	--------	199×10^3	14.0	--------
Ti-6Al-4V	225	17.0	--------	185	7.0	--------
solution-	218	14.0	--------	208	5.0	--------
treated	--------	----	--------	220	8.0	--------
	--------	----	--------	219	4.5	--------
Av. ----	223×10^3	16.0	--------	206×10^3	7.7	--------

ranged from clean to discolored. Etched surfaces had occasional deposits of corrosion products.

Figure 3–13 shows a schematic drawing of the tensile loading apparatus, the test chamber, the liquid-nitrogen cryostat, and the supply piping for purging, filling, and emptying the test chamber. The tensile load was generated by a hydraulic ram mounted at the top of the loading frame. Hydraulic fluid under pressure was metered to the ram by a needle valve from a previously charged accumulator. The tensile load on the specimen was measured by a load cell that utilized strain gages for load indication. This load cell was mounted so that it was in compression when load was applied to the test section (fig. 3–13).

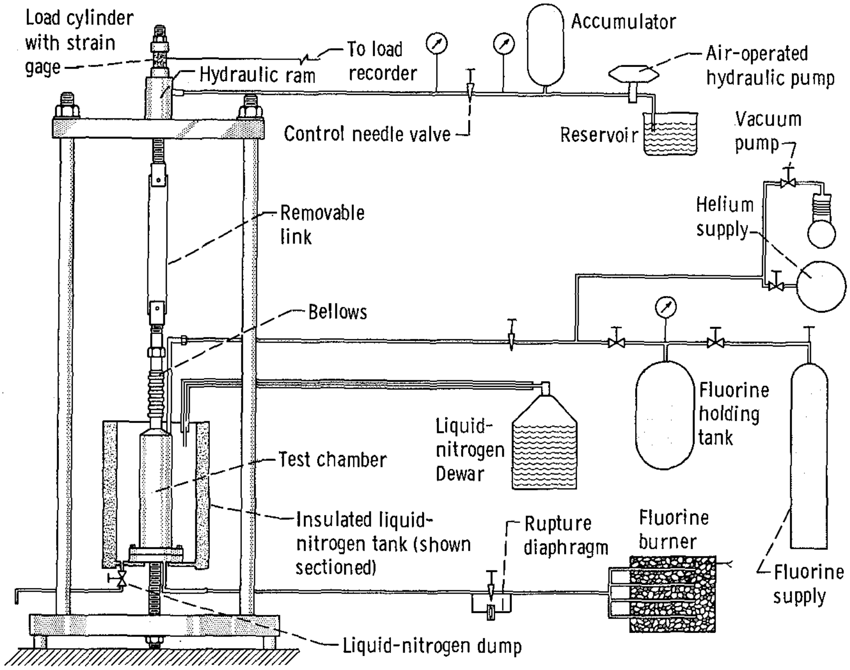


FIGURE 3-13.—Schematic diagram of test setup for Lewis tensile stress tests (ref. 18).

When the test chamber was filled with liquid fluorine, the smooth specimens were loaded to a stress value equal to 90 percent of the yield strength of the material at a temperature of −320° F (liquid-nitrogen boiling temperature). The notch specimens were loaded to 90 percent of the failure stress of duplicate notch specimens in liquid nitrogen. This load was maintained for 2 hours so that the specimens were under stress during the time of exposure to fluorine. After this time, the load was increased until fracture resulted. All specimens were loaded to fracture at strain rates of about 0.005 inch per inch per minute.

For smooth tensile specimens, the hold stress applied was 90 percent of the 0.2 percent yield strength of the material tested in liquid nitrogen. For notch specimens, the hold stress was 90 percent of the failure stress in liquid nitrogen. The time of exposure was 2 hours in this case also.

An interesting aspect of these tests (ref. 18) was that titanium specimens were tested to failure in liquid fluorine without ignition (despite the exposure of a nonpassivated surface by the fracture). Titanium has shown a tendency to ignite when subjected to impact in a liquid-oxygen environment (table 3-VIII), and thus its use in liquid fluorine has been discouraged. The Lewis tests indicated that the use of titanium is feasi-

TABLE 3-VIII.—SUMMARIZED IMPACT IGNITION (REF. 19)

Number of tests	Striker configuration	Number of samples at impact	Energy level, ft-lb	Degree of ignition		
				Moderate	Slight	None
Monel striker, titanium sample						
5	Flat, smooth	5	2.6	--	--	5
2	Flat, rough	2		1	--	1
2	Hemispherical	2		[a]1	--	1
2	Chisel point	2		--	[a]2	--
3	Pointed, conical	3		--	[a]3	--
Titanium striker, titanium sample						
8	Flat, smooth	2	40.0	1	1	--
		2	55.0	1	1	--
		4	58.0	--	1	3
4	Flat, grooved	2	55.0	1	--	1
		2	58.0	2	--	--
16	Pointed, conical	3	2.6	--	1	2
		3	6.0	2	1	--
		2	9.0	1	1	--
		1	35.0	1	--	--
		2	50.0	1	1	--
		2	55.0	1	1	--
		2	58.0	--	1	1
		1	61.0	--	--	1
9	Hollow, pointed	4	6.0	--	1	3
		4	10.0	1	1	2
		1	38.0	1	--	--
Stainless-steel or aluminum striker, aluminum sample						
8	Flat, grooved	8	58.0	1	--	7
4	Pointed, conical	2	30.0	--	--	2
		[b]2	58.0	--	--	2
Titanium striker, titanium sample, liquid oxygen						
10	Flat, smooth	1	60.0	--	1	--
		1	55.0	--	1	--
		8	65.0	--	--	8
9	Conical, pointed	9	65.0	[c]5	4	--
3	Flat, rough	3	65.0	--	1	2
4	Flat, grooved	4	65.0	2	--	2

[a] Ignition indicated by disappearance of striker tip. No evidence of sample igniting.
[b] Aluminum striker.
[c] One sample caught fire and burned almost completely.

ble in liquid-fluorine systems, but it should be thoroughly tested for the particular application before use with fluorine.

3.2.3.3 *Flexure tests.*—In several tests lasting up to 6 hours, flexing thin metal strips in liquid fluorine once per second produced no measurable effects (ref. 19). The flexure tests were performed on copper, brass, aluminum, and Monel immersed in liquid fluorine and were intended to provide some information on the flexibility of the fluoride film. If increased corrosion had resulted, it would have provided evidence that a fluoride film was being lost and re-formed, and that the film was not flexible. The negative results indicate that the fluoride film is not affected by the flexing of metals exposed to fluorine.

3.2.3.4 *Impact tests.*—As reported in reference 19, results were obtained that "were not very reproducible and in no case with liquid fluorine did ignition become general." These tests involved the impact of various shapes of strikers on impact plates beneath the surface of liquid fluorine or liquid oxygen (table 3-VIII).

Ignition was observed by all types of strikers at different impact levels on two titanium alloys tested in liquid fluorine. It should be noted that ignition of titanium with liquid oxygen was more severe than with fluorine (ref. 19). In one case (of 26 tests with oxygen) ignition became general, and the sample burned completely; in each case with fluorine, though reaction was initiated, it failed to propagate itself. Reference 19 states, "Ignition, when it was observed, was indicated by the formation of small craters and gullies together with droplets of melted metal [either] on the sample or on the striker face."

The data (table 3-VIII) provided little information for the compatibility of metals with fluorine; however, when compared with equivalent data for liquid oxygen or when impact ignition energies are compared for different materials, relative reactivities may be obtained for comparable energy values. These values may also be used in comparison with calculated localized energies that may be present in a given system.

As another part of the same series of tests (ref. 19), tubes of various metals were filled with liquid fluorine and struck on the outside at known impact levels. The degree of reaction on the inside of these tubes was not affected by intensive impact by pointed strikers on the outside of the tubes. Vibration of several samples after impacts, at 30 cycles per second, also produced no effects (ref. 19).

3.2.4 Ignition Temperatures of Metals in Fluorine Atmospheres

An experiment was performed (in cooperation with NASA Lewis) to determine ignition temperatures of metals in fluorine atmospheres (ref. 16). In these tests, metal wires were heated electrically in a chamber

TABLE 3-IX.—IGNITION TEMPERATURES OF METALS IN FLUORINE (REF. 16)

(a) Technique A.

Metal	Wire diameter, in.	Ignition temperatures, °C	Average ignition temperature, °C	Maximum variation from average, percent
Aluminum ---	0.010 .016	----	(a)	----
Copper ------	0.0123	725 645 670 670 747	692	8.0
Iron ---------	0.014	677 667 667 676	672	0.8
Molybdenum -	0.0149	214 207 188 220 188	205	8.3
Monel -------	0.010	437 423 348 377	396	12.0
Nickel ------	0.008 .0155 .0154 .0155 .0155 .0152	1168 1096 1219 1195 1209 1084	1162	6.0
Stainless steel 302	0.020	749 796 611 570	681	13.0
Tungsten ----	0.0153	260 332 263 275	283	18.0

TABLE 3-IX.—IGNITION TEMPERATURES OF METALS IN FLUORINE (REF. 16)—Concluded

(b) Technique B.

Metal	Wire diameter, in.	Maximum wire temperature, °C	Ignition delay, sec	Ignition temperature range, °C	Activation energy, kcal/mole
Copper	0.012	905	0.8	689 to 701	39.5
		852	1.0		
		810	.6		
		767	.8		
		701	1.2		
		689	No ignition		
Iron	0.014	730	1.0	618 to 644	16.3
		676	1.6		
		648	2.0		
		644	2.2		
		618	No ignition		
Nickel	0.015	1357	0.6	1253 to 1266	----
		1306	1.2		
		1266	.6		
		1253	No ignition		

[a] An average of four tests gave an ignition temperature greater than the melting point.

(bomb) containing fluorine, and temperatures were calculated from current and voltage readings by using resistivity-temperature data. Two procedures were used, and a comparison of results is given in table 3-IX.

Technique A.—An evacuated bomb was filled with gaseous fluorine at atmospheric pressure, and the temperature of the specimen was gradually increased by the variable resistor. The voltage and current at which the wire burned out were used, in conjunction with resistivity data, to calculate the temperature at ignition (table 3-IX).

Technique B.—The test specimen was brought to a predetermined temperature in the evacuated bomb before the introduction of fluorine. Fluorine was then admitted and the time (ignition delay) required for the reaction to go to completion was measured with a stop watch (table 3-IX). As shown in the table, ignition occurred at different temperatures for the different metals, but only the range is given. This procedure was used to obtain ignition-delay—temperature curves.

In general, molybdenum, Monel, and tungsten exhibited the lowest ignition points of the metals tested, with values ranging from 200° to

400° C. Aluminum, copper, iron, and 302 stainless steel ignited between 600° and 700° C. Nickel ignited at 1153° C.

3.3 COMPATIBILITY OF NONMETALS WITH FLUORINE AND FLOX MIXTURES

Fluorine-compatible nonmetallic materials would be extremely desirable for use in fluorine or FLOX systems, particularly when the design problem involves modification of an existing launch vehicle to make it fluorine or FLOX compatible. In this case, the problem would be to find materials for given seal, gasket, and other applications to replace currently used materials. For this reason, investigations were required to define the compatibility of materials suitable for use in fluorine or FLOX environments. These studies were conducted at Lewis in three separate programs:

(1) Studies of the effects of exposure of various nonmetals to gaseous and liquid-fluorine atmospheres at atmospheric pressure and 1500 pounds per square inch gage under static conditions
(2) Studies of the effects of exposure of various nonmetals to gaseous and liquid fluorine and FLOX under static conditions and atmospheric pressure
(3) Studies of the effects of gaseous and liquid fluorine and FLOX under flow conditions with pressures up to 1250 pounds per square inch gage and flow velocities of 280 feet per second (liquid) and pressures to 400 pounds per square inch gage and flow velocities to 900 feet per second (gaseous)

Results of the static exposure tests are discussed in the following sections. The dynamic tests are discussed in detail in section 3.3.3. Samples were deliberately tested to destruction to determine compatibility limits as affected by the various parameters.

3.3.1 Static Studies

In the early phases of fluorine work at Lewis, investigations were conducted (refs. 4 and 23) to determine the compatibility of nonmetals with fluorine (1) to classify relative compatibility of nonmetals and (2) to determine any nonmetals suitable for use as bearings and seal materials, sealants, and lubricants for possible fluorine service. These studies involved static exposure to both gaseous and liquid fluorine and were conducted first at atmospheric pressure and later at 1500 pounds per square inch gage. Liquid-fluorine tests were conducted at −320° F, and gaseous fluorine tests were conducted at room temperature. The materials investigated and the results are given in table 3-X.

TABLE 3-X.—NONMETALS EXPOSED TO GASEOUS AND LIQUID FLUORINE (REFS. 4 AND 23)

Sample [a]	Sample exposed to–				Sample injected into liquid fluorine at 1500 psig pressure
	Liquid fluorine at atmospheric pressure	Gaseous fluorine at atmospheric pressure [b]	Liquid fluorine at 1500 psig pressure	Gaseous fluorine at 1500 psig pressure [b]	
	Liquid				
Kel-F LO No. 10 (M. W. Kellogg Co.)	No reaction	No reaction	No reaction	Reaction [c]	Reaction
Fluorolube HO (Hooker Electrochemical Co.)	↓	↓	↓	Reaction [c]	(d)
N-43, $(C_4F_9)_3N$ (Minnesota Mining & Mfg. Co.)	↓	↓	↓	Reaction [e]	Reaction
Tap water	↓	↓	↓	Reaction	No reaction
Cenco Hyvac Oil (Central Scientific Co.)	Not tested	Burned	Not tested	Not tested	Not tested
Glyptal (General Electric Co.)	Not tested	Burned	Not tested	Not tested	Not tested
Dow Corning 200 fluid (20 centistokes)	Exploded	Burned	Not tested	Not tested	Not tested
Water glass	Not tested	Burned	Not tested	Not tested	Not tested
Safety Solvent 178 (Fine Organics, Inc.)	↓	↓	↓	↓	↓
Leak-Tec (American Gas & Chemicals, Inc.)	↓	↓	↓	↓	↓
Leak-Tec with glycerine	↓	↓	↓	↓	↓
Dry JP-4 fuel	↓	↓	↓	↓	↓
Carbon tetrachloride	↓	Exploded	↓	↓	↓

Grease					
Kel-F Med. Wax (M. W. Kellogg Co.)	No reaction	No reaction	Reaction[f]	Reaction	Not tested
Kel-F No. 1 Grease (M. W. Kellogg Co.)	(d)	↓	(d)	(d)	↓
Fluorolube LG (Hooker Electrochemical Co.)	(d)	↓	(d)	(d)	↓
Fluorolube MG (Hooker Electrochemical Co.)	(d)	↓	(d)	(d)	↓
Permatex No. 3 (Permatex Co.)	No reaction	No reaction	Reaction	Reaction	Not tested
Q-Seal (Quigley Co.)	No reaction	↓	No reaction	↓	↓
Blue Goop (Crawford Fitting Co.)	Exploded	↓	Not tested	↓	↓
Molylube (Bel-Ray Co., Inc.)	Exploded	↓	Not tested	↓	↓
Plast-O-Seal (The Colonial Plastics Mfg. Co.)	Burned	↓	Not tested	↓	↓
Permatex No. 1 (Permatex Co.)	Not tested	Burned	Not tested	Not tested	Not tested
Permatex No. 2 (Permatex Co.)	↓	↓	↓	↓	↓
X-Pando seal *coating* (X-Pando Corp.)	↓	↓	↓	↓	↓
Tyte Unyte (J. C. Whitlam Mfg. Co.)	↓	↓	↓	↓	↓
White lead	↓	↓	↓	↓	↓
Solid					
Ruby (Al_2O_3)	No reaction	No reaction	No reaction	No reaction	Not tested
Teflon (E. I. du Pont de Nemours & Co.)	↓	↓	No reaction	No reaction	↓
Fel-F Solid (M. W. Kellogg Co.)	↓	↓	Reaction[f]	Reaction	↓
Kel-F Elastomer 5500 (M. W. Kellogg Co.)	↓	↓	No reaction	Reaction	↓
Graphitar (United States Graphite Co.)	↓	↓	No reaction	Reaction	↓

[a] Samples are listed by trade name in most cases; the compositions were not available.

[b] Ref. 4.

[c] Reacted when exposed surface area was increased.

[d] Not tested; Kel-F and Fluorolube materials are all polymers of chlorotrifluoroethylene.

[e] Reacted in two of four tests.

[f] Reacted in one of two tests.

TABLE 3-X.—NONMETALS EXPOSED TO GASEOUS AND LIQUID FLUORINE (REFS. 4 AND 23)—Concluded

Sample [a]	Sample exposed to–				Sample injected into liquid fluorine at 1500 psig pressure
	Liquid fluorine at atmospheric pressure	Gaseous fluorine at atmospheric pressure [b]	Liquid fluorine at 1500 psig pressure	Gaseous fluorine at 1500 psig pressure [b]	
Powdered Graphitar (United States Graphite Co.)	Not tested	Burned	Not tested	Not tested	Not tested
Neoprene-covered Fiberglas	Exploded	No reaction	↓	Reaction	↓
N-43 plus neoprene-covered Fiberglas	Not tested	No reaction	↓	Reaction	↓
Plexiglas (Rohm & Haas Co.)	No reaction	No reaction	Reaction	Reaction	Not tested
Tygon tubing (U. S. Stoneware Co.)	↓	↓	Reaction	↓	↓
Vinylite (Carbide and Carbon Chemicals Co.)	↓	↓	No reaction	↓	↓
Pennsalt PCC (Pennsylvania Salt Mfg. Co.)	↓	↓	No reaction	↓	↓
Pennsalt PCI (Pennsylvania Salt Mfg. Co.)	↓	↓	Reaction [f]	↓	↓
Flux on silver-soldered copper-to-brass joint	↓	↓	Not tested	↓	↓
Slag on stainless-steel weld joint	No reaction	No reaction	No reaction	Reaction	Not tested
Flux on silver-soldered stainless-steel joint	No reaction	No reaction	Reaction	Reaction	↓
Dow Corning Elastomer	Not tested	Burned	Not tested	Not tested	↓
Molykote Type Z Powder (Bel-Ray Co., Inc.)	↓	↓	↓	↓	↓
Litharge and glycerine	↓	↓	↓	↓	↓
Palmetto (Greene, Tweed & Co.)	↓	↓	↓	↓	↓

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[a] Samples are listed by trade name in most cases; the compositions were not available.

[b] Ref. 4.

[f] Reacted in one of two tests.

Most of the materials were not sufficiently compatible for use in fluorine systems; however, the tests did demonstrate the typical characteristics of fluorine in showing remarkable inhibition to reaction with many nonmetals under nonflow or static conditions. Recognition of this fact is important in dealing with fluorine. Later investigations under dynamic conditions with some of the more resistant materials (section 3.3.3) substantiate this conclusion.

Consistent results were obtained in both liquid and gaseous tests in indicating that an increase in pressure (0 to 1500 psig) increased reactivity. Under gaseous conditions, all but two of the materials reacted when the pressure was increased to 1500 pounds per square inch gage.

3.3.2 **Static Compatibility Tests**

Reactivity of elemental fluorine had been defined by earlier work (section 3.3.1), but little information existed on the effects of reactivity to be expected from addition of oxygen to fluorine. To define these effects, a program involving static exposure of nonmetals to both fluorine and FLOX was conducted (ref. 24). The resulting information was the basis for later dynamic studies (section 3.3.3).

In the static liquid FLOX compatibility test program (ref. 24), the sample was placed on the movable sample holder rod (fig. 3–14),

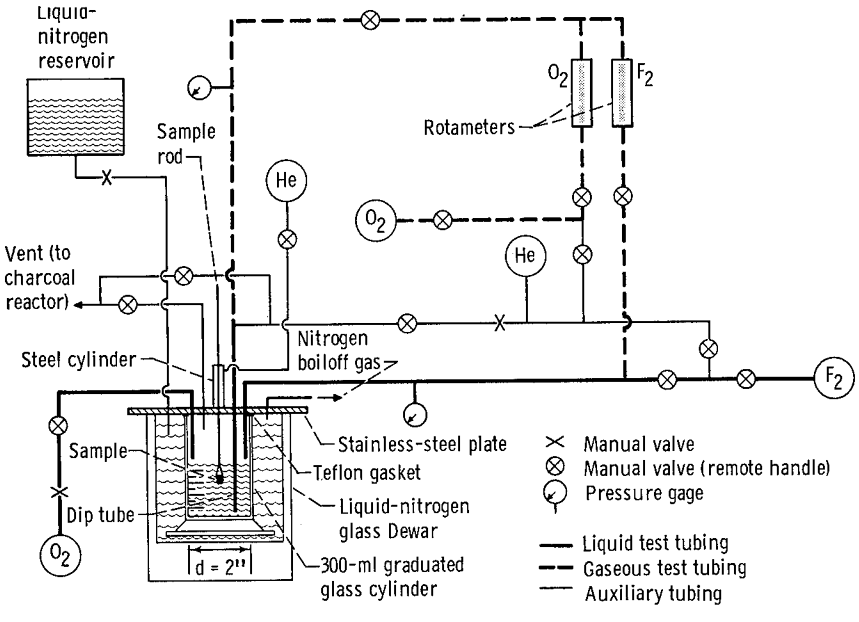


FIGURE 3–14.—Schematic drawing of FLOX system for static tests.

inserted by remote control into the FLOX mixture, and exposed to FLOX for 15 seconds. The sample was then agitated for another 45 seconds. If no reaction occurred, the sample was withdrawn into the helium-inerted tube. More fluorine was added to increase the FLOX concentration and the sample reimmersed. If the sample survived the maximum FLOX concentration used (80 to 85 percent), it was then immersed and agitated in pure liquid fluorine for 5 minutes. If the sample survived, it was removed, inspected, and reweighed.

In the gaseous tests, the sample was held stationary on the sample holder (fig. 3–14). Gaseous FLOX, at controlled concentration and pressure (2 psig or less), was slowly passed through the test chamber for 3 minutes at each concentration. The concentration was increased by increasing the rate of fluorine flow relative to the oxygen flow.

Results for all the materials tested statically in gaseous and liquid FLOX are given in the form of a bar graph in figure 3–15 (ref. 24). Identification and structures of materials tested are given in table 3-XI. In the figure, the gap between nonreaction and the reaction symbols is explained by the fact that concentration was increased incrementally, and this gap represents an unknown region of reactivity. Examination of the results indicates that reactivity with FLOX is a function of fluorine concentration. It must be emphasized, however, that these results were obtained under carefully controlled conditions. The reaction point in the figure represents the *maximum* concentration these materials may withstand under ideal static conditions. In practice, a wide margin of safety should be used to allow for variation of quality control in production of the material.

In the liquid testing, when a reaction occurred it was either an explosive reaction or a relatively slow-burning surface reaction. The nature of the reaction seems related to the degree of porosity of the material and its ability to absorb fluorine. When a reaction occurred between a porous material and fluorine or FLOX, it was usually quite violent. Therefore, in the physical makeup of the nonmetallic materials porosity appears to have an important effect on the type of reaction. The reactions that occurred after longer time delays seem dependent on a surface initiation with a highly variable and unpredictable induction period. The explosive reactions observed were similar to those observed between fluorine and water or crystalline carbon (refer to section 3.1.2).

The gaseous static FLOX tests were run at atmospheric temperature and pressure conditions. Since a temperature difference of about 350 F° existed between liquid and gaseous FLOX, it was initially expected that, with gaseous FLOX at the higher temperature, the fluorine concentration required for reaction would be less than that required for the liquid exposure. Normally, an increase in temperature increases the possibility of ignition as well as the reaction rate; however, as figure 3–15 shows,

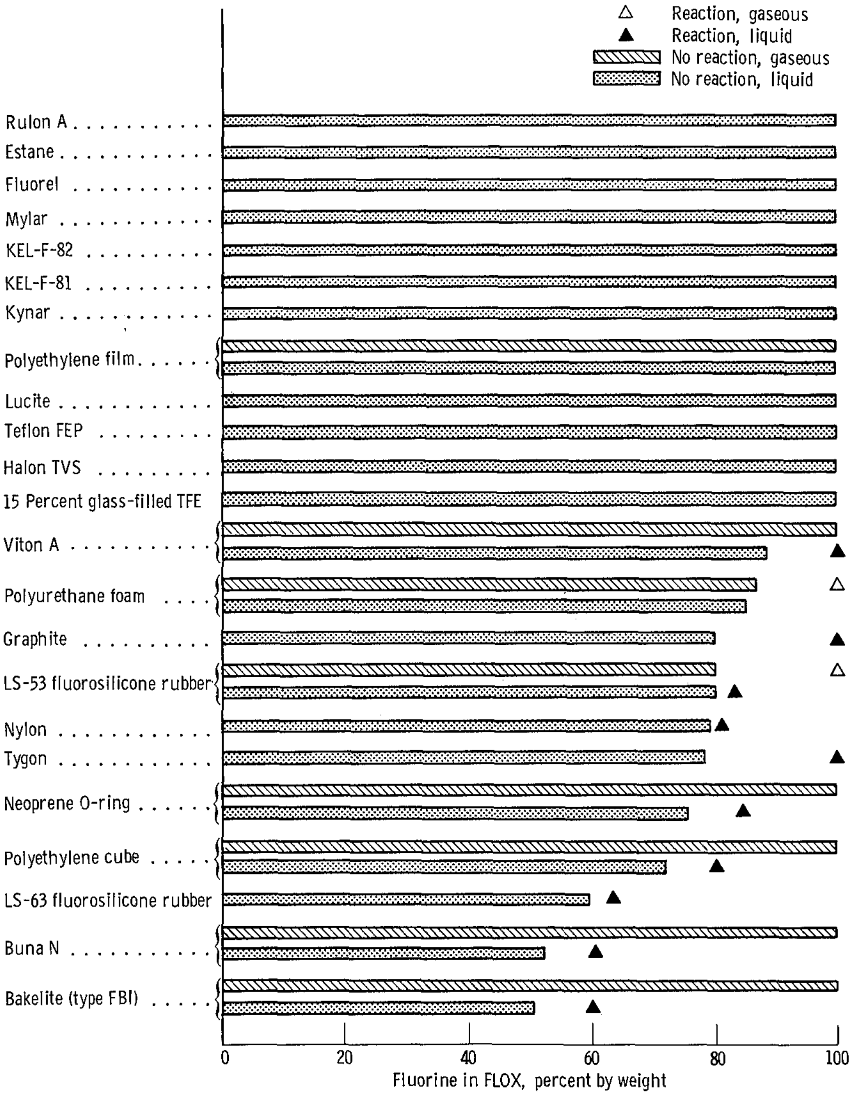
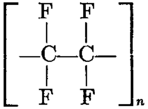
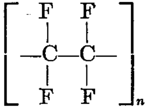
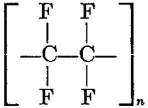
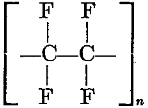
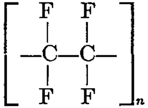
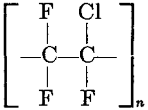


FIGURE 3-15.—Static compatibility test results for solid ~~nonmetals in~~ FLOX. Liquid FLOX temperature, —320° F; gaseous FLOX temperature, 20° to 40° F; pressure, atmospheric (ref. 24). (These results should not be used as a guide in selecting materials to withstand dynamic conditions or pressures greater than atmospheric.)

reactions occurred more readily in liquid than in gas for particular concentrations. Since the only parameter changed here was temperature, the greater reactivity appears to be caused by the higher molecular density (fluorine molecules per unit volume) of the liquid; that is, the

TABLE 3-XI.—TEST MATERIALS IDENTIFICATION (REF. 24)

Trade name	Chemical name or description	Molecular structure
Teflon TFE	Polytetrafluoroethylene	 $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right]_n$
Halon TFE, G-80	Polytetrafluoroethylene	 $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right]_n$
Rulon A	Polytetrafluoroethylene with MoS_2 filler	 $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right]_n + MoS_2$
Nickel-filled Teflon	Polytetrafluoroethylene with nickel-powder filler	 $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right]_n + Ni$
15-Percent glass-filled Teflon	Polytetrafluoroethylene with glass fibers	 $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right]_n$ +Glass
Kel-F 81	Polychlorotrifluoroethylene (CTFE)	 $\left[-\overset{F}{\underset{F}{C}}-\overset{Cl}{\underset{F}{C}}- \right]_n$

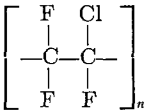
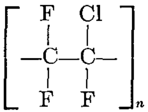
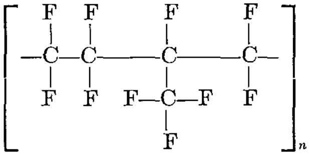
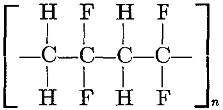
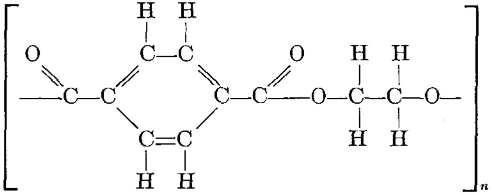
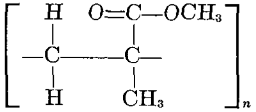
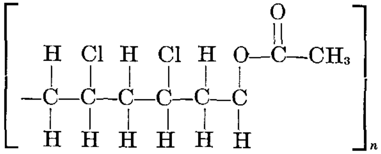
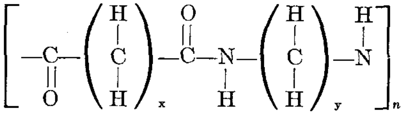
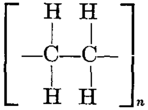
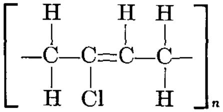
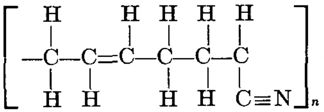
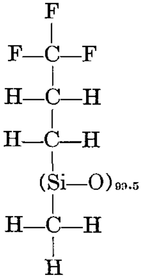
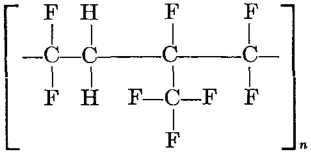
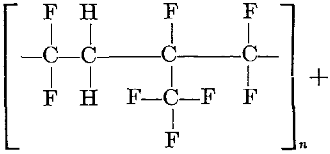
Plaskon 2400 ----------	Polychlorotrifluoroethylene (CTFE)	
Halon TVS (now called Plaskon 2200)	Polychlorotrifluoroethylene (CTFE)	
Teflon FEP ----------	Fluorinated ethylene propylene	
Kynar ----------	Vinylidene fluoride ----------	
Kel-F 82 ----------	Copolymer of CTFE and 3 mole percent vinylidene fluoride	----------
Mylar ----------	Polyethylene terephthalate --	

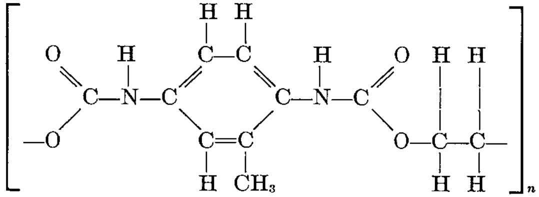
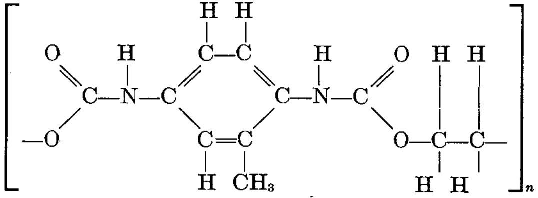
TABLE 3-XI.—TEST MATERIALS INDENTIFICATION (REF. 24)—Continued

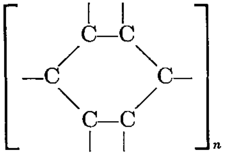
Trade name	Chemical name or description	Molecular structure
Lucite	Polymethyl methacrylate	
Tygon	Polyvinyl chloride-acetate	
Nylon	Polyamide	
Bakelite	Phenol formaldehyde	Not available
Polyethylene	Polyethylene	
Neoprene	Polychloroprene	 +Carbon black (a)

Buna N	Copolymer of acrylonitrile and butadiene	 +Carbon black	[a]
LS-63 Rubber	Trifluoropropyl methyl polysiloxane	 +Curing agents	[a]
LS-53 Rubber	Trifluoropropyl methyl polysiloxane		
Viton A	Copolymer of vinylidene fluoride and hexafluoropropylene	 +Carbon black	[a]
Fluorel	Copolymer of vinylidene fluoride and hexafluoropropylene	 +Carbon black	[a]

[a] Simplified structure in uncured state.

TABLE 3-XI.—TEST MATERIALS IDENTIFICATION (REF. 24)—Concluded

Trade name	Chemical name or description	Molecular structure
Polyurethane foam	Polyurethane	 +Curing agents (a)
Estane	Polyurethane rubber	 +Carbon black (a)

Graphite ----------------	Crystalline carbon ----------	
CPE 401 (BR 93) with EPON 828	Amorphous chlorinated polyethylene	Unknown
CPE 402 (TDX 176) with tribase E	Amorphous chlorinated polyethylene	Unknown
CPE 403 with EPON 828---	Semicrystalline chlorinated polyethylene	Unknown

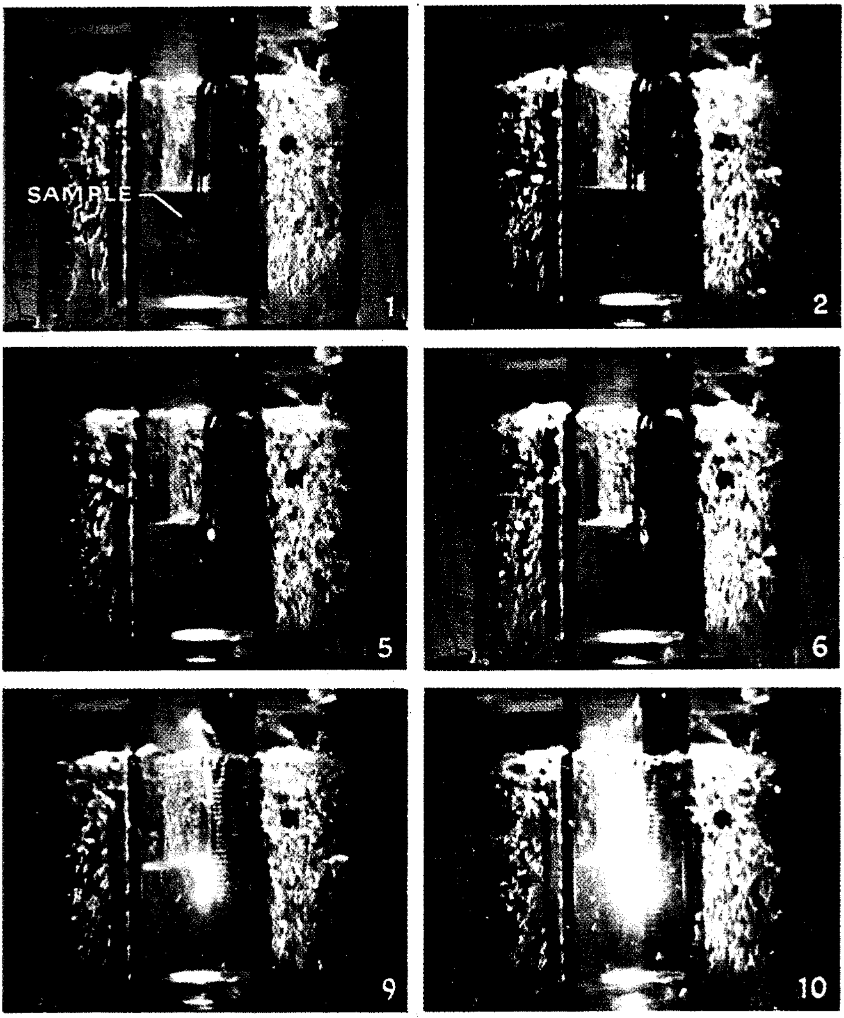
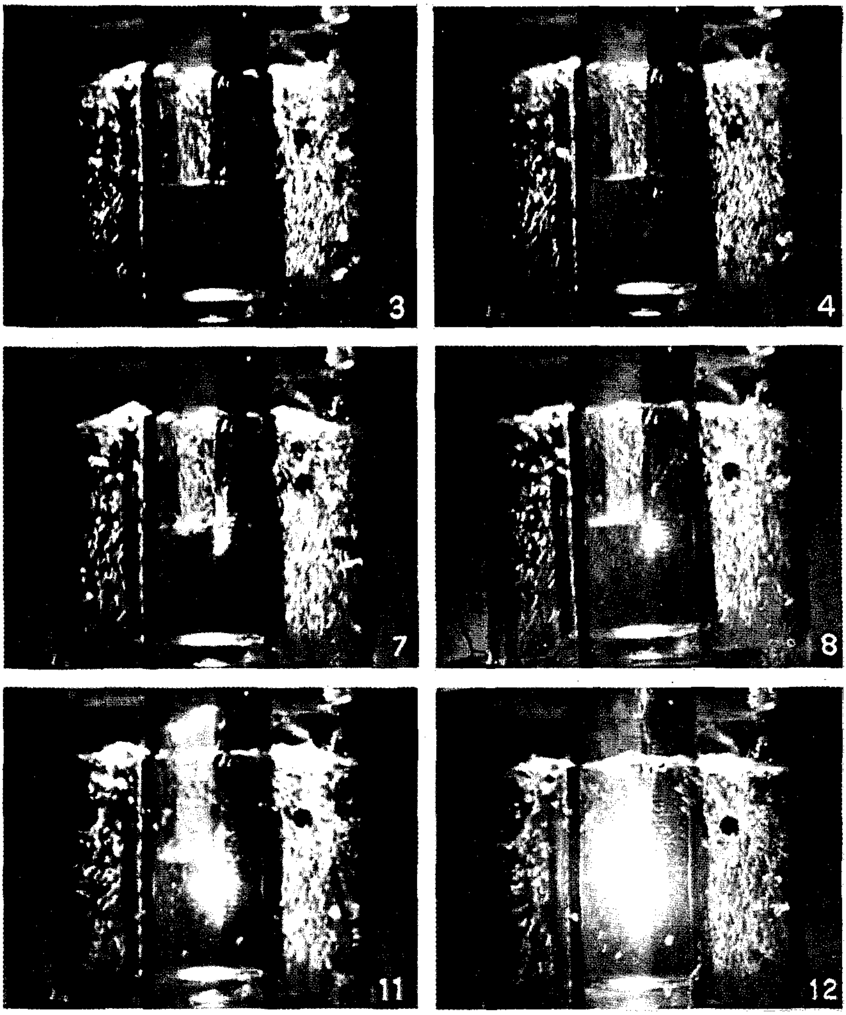


FIGURE 3–16.—Typical slow-burning surface reaction of neoprene

effect of the greater availability of fluorine atoms to participate in the reaction in the liquid case seems to exceed the effect on reactivity normally obtained from an increase in temperature. This explanation was also supported by the results of the high-pressure tests (section 3.3.1). In that series of tests, the increase in the molecular density of the gas at 1500 pounds per square inch gage, as well as the temperature effect, caused a higher reactivity than in the liquid case. Therefore, the higher enthalpy of the room-temperature gaseous system at atmospheric pres-



O-ring in 83.5 percent FLOX. Film speed, 24 frames per second.

sure was not in itself sufficient to cause higher reactivity of the gas, but by increasing the pressure to 1500 pounds per square inch gage with resulting increase in molecular density, the reactivity exceeded that of the liquid. This reactivity factor is further discussed in section 3.3.3.5.

A typical slow-burning surface-reaction sequence (fig. 3–16) shows a neoprene O-ring being tested in 83.5-percent liquid FLOX (83.5 percent fluorine by weight in a fluorine-oxygen mixture). The reaction, once initiated, seemed to propagate itself over an increasingly large area;

burning was smooth and quiet. The sequence shown occurred in 1/2 second.

Samples that exhibited reaction delay in the gaseous tests were observed to smolder before igniting. In other words, the material reacted slowly until its combustion temperature was reached, at which time it ignited.

3.3.3 **Dynamic Tests**

A dynamic test program (ref. 24) was carried out to define velocity effects on reactivity of selected nonmetals with various FLOX concentrations, since experience with fluorine system failures showed that most

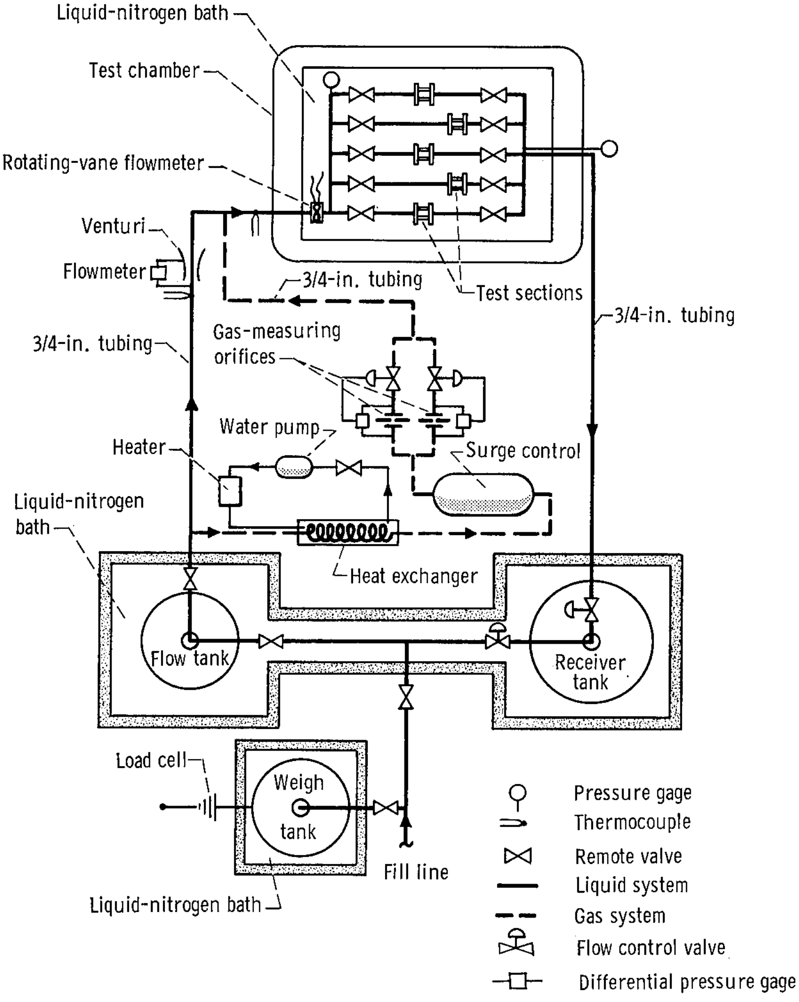


FIGURE 3–17.—Schematic drawing of FLOX system for dynamic tests (ref. 24).

ignitions occurred with combinations of high pressures and high velocity. Test data from this program revealed that reactivity varies as a function of increasing flow velocity and increasing FLOX concentration in a predictable manner. Generally, the fluorocarbon polymers, particularly the fully fluorinated straight-chain polymers, were most compatible with fluorine and FLOX (ref. 24). The test program was essentially divided into three phases: (1) an initial study to determine the effects of pressure at flow velocity, (2) a series of liquid-phase FLOX tests to define the effects of flow velocity and concentration on the reactivity of FLOX with selected nonmetals, and (3) a series of gaseous-phase tests to define the effects of flow velocity, FLOX concentration, and ambient temperature on the reactivity of FLOX with selected nonmetals.

The test apparatus used for the dynamic tests is shown schematically in figure 3–17. The specimen materials were fabricated into tubular orifices (see fig. 3–18) and installed in the test legs of the apparatus.

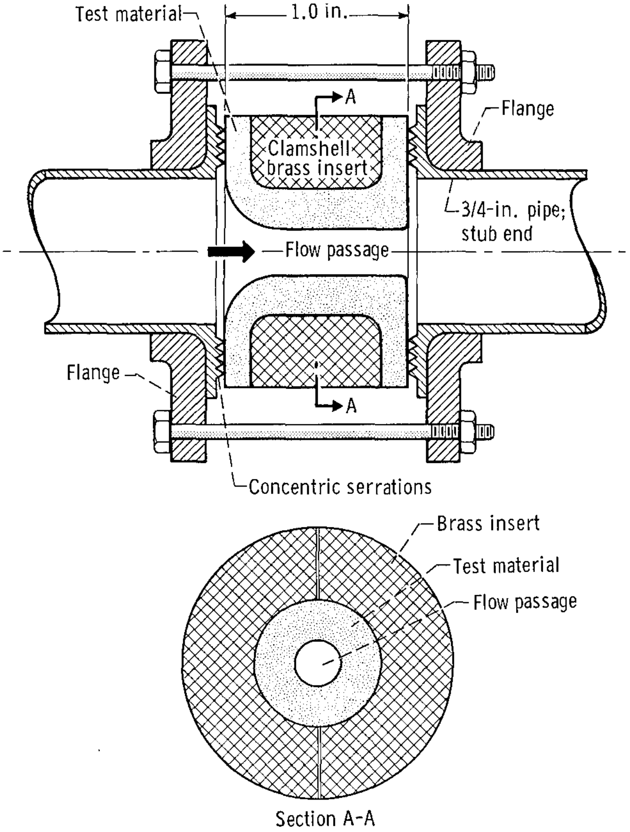


FIGURE 3–18.—Dynamic FLOX test-specimen holder (ref. 24). (Not drawn to scale.)

Flow through the specimen was achieved by pressurizing the flow tank with helium gas to the required pressure to obtain maximum flow, while maintaining only slightly more than atmospheric pressure in the receiver tank. The flow rate was then controlled by operation of a flow-control valve located downstream from the specimen. Flow quantities were measured by the turbine flowmeter and venturi meter.

The testing procedure for this program involved increasing velocity in increments (for each FLOX concentration); smaller increments were chosen as the suspected reaction point was approached. Successive runs were made through each specimen (at increasingly higher pressures in the flow tank to provide higher maximum velocities) until reaction occurred.

The first phase of testing involved varying pressures up to 400 pounds per square inch gage at a flow velocity of 12.2 feet per second. Since no reactions occurred for the materials tested, it was concluded that the effects of pressure on reactivity (from the pressurization required to achieve flow) would be negligible when compared with the effect from velocity. Since a pressure effect is present in any confined flow situation, the velocity effects on reactivity should be valid for an equivalent condition in an operational system.

The main conclusions drawn from the dynamic tests (ref. 24) are as follows:

(1) Some nonmetallic materials may be considered for use in rocket systems with fluorine or FLOX under controlled conditions of exposure; however, because of possible variations in quality and because nonmetals are more sensitive to contamination than metals in a fluorine environment, a margin of safety should be provided based on the acceptable level or risk for the particular application. Where flight reliability is required, qualification testing must be performed.

(2) Generally, the highly fluorinated and highly chlorinated materials are more suitable for use in fluorine or FLOX systems than materials containing atoms such as hydrogen in their molecular structures or materials impregnated with some noncompatible additive. Of all materials tested, the polytetrafluoroethylenes, Halon TFE and Teflon TFE, are the most promising for practical application in fluorine or fluorine-oxygen environments.

(3) The strong significance of flow velocity on reactivity of nonmetallic materials with fluorine or FLOX indicates that some of these materials are suitable for use as static seals if it is assumed that no contamination is present. Exposure to direct flow (particularly in the liquid phase) should be avoided except under conditions where the risk is acceptable.

(4) The orderly molecular arrangement of the more crystalline

materials makes them less susceptible to fluorine attack than the amorphous materials with their irregular molecular alinement. A material selected for use should therefore be of the highest crystalline form available for the particular material.

(5) The reactivity of nonmetallic materials with fluorine and FLOX increases as a function of molecular density (number of molecules per unit volume) present at the point of reaction initiation.

3.3.3.1 *Reactivity profiles from liquid tests.*—From data obtained in the dynamic tests, reactivity profiles (flow velocity at burnout as a function of FLOX concentration at burnout) were generated for selected materials (ref. 24). Since a material must be tested to burnout at several concentrations in order to generate a reactivity profile, only the materials of greatest interest were chosen. A composite of these reactivity profiles is shown in figure 3–19. (Fig. 3–20 shows those materials for which only a single test was made.)

It should be emphasized that the data were obtained under carefully controlled conditions. The reaction line in the figure represents the *maximum* concentration and/or velocity these materials may withstand under ideal conditions. In practice, a wide margin of safety should be used. Differences in reactivity with fluorine are possible with supposedly identical materials because of variations in fabrication processes, which may produce voids, impurities, or other differences in the material. Therefore, materials selected for use in a fluorine or FLOX environment

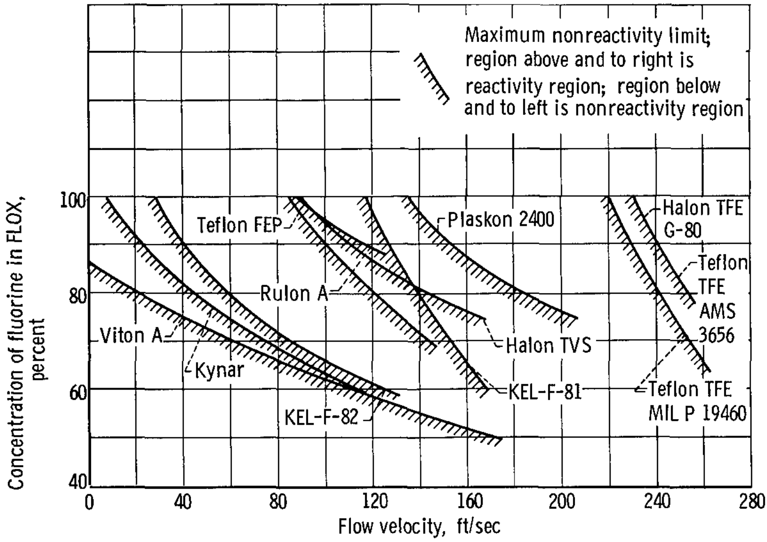


FIGURE 3–19.—Composite liquid FLOX reactivity profiles.

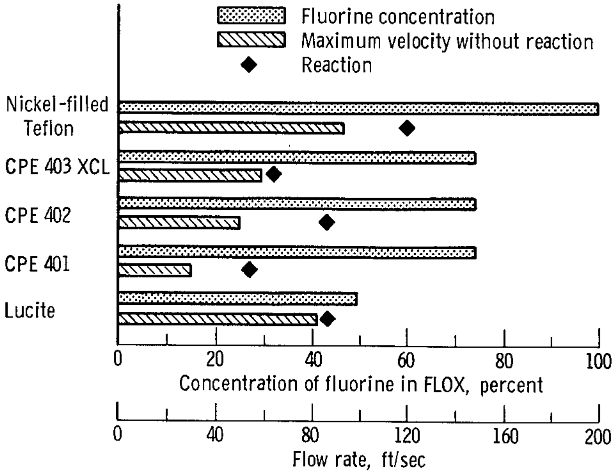


FIGURE 3-20.—Dynamic liquid FLOX compatibility tests (single data points, ref. 24). Pressure range, 100 to 400 pounds per square inch gage; temperature, —320°F; specimen configuration, 0.25-inch orifices.

should be of the highest possible quality. It should be remembered that the activation energy required to initiate reaction with these nonmetallic materials is not appreciably greater than the energy level that exists under some normal exposure conditions. This is particularly true when these materials are exposed to the flow of liquid fluorine or FLOX. Therefore, when exposure includes a high flow rate of liquid fluorine (or FLOX of high concentration) only a relatively small increase in flow rate, or the presence of a minor amount of contamination, could result in reaction initiation. Because of the lack of statistical test information, no fixed factor of safety can be given; the margin to be used should depend on the acceptable level of risk for the particular application. In all applications of nonmetallic materials, the severity of environmental conditions should be minimized by avoiding direct exposure to flow if possible. The most FLOX-compatible materials that fulfill physical requirements should be chosen when nonmetals must be used.

3.3.3.2 *Typical reaction.*—A specimen of Lucite was tested to failure under dynamic conditions (ref. 24) because it is transparent and the reaction initiation and propagation can be photographed easily. Reaction of this material occurred at a flow velocity of 84 feet per second and is shown in figure 3-21. (Distortion was caused by photographing through liquid nitrogen.) In this close-up view, the first frame shows FLOX passing through the specimen. The second frame shows reaction initiation (about 1/24 sec later). A projection review of the original film showed that this reaction was initiated at the inlet near the end of

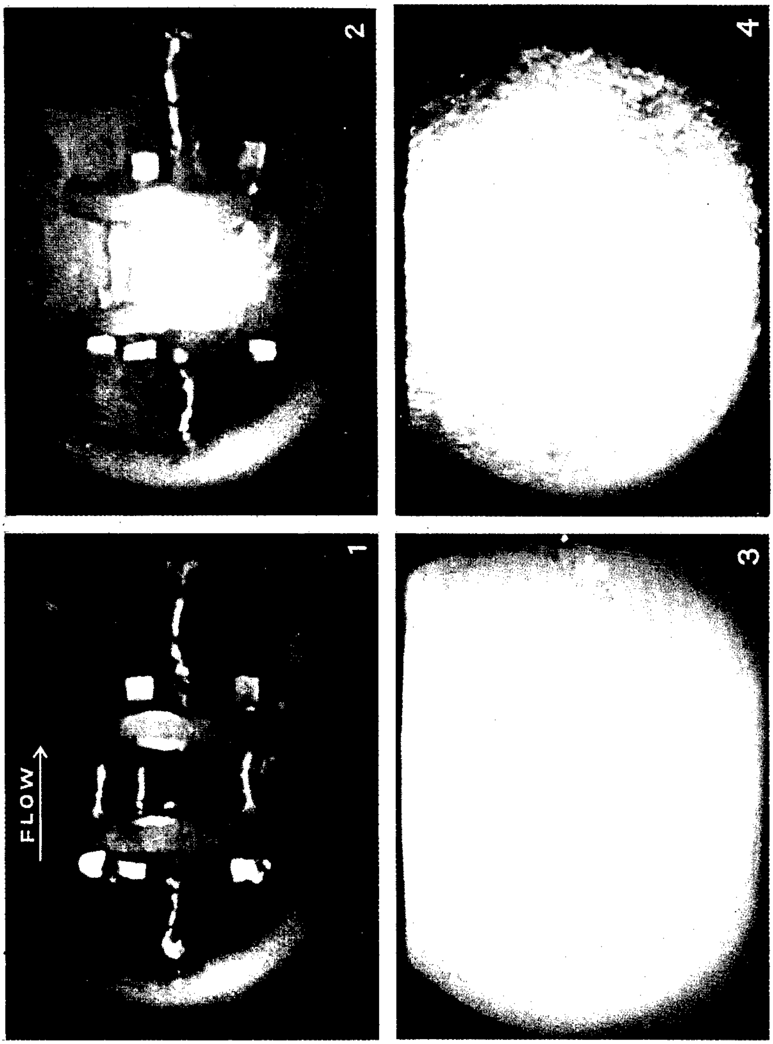


FIGURE 3-21.—Dynamic FLOX compatibility test of Lucite specimen. Film speed, 24 frames per second; time interval between frames, 1 and 2, and 3 and 4, 9 seconds (ref. 24).

the throat curvature (see fig. 3–21) of the test specimen (not visible in the figure since contrast was lost in making the print). Reaction was then propagated over the entire surface of the channel in the specimen. The remaining frames in figure 3–21 show the reaction at increasing stages in its progression.

3.3.3.3 *Gaseous dynamic testing.*—High-velocity flow tests were performed with pure gaseous fluorine to explore the effect of velocity on reactivity (ref. 24). Table 3-XII shows nine materials that were fabricated into 1/4-inch orifices and exposed to 30-second test runs at increasing velocities. These materials withstood maximum conditions of gaseous fluorine flow of 900 feet per second (sonic flow) for several seconds and average velocities of 700 to 880 feet per second for the test run. Table 3-XIII shows three materials that were fabricated into 1/8-inch orifices and exposed from 5 to 30 minutes to sonic flow rates. While all the materials tested survived exposure to sonic flow rates, only the TFE (table 3-XIII) held up under the maximum 30-minute time obtainable with the test apparatus and procedure (see section 3.3.3.5).

TABLE 3-XII.—GASEOUS FLUORINE COMPATIBILITY TESTS (REF. 24)

Material (1/4-in. tubular orifices)	Duration of sonic velocity of 900 ft/sec, sec	Average velocity for 30-sec period, ft/sec
Halon TFE	10	825
Teflon TFE	[a] Unknown	[a] Unknown
Rulon A	11	750
Kel-F-81	4	825
Teflon FEP	5	750
Halon TVS	8	700
Kel-F-81 amorphous	9	850
Kel-F-82	16	880
Kynar	2	825

[a] Instrument malfunction.

TABLE 3-XIII.—GASEOUS FLUORINE TIME-EXPOSURE TESTS (REF. 24)

Material (1/8-in. tubular orifice)	Velocity without reaction, ft/sec	Time, min	Velocity that caused reaction, ft/sec	Time, min
TFE	900 (sonic)	30	No reaction	30
Kel-F-81 amorphous	372	30	900 (sonic)	5
Kel-F-82	279	30	900 (sonic)	15

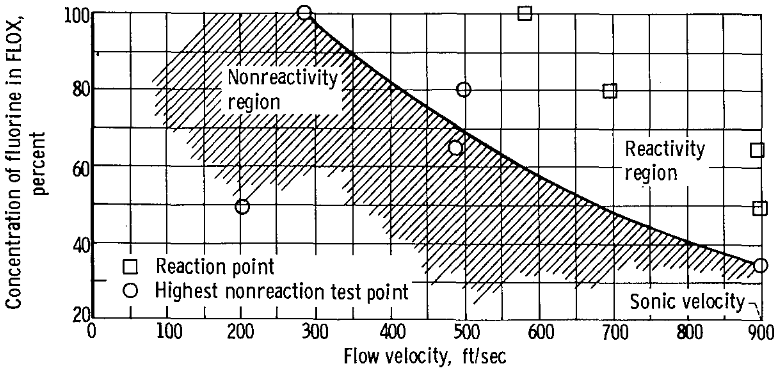
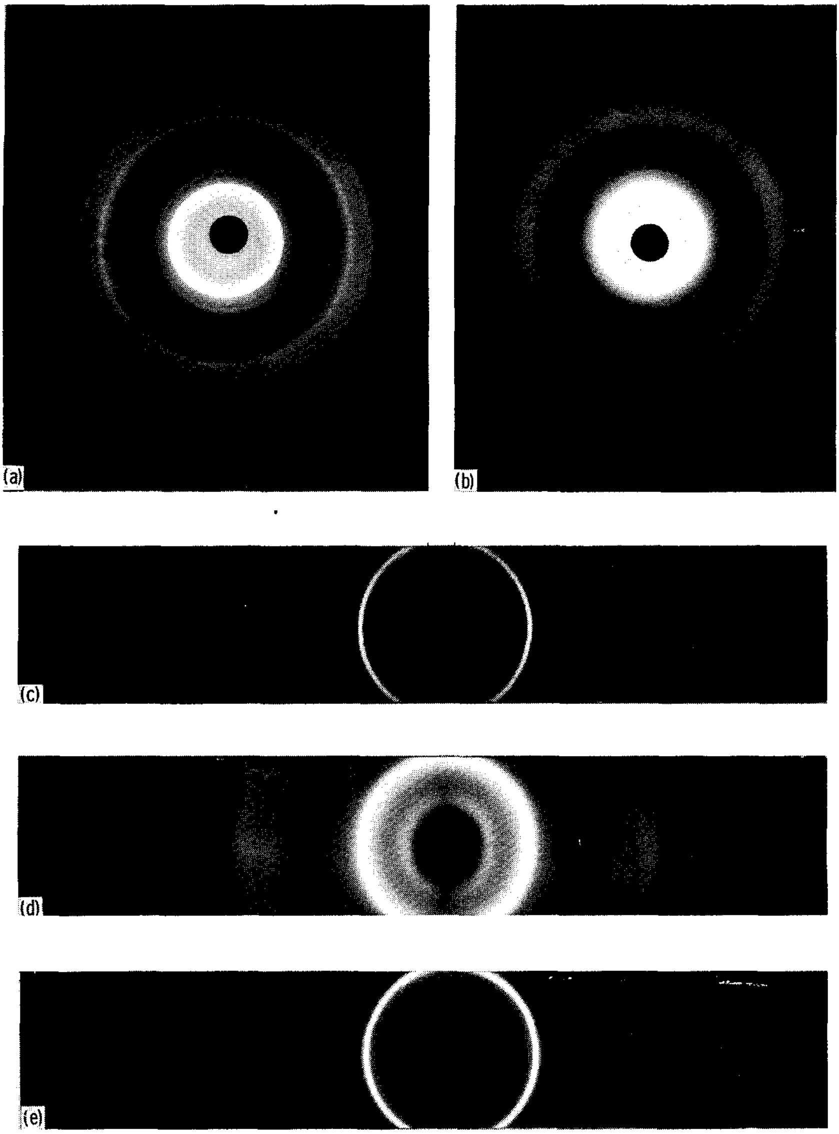


FIGURE 3-22.—Gaseous FLOX reactivity profile for Viton A (ref. 24). Temperature, 60° F; sample configuration, 0.20-inch orifice.

A reactivity profile for Viton A is shown in figure 3-22 (the only material for which the required test runs were made). The explanations of the curve and precautions given for application of the liquid reactivity profiles also apply for this figure. From these limited data, it appears possible that a step occurs in the reactivity profile for Viton A at sonic velocity, although the curve does not indicate this. Reactions for this material usually occurred at sonic velocity, before the backpressure buildup reduced the velocity. Only at the 34-percent-FLOX concentration was sonic flow maintained (for 9 sec) without reaction; after this time, the velocity decreased to an average of 700 feet per second for 60 seconds.

3.3.3.4 *Crystallinity effects on reactivity.*—Tests of chlorotrifluoroethylenes in crystalline and amorphous forms revealed that the crystalline form was more resistant to reaction than the amorphous form (ref. 24). This led to an attempt to control crystallinity in materials.

X-ray diffraction photographs were taken in the Lewis diffraction laboratory in an attempt to measure the crystallinity of Kel-F and other materials. These studies provided a means for making comparisons of crystallinity among different materials. Figure 3-23 shows X-ray diffraction photographs of five different materials. The relative degree of crystallinity is estimated from the relative sharpness of the diffraction rings. Teflon TFE appears to be more crystalline than Teflon FEP. The difference in crystallinity is similarly apparent between crystalline and amorphous Kel-F-81. The figure also shows that heat-treated Kel-F-81 amorphous has a degree of crystallinity similar to crystalline Kel-F-81. These photographs demonstrate that the heat-treating process transforms the amorphous material to a more crystalline state. Also, this crystalline form is more resistant to reaction than the amorphous form from which it was created.



(a) Teflon TFE. (b) Teflon FEP.

(c) Crystalline Kel-F-81.

(d) Kel-F-81 amorphous.

(e) Kel-F-81 amorphous (heat treated).

FIGURE 3-23.—X-ray diffraction patterns (ref. 24).

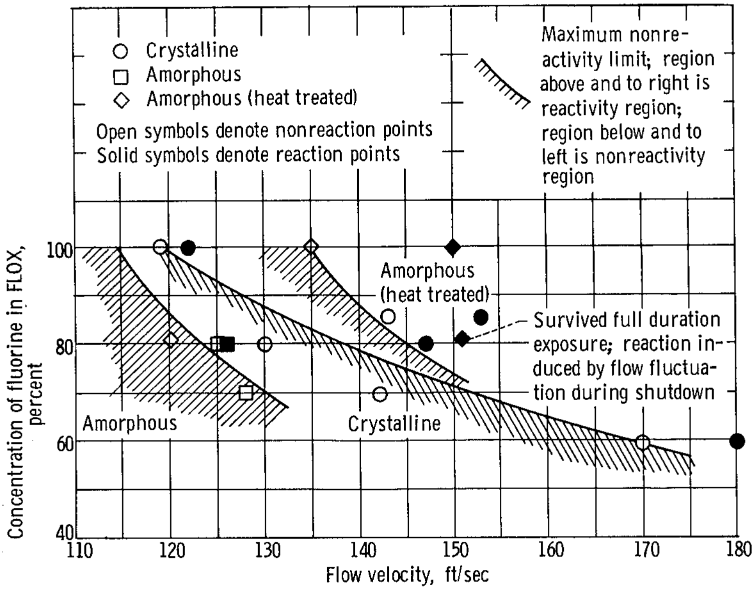


FIGURE 3–24.—Liquid FLOX compatibility profiles for crystallinity effects for Kel-F-81 (ref. 24).

Different degrees of crystallinity are obtained by varying the cooling rate during the molding process, where faster cooling rates produce more amorphous materials. Since test data show that Kel-F-81 amorphous reacted under less severe conditions than crystalline Kel-F-81, an attempt was made to transform Kel-F-81 from the amorphous to the crystalline form by heating two amorphous specimens to a temperature just below the melting point and allowing them to cool slowly (33 F°/hr). Theoretically, this treatment should transform the material from amorphous to crystalline. These specimens were tested in the same manner as the other Kel-F-81 specimens and gave a reactivity profile that falls in the same general position as that of the crystalline Kel-F-81 (fig. 3–24). On the basis of the limited number of data points taken, the heat-treating process increased the resistance of the material to FLOX (which indicates that the orderly arrangement of the molecules in the crystalline form makes the material less susceptible to fluorine attack than in the amorphous form with its irregular molecular alinement). When one of the fluorocarbons is being selected for use in fluorine systems, the most crystalline form available should be used.

3.3.3.5 *Other factors affecting reactivity.*—Some factors other than velocity and FLOX concentrations were also observed as affecting reactivity (ref. 24):

(1) Exposure time: In order to attain sustained high velocities to gain information on the effect of exposure time, it was necessary to reduce the specimen orifice diameter from 1/4 to 1/8 inch to provide longer run times. Three specimens were tested (table 3-XIII), and sustained velocities up to a maximum of sonic were attained in each case. TFE successfully withstood pure gaseous fluorine flow at sonic velocity of 900 feet per second for 30 minutes; Kel-F-81 amorphous ignited after 5 minutes at 900 feet per second. All three specimens had just previously been exposed to lower flow velocities (see table 3-XII) for 30 minutes without reacting.

A Viton A specimen was exposed to gaseous 50-percent-FLOX flow at 200 feet per second for 30 minutes. There was no reaction at this velocity during the extended time run. In order to obtain an additional data point for this material, the specimen was then subjected to sonic velocity of 900 feet per second. The specimen reacted almost immediately.

The effect of exposure time on reactivity of liquid FLOX was not specifically examined; however, many short-duration test runs were consistently made on the same test specimen with no effect until the reaction conditions for the material (concentration and velocity) were reached. The reaction points seemed to be independent of the total exposure time leading up to the reaction conditions. Additionally, past Lewis experience has shown that TFE can be used successfully in valves for packing and seals for prolonged time periods (several months of intermittent use without effect is not uncommon). Therefore, exposure time in itself is probably not a significant factor in reactivity of either gaseous or liquid fluorine or FLOX. It may have some effect at marginal FLOX concentrations and flow velocities; however, some very long run times, hours rather than minutes, would be needed to verify this possibility.

(2) Phase effects: Normally, at a higher temperature, a material is closer to its enthalpy of activation. However, reviews of both static and dynamic test results revealed that both FLOX and fluorine were much more reactive as cryogenic liquids than as ambient gases. According to reference 24, the higher molecular density in the liquid phase had more of an effect on reaction initiation than did the higher temperature of the gaseous phase. The decreased reactivity due to the diluent effect of oxygen in a FLOX mixture also seems to substantiate the premise that reactivity is partly a function of the molecular density of fluorine at a potential reaction zone.

The effect observed during static tests is discussed in section 3.3.3. The greater reactivity of the cryogenic liquid was also noticed in the dynamic tests. A comparison between the liquid and the gaseous reactivity profiles for Viton A (figs. 3–19 and 3–22) shows that much higher velocities were required to obtain reactions with gaseous FLOX than with liquid FLOX at similar concentrations. This fact, together with the fact that many other materials which did not react with gaseous fluorine at sonic velocity did react with liquid FLOX at much lower velocities, is evidence that the cryogenic liquid is more reactive than ambient temperature gas at pressures up to 400 pounds per square inch gage. The effect of higher molecular density for the liquid seems to exceed the effect on reactivity that is normally characteristic of increases in temperature and enthalpy.

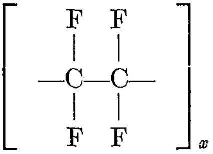
(3) Contamination: The importance of cleanliness in a fluorine system is generally well recognized. All fluorine or FLOX systems should be free from moisture, dirt, oil, grease, and other such contaminants. Reactions of fluorine or FLOX with significant accumulations of foreign materials can trigger a reaction with the system, and particularly with any nonmetallic components. (Cleaning procedures for fluorine systems are included in chapter 6. The cleaning procedure used for the nonmetallic samples tested in this program is included in section 6.2.1.)

3.3.3.6 *Reaction rates.*—With explosive reactions, it was observed that a large portion of the test specimen usually remained after reaction (with either the liquid or the gas). Graphite, which is a very porous material, reacted explosively with 100-percent liquid fluorine after a $1\frac{1}{2}$-minute delay. After the test, 85 percent of the sample remained intact. Reaction characteristics of crystalline and amorphous carbon are not alike. Amorphous carbon is hypergolic with fluorine even at very low concentrations and will burn smoothly even with liquid fluorine or FLOX, while crystalline carbon shows a strong initial inhibition to reaction with fluorine, but reacts explosively when reaction occurs. If reaction is initiated, however, it is self-sustaining and produces the same reaction products as amorphous carbon (mainly carbon tetrafluoride gas, refer to section 3.1.2.2).

Rulon A, which is polytetrafluoroethylene (TFE) impregnated with a molybdenum disulfide filler (for better wear characteristics), reacted explosively, whereas the nonimpregnated polytetrafluoroethylene burned smoothly. Fluorine should have the tendency to react with molybdenum disulfide (see Molylube in table 3-X), and therefore the presence of the filler affected not only the material reaction point but also its rate of reaction. Kynar, which is an unimpregnated resin, also reacted explosively. As shown in table 3-XII, however, this material contains many hydrogen atoms in the side links of its molecular structure. There was a general tendency for materials with high hydrogen content to react explosively. As in the case of graphite, the materials may absorb FLOX interstitially to a certain depth, and the ensuing reaction may involve only the portion of the material that has absorbed FLOX. The explosive reaction then separates the reacted material from the unreacted material and prevents further reaction. In slower burning reactions, ignition began at the surface of the material, progressed over an increasingly large area, and burned inward until the source of reactant was depleted.

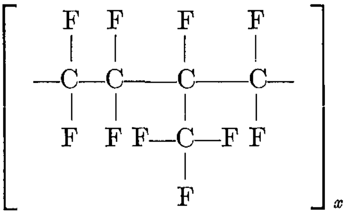
3.3.3.7 *FEP-TFE discrimination.*—During compatibility tests for polymeric materials (ref. 24), polytetrafluoroethylene (TFE) proved to be preferable to FEP (fluorinated ethylene propylene) for use in fluorine or FLOX systems (fig. 3–19). However, a reliable method was required to discriminate between the two basic types, since a particular stock item (with the same physical appearance) could be formed from either material. To define some simple tests to differentiate between these two materials, studies were conducted at Lewis with the following results:

(1) TFE characteristics: At ambient temperatures, polytetrafluoroethylene (TFE) resin tends to be crystalline and very opaque. If no pigments have been added, it is normally a milky-white color that can vary to light gray or light brown. Unless some type of cold-forming process is used, the material will not adhere to itself below 620° F; above this temperature it becomes amorphous and sublimes. The molecular structure for this material is



$$\left[-\mathrm{CF_2}-\mathrm{CF_2}-\right]_x$$

(2) FEP characteristics: Fluorinated ethylene propylene (FEP) tends to be more translucent (than TFE) at ambient conditions. It does not sublime like TFE, but becomes a very viscous fluid above a 500° to 530° F range. In addition, the material adheres to itself above this melting point range. The structure of the material is



$$\left[-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{CF(CF_3)}-\mathrm{CF_2}-\right]_x$$

(3) Sample differentiation tests: To determine whether the material to be used is TFE or FEP, the following general tests were used and can be applied in the field:

(a) Melting point test: The sample is heated to between 530° and 600° F. The Lewis tests indicated that the sample will melt if it is FEP, while if it is TFE, corners will remain sharp and no signs of slumping will be apparent.

(b) Adherence test: When samples are stacked on top of each other and heated to 600° F, the FEP samples will fuse together, while TFE samples will show no signs of cohesion.

(c) Deformation test: A weight (15 g) is suspended from the sample by a wire looped over the sample. The sample is then furnace heated to 550° F to check deformation from an applied load. After 10 minutes at 554° F, the TFE should show no signs of elongation, while the FEP sample should be completely cut through by the weight.

3.3.4 Investigation of Soft-Seal Material Applications

In the course of developing a zero-leak shutoff valve design concept (section 4.4.1), tests were run on six soft-seal materials in 100-percent-fluorine environments (ref. 5). The tests employed a minimum-exposure technique, in which the specimen was surrounded to a maximum degree with metal to increase local thermal conductivity (see section 3.1.1.3). It was expected that reaction of the fluorine with seal materials would thus be minimized. That this occurs is borne out by the test results with nitroso rubber, which could normally be expected to burn when exposed to the flow of liquid fluorine.

The materials tested included

(1) Nitroso rubber
(2) High-percentage glass-filled tetrafluoroethylene (Fluorogreen E-600 and Fluorobrown)
(3) High-percentage metal-filled tetrafluoroethylene
    (a) Nickel filled
    (b) Copper filled
    (c) Bronze filled

In the design of the test-valve seal retainer, the soft-seal material was protected by minimizing its exposed surface area (refer to section 4.4.1). This, together with the heat-dissipating characteristic of the surrounding metal, tended to inhibit a combustion reaction (refer to section 3.1.1.3).

Test results showed surface decomposition in the nitroso rubber sample over its shielded area as well as over its exposed annulus. A layer of porous, gumlike parent material covered the entire specimen after an exposure of 61 seconds. After 178 seconds of exposure, the annulus of the glass-filled polytetrafluoroethylene (Fluorobrown) was pitted because of noncombustive reaction with the fluorine. Approximately one-sixth of the specimen was lost in this manner. The Fluorogreen E-600 showed no evidence of deterioration after 63 seconds of exposure.

Under visual examination after exposure, neither chemical change nor fiber migration due to erosion was observed in the metal-filled polytetrafluoroethylene sample. A comparison of the weights of the samples before and after testing quantitatively confirmed the observation. Thus, no conclusion could be made regarding any inhibiting effect on chemical reaction from addition of metal fillers to polytetrafluoroethylene.

The major value of these tests was in demonstrating

(1) That fluorine compatibility of a material can be enhanced by protecting it from the flow stream and by minimizing surface exposure
(2) That high thermal conductivity reduces the tendency to combustive reactions

3.4 FLOX SPILL TESTS ON COMMON MATERIALS

The use of fluorine or FLOX as an oxidizer at rocket installations requires data on reaction characteristics to be expected if fluorine or FLOX is spilled on some common materials (sand, slag, etc.). To gain information on hypergolicity, cloud formation, and other reaction characteristics with some of these materials, tests were conducted at Plum Brook in 1964 (ref. 25), by spilling 5- to 10-pound quantities of fluorine, FLOX, and liquid oxygen onto test specimens of representative materials that might be used in rocket installations.

The test apparatus, shown in figure 3–25, consisted of a $3\frac{1}{2}$-gallon liquid-nitrogen-jacketed stainless-steel tank with appropriate fill and vent lines, a remotely controlled spill valve, and a spill pipe. The valve was insulated with asbestos padding, and the spill pipe was cooled by a liquid-nitrogen coil and purged with helium. Spills were made on samples contained in 12-inch-deep 3-foot-square stainless-steel pans.

The results of the tests (ref. 25) are included in tables 3-XIV and 3-XV. Spills listed are those made with 100-percent fluorine and 30-percent FLOX (30-percent fluorine by weight in liquid oxygen). Spills were also made with liquid oxygen to gain comparative data and these are included in table 3–XVI.

In the spills involving use of 30-percent FLOX, 10-pound quantities were spilled on various materials. It was observed that when no reaction occurred, the toxic vapors merely drifted downwind close to the ground. In other cases, with spills on asphalt, for example, there was a small reaction with little heat release. In such cases, the reaction cloud rose at very low angles. In some reactions, for example, 30-percent FLOX with JP-4 fuel, several rapid microexplosions occurred over a period of 1 to 2 seconds. A yellow fireball formed and expanded to a diameter of 25 to 30 feet (fig. 3–26), and a turbulent black cloud emerged

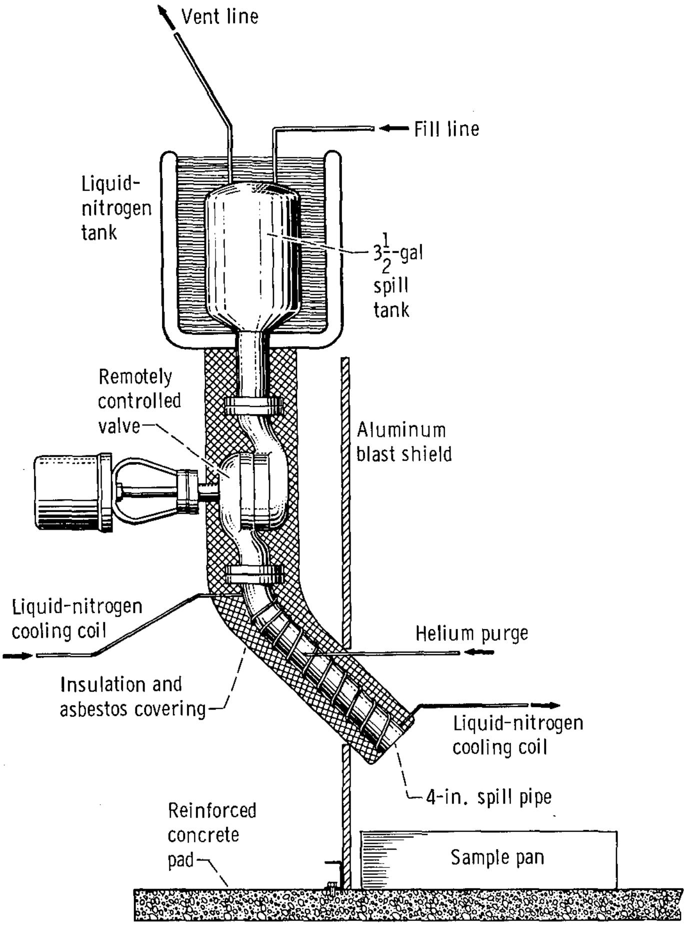


FIGURE 3-25.—Apparatus used for FLOX spill tests (ref. 25).

from the fireball. A marked "stack" effect was produced as the cloud rose rapidly and almost vertically. An atmospheric fire on the JP-4 fuel surface continued for more than 1 minute before it was manually extinguished. The loud sputtering effect or multiple explosions were also noticed when FLOX was spilled on JP-4-fuel-soaked sand and oil-soaked sand. Slow-motion close-up motion pictures of the reaction with oil-soaked sand distinctly showed three large reactions and about five smaller ones, all of which occurred within less than 1 second. In an attempt to smooth out the multiple explosion effect of the FLOX–JP-4 fuel reaction, 30-percent FLOX was spilled into a JP-4 fuel stream. As shown in table 3-XIV, the multiple explosions still occurred. A similar test was made with a coarse spray of JP-4 fuel. Multiple

TABLE 3-XIV.—RESULTS OF 30-PERCENT-FLOX SPILL TESTS (REF. 25)
[FLOX spill quantity, 10 lb.]

Test material		Weather conditions		Reaction	Cloud or vapor	Moisture content, percent		Acid content, pH	
Substance	Weight, lb	Wind speed, mph	Temperature gradient from 2.5 to 30 ft			Before	After	Before	After
Concrete slab	480.0	8	—0.8 F°	None	Vapors drifted close to ground	----	----	----	----
Sand	475.0	3	—2.0 F°	None	Vapors drifted close to ground	1.00	1.34	----	----
Rich soil	311.0	8	0	Bright flame	White cloud rose high at about 45° angle	8.81	12.17	----	----
Asphalt (from building)	177.0	8	0	Sputtered, small flames	Gray cloud drifted close to ground	----	----	----	----
Oil-soaked sand	478.0	8	0	Several loud, rapid explosions	Gray cloud rose high at about 45° angle	1.03	1.31	----	----
Charcoal	180.0	8	0	Large, smooth, brilliant fireball	White cloud rose high at about 60° angle and disappeared	5.94	17.95	----	----

Limestone slab	332.0	5	—1.0 F°	None	Vapors drifted close to ground	----	----	----	----
Lake water (5 gal)	41.7	1	—1.0 F°	None	Vapors drifted close to ground	----	----	8.30	2.30
JP-4 fuel-soaked sand	478.4	2	0.5 F°	Loud sputtering, large flames	Dark cloud rose high at about 60° angle	14.23	1.83	----	----
JP-4 fuel (3 gal)	20.1	2	0	Several loud, rapid explosions; large fire-ball	Black cloud rose high, almost vertically	----	----	----	----
Asphalt (from road)	258.0	2	1.0 F°	Loud sputtering, small flashes	Gray cloud rose at about 15° angle	0.08	0.37	----	----
Water-soaked sand	552.0	1	1.0 F°	None	Vapors drifted close to ground	19.28	14.97	8.40	7.60
Lake-water spray	Not measured	5	—1.9 F°	None	Vapors drifted close to ground	----	----	6.70	1.30
JP-4 fuel stream (bad timing)	6.7	5	—1.9 F°	Several loud, rapid explosions; large fire-ball	Black cloud rose high at about 60° angle	----	----	----	----

TABLE 3-XIV.—RESULTS OF 30-PERCENT-FLOX SPILL TESTS (REF. 25)
[FLOX spill quantity, 10 lb.]—Concluded

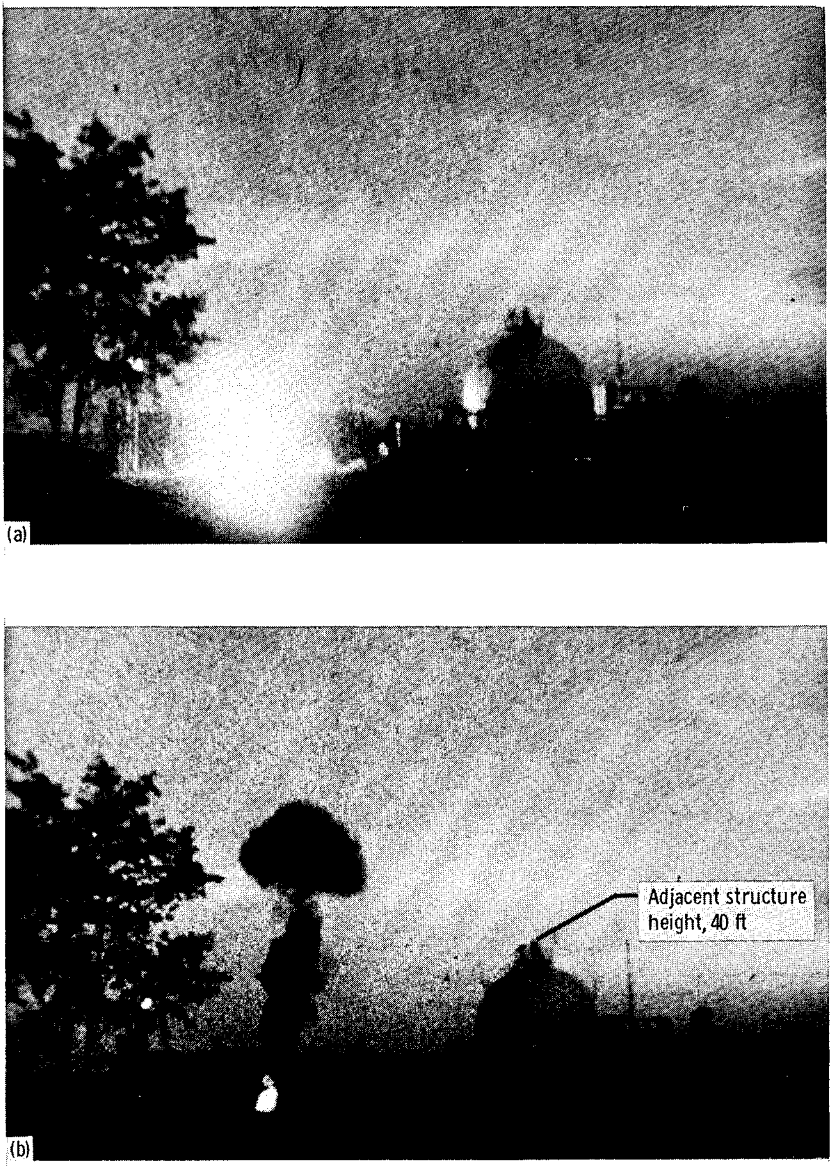
Test material		Weather conditions		Reaction	Cloud or vapor	Moisture content, percent		Acid content, pH	
Substance	Weight, lb	Wind speed, mph	Temperature gradient from 2.5 to 30 ft			Before	After	Before	After
JP-4 fuel (coarse spray)	6.7	5	—2.0 F°	Very rapid, smooth explosions; large fireball	Black cloud rose high at about 70° angle; smoke ring formed	----	----	----	----
JP-4 fuel stream (good timing)	6.7	5	—2.2 F°	Several loud, rapid explosions; large fireball	Black cloud rose high at about 50° angle	----	----	----	----
Coke (low grade) ---	265.0	3	—2.0 F°	Small reaction, small flame	Gray cloud had very little rise	2.56	5.77	----	----
Crushed limestone--	462.0	3	—2.0 F°	None -------------	Vapors drifted close to ground	----	----	----	----

TABLE 3-XV.—RESULTS OF 100-PERCENT-FLOX (PURE FLUORINE) SPILL TESTS (REF. 25)

Test material		Weather conditions		Liquid-fluorine spill quantity, lb	Reaction	Cloud or vapor	Moisture content, percent		Acid content, pH	
Substance	Weight, lb	Wind speed, mph	Temperature gradient from 2.5 to 30 ft				Before	After	Before	After
Crushed limestone	411.0	15	0	10	Sputtered, small yellow flames	Gray cloud rose at low angle	----	----	----	----
Sand --------	320.0	5	—0.7 F°	10	Bright flame -----	White cloud rose at about 45° angle	2.70	4.20	----	----
Water-soaked sand	321.0	5	0	10	Strong explosion--	Light gray cloud rose at about 40° angle	16.30	12.68	8.70	3.55
Asphalt (from road)	275.0	5	0	5	Sputtered, small flashes	Gray cloud rose at low angle	0.03	0.05	----	----
Lake water (5 gal)	41.7	12	—1.1 F°	5	Loud, sharp detonation	White cloud rose at about 30° angle	----	----	8.15	1.35
JP-4 fuel (2 gal)	13.4	5 to 10	0	5	Smooth, fast-burning, large fireball	Black cloud rose almost vertically	----	----	----	----

TABLE 3-XVI.—LIQUID-OXYGEN COMPARISON SPILL TESTS (REF. 25)

Test material		Weather conditions		Liquid-oxygen spill quantity, lb	Reaction	Cloud or vapor
Substance	Weight, lb	Wind speed, mph	Temperature gradient from 2.5 to 30 ft			
JP-4 fuel (1 gal)	6.7	8	—2.0 F°	5	None	Vapors drifted close to ground
JP-4 fuel (2 gal) with spark-plug igniter	13.4	8	—2.0 F°	10	Loud, sharp detonation	Black cloud rose fast and high, almost vertically



(a) Fireball.

(b) Reaction cloud (2.5 sec later).

FIGURE 3–26.—Spill tests of 30-percent FLOX onto JP-4 fuel at Plum Brook.

explosions were again noticed but the reactions were very rapid, less severe, and considerably smoother. In this test, a large, distinct, horizontal smoke ring formed and moved slowly upward.

When 30-percent FLOX was spilled into lake water, there was no reaction; however, a later chemical analysis revealed that the acid content (presumably hydrogen fluoride) of the water had increased considerably after the spill. In order to obtain greater contact surface area, 30-percent FLOX was also spilled into a shower-head spray of lake water. Again there was no reaction, and again the acid content of the water was increased considerably.

When 30-percent FLOX was spilled onto charcoal, a smooth, quiet, brilliant flame occurred over a period of 2 to 3 seconds. Many minute sparks swept upwards within the flame. A faint white cloud rose rapidly at about a 50° angle and disappeared. The flame was so brilliant that observers approximately 140 yards away viewing through 7x50 binoculars experienced a delay of about 10 minutes in return to normal vision. For results of this and other FLOX spills, see tables 3-XIV and 3-XV.

In all cases, 100-percent fluorine reacted with the materials on which it was spilled, even crushed limestone (table 3-XV). These results are also given in table 3-XIV. A strong detonation occurred when fluorine was spilled on lake water. An almost instantaneous small flash of white light was observed, and a strong shock wave was felt by observers 140 yards away. The white cloud formed after the explosion rose at an angle of only about 30°, indicating a relatively small heat release from reaction of only a limited amount of the fluorine spilled with the water; the rapid energy release from the blast apparently blew the remaining fluorine from the reaction site before it could react. The heat content of the cloud then represented the heat release from a small instantaneous reaction.

It was observed that when 100-percent fluorine was spilled on JP-4 fuel, smooth burning occurred, as opposed to the multiple explosions previously mentioned with the 30-percent-FLOX spills. A yellow fireball about 25 feet in diameter was observed and the resultant black cloud rose rapidly, almost vertically, then drifted downwind and slowly dissipated.

Several significant trends were noticed in these spill tests. When there was no reaction, the FLOX, liquid oxygen, fluorine, or hydrogen fluoride vapors drifted slowly downwind close to the ground. When a reaction did occur, the rate of rise and angle of rise of the resultant toxic cloud were dependent on the amount of heat produced by the reaction.

The smoothness of the 100-percent fluorine–JP-4 fuel reaction compared with the multiple explosion effect of the 30-percent-FLOX–JP-4 fuel spill and the violent detonation of the liquid-oxygen–JP-4 fuel spill indicated that the reaction was smoother with more fluorine present in the FLOX mixture.

In spills on lake water, it was noted that no reaction occurred with 30-percent FLOX, even into a water spray; yet a violent explosion occurred when 100-percent fluorine was spilled on lake water. The indication is that there is some concentration between 30 and 100 percent at which FLOX will react with water, and the reaction will probably be very rapid.

Additional work has been conducted in studies (ref. 26) involving large-scale FLOX spills; results of these tests are discussed in sections 5.2.1.4 and 5.2.3.

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Chapter 4. Components and Subsystems Design, Fabrication, and Installation Considerations

Design criteria for liquid fluorine and FLOX storage, transfer, flow-control components, instrumentation, and disposal systems are included in this chapter. Emphasis is placed on components that would find application in large-scale test or launch facilities. In general, criteria applicable to any cryogenic are applicable to fluorine and FLOX. Additionally however, because of the reactive nature of fluorine, consideration must be given to compatibility of materials, fabrication and installation of components, and facility preparation. The consideration of these factors is included in the design criteria discussed in the following sections, but it should be noted that achieving and maintaining cleanliness and the prevention of contamination by moisture and other foreign materials (see sections 3.2, 3.3, 5.2, and 6.2) are of equal importance to good engineering and design of fluorine systems.

4.1 LIQUID FLUORINE AND FLOX STORAGE TANK AND TRANSFER LINES

Some of the design considerations are presented that must be taken into account when deciding on the type of storage to use at the particular facility. Three major types of storage may be used:

(1) Facility storage and supply tanks are large quantity tanks that can contain normal facility requirements for one or several test runs or launches. They form an integral part of the launch or test site, are permanently interconnected (by transfer lines) with use areas, disposal equipment, and associated pressurization equipment, and store fluorine or FLOX on a long-term basis.

(2) Use (or run) tanks are normally used at a test facility for short-term supply of fluorine or FLOX. These storage tanks may be either permanent or temporary.

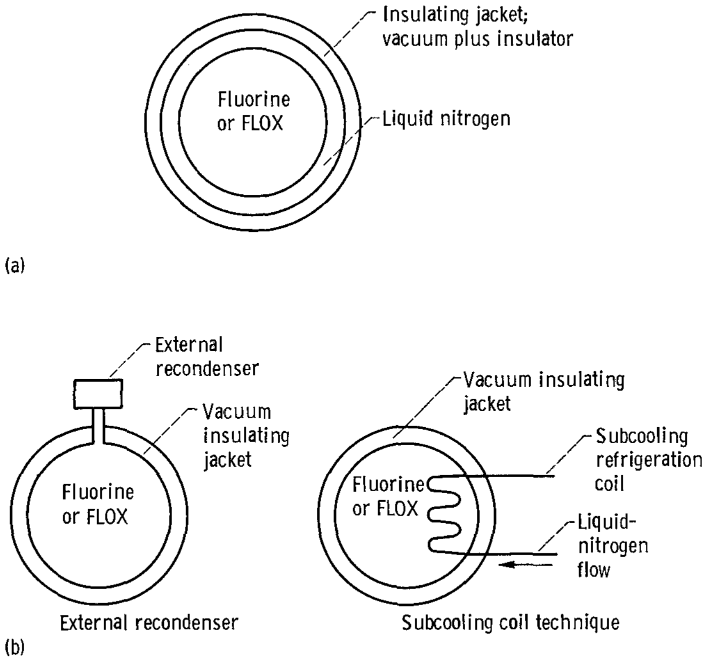
(3) Mobile storage and transport systems are trailer-mounted storage tanks with capacities up to 5000 pounds (in present equipment). These tanks are used for resupply of facility storage or use tanks and (if facility requirements dictate) can be used instead of facility storage tanks.

4.1.1 Facility Storage Tank Design Considerations

Selection and design of the storage tank should provide for no-loss storage for long periods of time from considerations of cost as well as safety. Some applications of storage tanks within a facility are discussed in chapter 5. Here, however, the major concern is the design considerations involved in selection of a particular method of storage.

Figure 4–1 shows the basic types of vessels that may be considered for facility storage purposes. The preferred Dewar for this application is the three-shell vessel that contains liquid fluorine or FLOX in a central container surrounded by an annulus filled with liquid nitrogen (−320° F) or other coolant to maintain the fluorine or FLOX at subcooled conditions. The outermost annulus of this storage tank is a vacuum container that is filled with an insulating powder (such as Santocell or Perlite) or that may contain reflective insulation or radiation shields to minimize radiation transfer of heat into the liquid-nitrogen annulus.

While liquid nitrogen is referred to herein as the coolant in the three-shell storage system, either liquid air (−312° F) or liquid oxygen (−298° F) might be used as a coolant in place of liquid nitrogen for FLOX storage. Use of liquid oxygen as a coolant (at atmospheric



(a) Three-shell Dewar fluorine-FLOX container.

(b) Possible conversions of existing liquid-oxygen tanks for use with fluorine and FLOX.

FIGURE 4–1.—Recommended storage tanks for fluorine or FLOX installations.

pressure) would allow storage of fluorine or FLOX at a higher vapor pressure, minimizing or eliminating the need for helium blanket pressurization during storage (depending on FLOX concentration and vapor pressure). By increasing the pressure on the coolant (e.g., by setting the relief valve to restrict release of the boiloff gases that result from the inward heat leak through the insulating annulus of the tank) and thus raising the temperature at which the coolant boils, fluorine or FLOX may be stored at various vapor pressures.

Another kind of vessel that can provide adequate no-loss storage, when properly modified, is the conventional two-shell Dewar currently used for liquid-oxygen or liquid-nitrogen storage. If it is used, however, this type of storage system requires addition of a reliquefaction system (internal subcooling coil or external recondensing system to liquefy boiloff vapors) to ensure no-loss storage of fluorine or FLOX. The last system allows the use of existing facilities that can be made to meet requirements for long-term refrigerated storage. A thorough inspection must be performed, however, to assure that tank construction meets compatibility requirements for fluorine or FLOX. Several disadvantages should be considered before deciding on the use of this type of storage:

(1) The insulating powders usually used in these tanks (such as Perlite) react combustively with fluorine and, since there are welds and piping in the tank wall surrounding the stored fluid, the possibility of a leak should be considered. In a tank with three-shell construction, the leakage of fluorine into the liquid-nitrogen annulus would be a less serious condition. Thus, the use of two-shell storage tanks would not provide a fail-safe storage system for fluorine or FLOX application unless the powdered insulation were removed and only the vacuum jacket used for insulation. A thorough radiographic inspection of all seams and joints (as well as the basic tank material) would be required to ensure perfect welds and minimize risks of possible leakage. Any inclusions, discontinuities, cracks, etc., must be cut out and rewelded to ensure a flawless, homogeneous surface.

(2) The cost of the refrigerating equipment to provide no-loss storage may well outweigh the advantages obtained from the use of existing storage equipment. This, as well as the refurbishment cost factors, must be determined for the particular facility.

Some of the advantages of the three-shell storage system are as follows:

(1) Fluorine or FLOX is separated from any contact with reactive insulating material by the liquid-nitrogen jacket; this allows the use of powdered insulation in the vacuum jacket and eliminates the possibility of accidental ignition from a leak in the inner shell.

(2) The system involves a minimum of mechanical equipment. Except for the possible need for helium blanket pressurization, the storage

tank is normally sealed off from all outside contact during static conditions and this reduces the possibility that contamination will be introduced into the system.

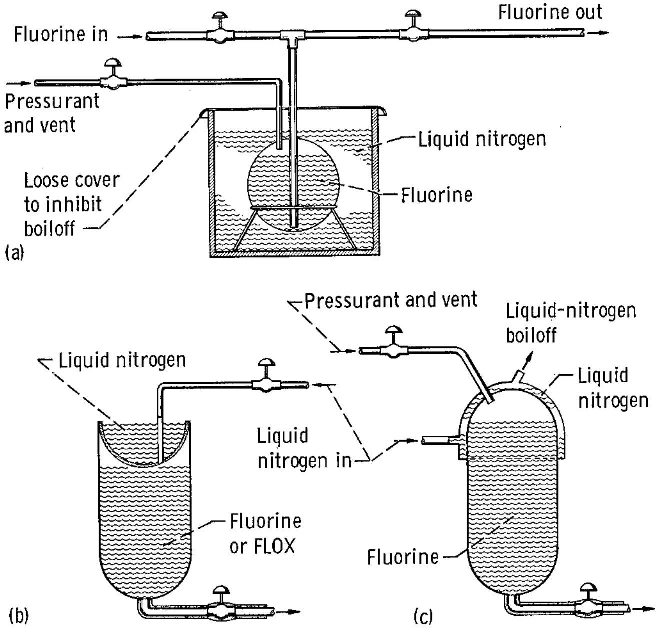
(3) There is no heat leak into the inner fluorine or FLOX container. The inner container remains subcooled (−320° F) until most of the liquid nitrogen has boiled off from the surrounding jacket.

(4) The system is fail-safe. Any fluorine in nitrogen boiloff gases would indicate loss of integrity in the inner shell, or an increased rate of boiloff of the liquid-nitrogen coolant would indicate problems in the insulating space that permit increased heat leak. Either condition would provide a warning to detank and make repairs.

Regardless of which storage tank system is selected for use in facility storage, design considerations must include proper fabrication techniques, compatibility of materials, and cleaning requirements.

4.1.2 **Use or Run Tanks**

The three basic tank designs shown in figure 4–2 have been used for



(a) Open-top immersion.

(b) Beanie, open top. (c) Beanie, capped.

FIGURE 4–2.—Schematic drawing of typical use-tank configurations employed in Lewis test facility operations.

fluorine containment at Lewis. In all these methods, liquid-nitrogen (or other coolant) is employed to subcool the fluorine or FLOX.

The first and simplest storage configuration (fig. 4–2(a)) is generally restricted to short use time, such as battleship tankage for test cell applications. This method involves immersion of the fluorine or FLOX container (normally made of stainless steel, Monel, or aluminum) in an open-top insulation bath of liquid nitrogen. Normal nitrogen boiloff provides a suitable thermal blanket for the bath; however, a loose cover or a layer of foam polystyrene balls floating on the liquid-nitrogen surface may be used to inhibit radiant heat transfer from the atmosphere.

For the techniques shown in figures 4–2(b) and (c), a coolant cap of liquid nitrogen is used to condense boiloff from the fluorine or FLOX in the closed container. The configuration of figure 4–2(b) was used in a Lewis test facility, and the configuration of figure 4–2(c) has been used for liquid fluorine tanks by Rocketdyne Division of North American Aviation Corporation. For test-cell applications, conventional insulation is usually added to minimize heat transfer.

4.1.2.1 *Selection of storage-vessel material.*—Preferred materials for the construction of pressure vessels for containing liquid fluorine or FLOX include stainless steels, 304L, 321, or 347, and Monel. Aluminum 61 (as well as other materials) may also be used if they meet the requirements for cryogenic use.

All metals that are to be in contact with the fluorine or FLOX must be X-ray inspected to ensure that no inclusions, cracks, discontinuities, or other imperfections are present. Any imperfection must be cut out and repaired to provide a homogeneous metal material.

An intermediate liquid-nitrogen shell would require the same materials for the same reason as the pressure vessels (300 series stainless steel has been the preferred choice in construction of mobile storage tanks primarily because of cost and strength requirements). Where cryogenic temperatures are not a factor, outer shell materials may include the mild steels (A-285-Gr-C, A-285-Gr-B, A-240-S, and A-283-Gr-C, ref. 1). It is important, however, to design this vessel in such a manner to avoid thermal shocks.

4.1.2.2 *Fluorine or FLOX container fabrication considerations.*—Two methods are recognized for connecting outlet lines into the storage tank: (1) dip tube and (2) bottom connection. While the use of dip-tube connections into the fluorine or FLOX tank is generally preferred, bottom connections into use or run tanks have been used successfully by Lewis for several years. When it is selected, however, the bottom connection should be subcooled (e.g., liquid-nitrogen jacketed) up to and preferably including the first transfer line shutoff valve in either storage or run tanks.

The primary objective in fluorine tank fabrication is to achieve a smooth crevice-free interior. Poor seam welds, which have flux and slag inclusion, pockets or bubbles, and oxidized surface flaking, are considered particularly undesirable. For this reason, the quality of the weld seams and/or the inlet and outlet connections (as well as the construction materials) is very important, and it is good practice to X-ray all welds, as well as all stock material used in fabrication to ensure good quality (refer to section 4.9). Reaction cannot occur if the container, its surface, and the fluorine or FLOX contents are maintained in the highest state of purity. It follows that pressurizing gas *must be free of moisture* or other contamination (refer to section 5.2.6.1).

4.1.3 Mobile Storage Tanks

Combination storage and transport tanks for liquid fluorine have been in use at Lewis facilities for several years without failure. These truck-transported trailers contain fluorine in amounts of 55 and 450 gallons in no-loss storage and are basically three-shell systems of the same type as shown in figure 4–1. The inner container holds fluorine in a subcooled liquid state, and the outer annulus is a vacuum-Perlite-filled insulation space. Experience with mobile storage containers at Lewis has shown average loss rates of liquid nitrogen of less than 3.5 percent per day (table 4-I). This loss rate indicates that, even without replenishment of the liquid-nitrogen coolant, the fluorine would be safe from boiloff for about 25 days. The three-shell construction is the only one used in mobile storage systems to date. This type of storage is the most reliable design available and is the only construction recommended for this type of service.

The present maximum fluorine trailer capacity is 450 gallons (about 5000 lb); however, an unpublished study performed by the General Chemical Corporation indicates that, as needs dictate, 1500-gallon-capacity (about 20 000 lb) trailers can be fabricated for use in large-scale launch or test facilities. Because of highway limitations, larger sizes than this would probably necessitate railroad transport. Selection of the most suitable delivery vehicle is considered to be a trade-off in the initial capital investment between trailers versus tank cars and the potential utilization of liquid fluorine or FLOX as an oxidizer in space vehicles.

Mobile fluorine storage trailer tanks have been built by Air Products, Incorporated; Stearns–Roger Manufacturing Company; and Process Engineering Company in cooperation with Allied Chemical Company. In addition, three 5000-pound trailers and one 10 000-pound trailer are currently being built by Cryovac, Incorporated. When these are completed, the mobile storage inventory for fluorine will be as shown in table 4-II.

TABLE 4-I.—DESIGN PARAMETERS FOR NASA LEWIS FLUORINE TRANSPORT TRAILERS (REFS. 2 AND 3)

Design consideration	Fluorine weight, lb	
	600	5000
Internal design pressure, psig:		
Inner shell	70	70
Intermediate shell	60	45
Outer shell	0	10
External design pressure, psig:		
Inner shell	60	45
Intermediate shell	0	10
Outer shell	14.7	14.7
Operating temperature limits, °F:		
Inner shell	80 to —320	80 to —320
Intermediate shell	80 to —320	80 to —320
Outer shell	650 to —20	650 to —20
Volume, gal:		
Inner container	55 (max.)	417
Intermediate annulus	60	338
Outer annulus	----------------	----------------
Thickness, in.:		
Inner shell	0.1875	0.250
Intermediate shell	.1875	.250
Outer shell	.250	.250
Materials:		
Inner shell	Monel	Monel
Intermediate shell	Stainless steel 304	Stainless steel 304
Outer shell	A-212, A-285	A-285, GrC
Tank length, in.:		
Inner shell	53.3	86.9
Intermediate shell	58.6	114.5
Outer shell	75	133.5
Tank diameter, in.:		
Inner shell	20	42
Intermediate shell	28	48
Outer shell	44.5	66
Support system	Transite blocks	Stainless-steel rods
Weight empty, lb	4000	10 000
Insulation	Perlite grade "PF"	Powder Perlite
Insulation thickness, in.	----------------	9

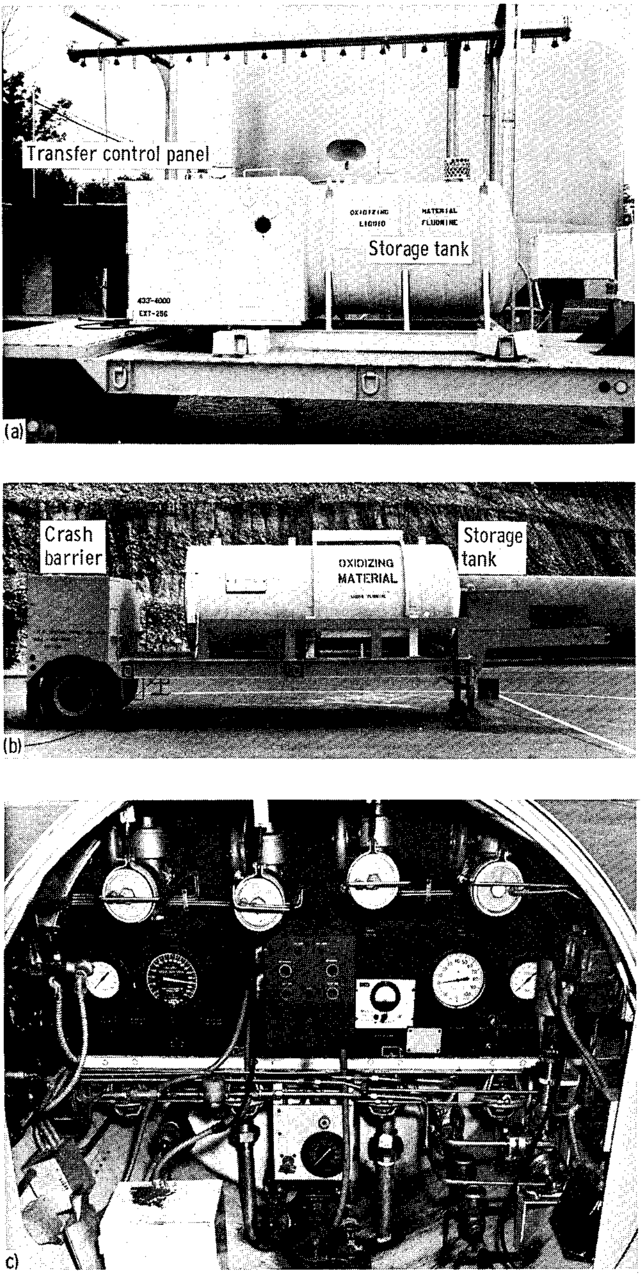
TABLE 4-I.—DESIGN PARAMETERS FOR NASA LEWIS FLUORINE TRANSPORT TRAILERS (REFS. 2 AND 3)—Concluded

Design consideration	Fluorine weight, lb	
	600	5000
Insulation pressure, μ	50 (max.)	10
Total heat leak (to liquid nitrogen), Btu/hr	40	120
Normal evaporation of coolant, percent/day	3.5 (max.)	2
Liquid line sizes, in.	$\frac{3}{4}$ (liquid-nitrogen fill and discharge)	1
Vent line diameter (liquid nitrogen), in.	1 reduced to $\frac{3}{4}$	2 reduced to $\frac{3}{4}$
Instrumentation:		
Liquid fluorine pressure gage	30 in. vacuum to 100 psig	[a]
Liquid nitrogen pressure gage	[a]	[a]
Liquid nitrogen level gage	[a]	[a]
Vacuum gage	[a]	[a]
Gaseous nitrogen vent (pressure) gage	[a]	[a]
Shock loading design for all assembly, g's:		
Vertically	3	3
Longitudinally	2	2
Laterally	1	1

[a] Installed in trailer.

TABLE 4-II.—INVENTORY OF FLUORINE TRAILERS

Owner	Number of trailers	Capacity, lb
NASA Lewis	2	5 000
NASA Lewis	2	600
U. S. Air Force	1	600
General Chemical Corporation	6	5 000
Minnesota Mining and Manufacturing Co.	1	5 000
United Technology Corp.	1	5 000
Pratt & Whitney Aircraft	1	5 000
Pratt & Whitney Aircraft	1	10 000

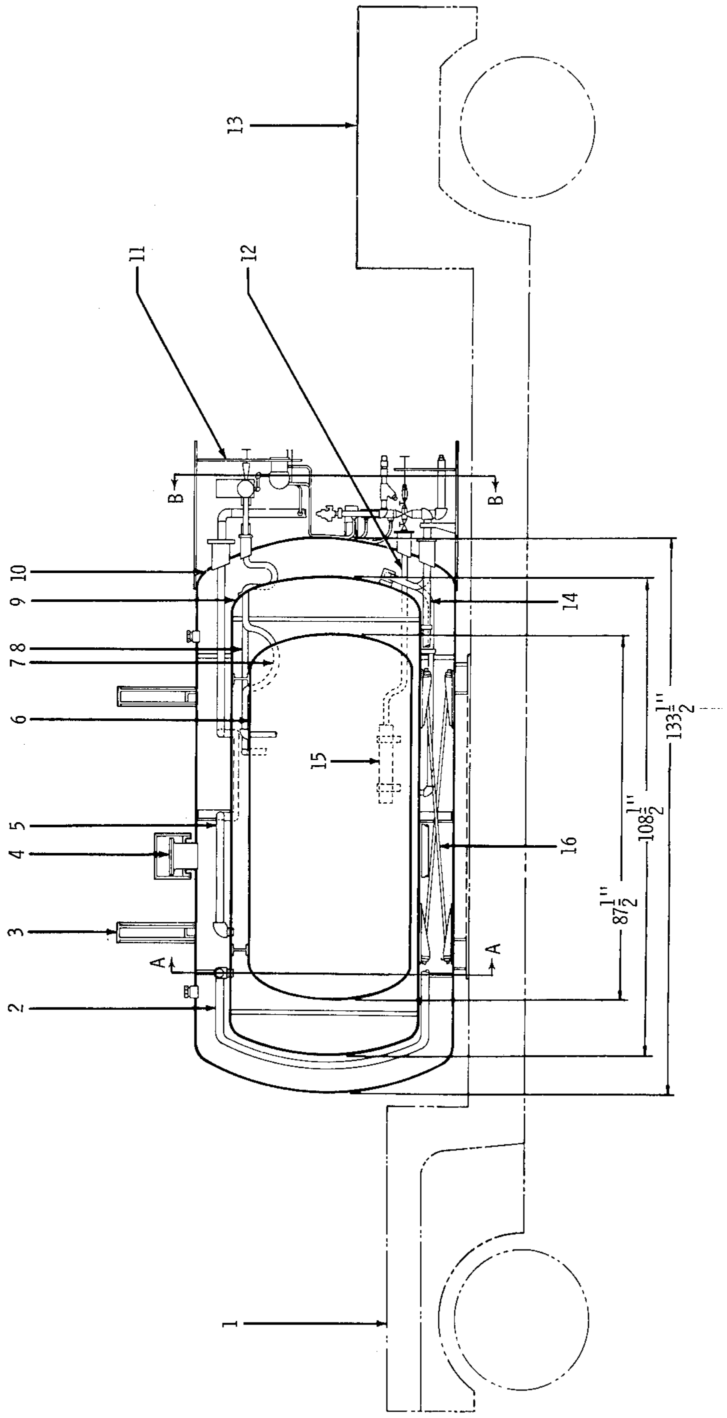


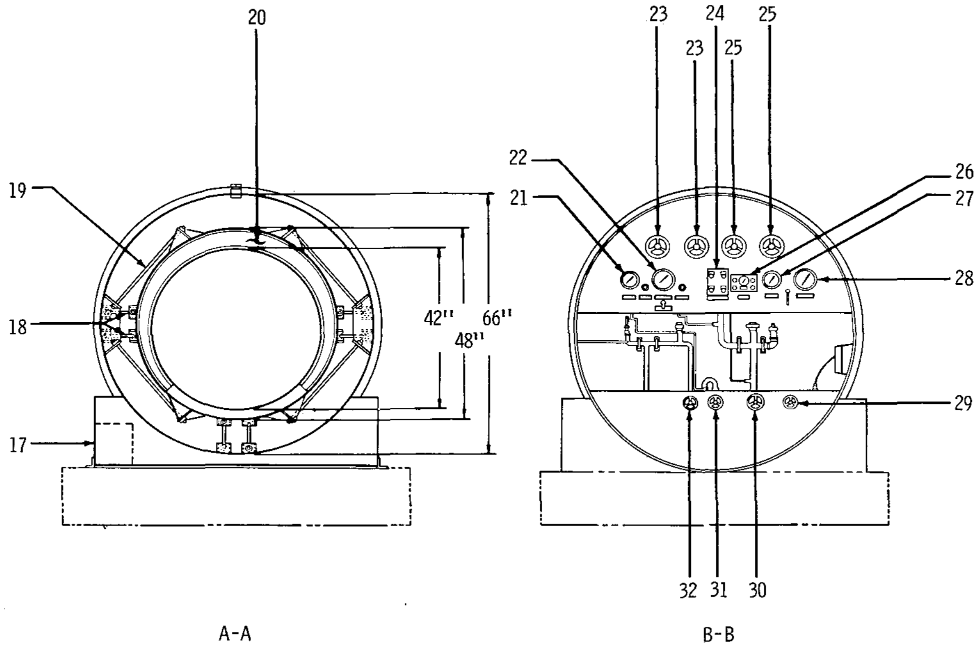
(a) Capacity, 600 pounds.

(b) Capacity, 5000 pounds.

(c) Control panel for 5000-pound trailer.

FIGURE 4-3.—Liquid-fluorine mobility storage trailer.


1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
A
A
B
B
87½"
108½"
133½"



1, Low bed trailer
2, Liquid-nitrogen fill line
3, Roll over protection guards
4, Pressure relief disk
5, Liquid-nitrogen vent line
6, Inner tank
7, Fluorine discharge line
8, Fluorine fill line
9, Intermediate tank
10, Outer tank
11, Barricade and instrument panel
12, Vacuum line
13, Crash barrier
14, Liquid-nitrogen discharge line
15, Vacuum filter
16, Bottom tension rods
17, Cradle support
18, Side tension rods
19, Suspension tie rods
20, Support rings
21, Liquid-nitrogen fill pressure gage
22, Liquid-nitrogen level gage
23, Fluorine discharge shutoff valves
24, Alarm panel
25, Fluorine fill shutoff valves (vent side)
26, Vacuum gage
27, Fluorine pressure gage
28, Nitrogen vent pressure gage
29, Vacuum line outlet valve
30, Liquid-nitrogen vent valve
31, Liquid-nitrogen discharge valve
32, Liquid-nitrogen fill valve

FIGURE 4-4.—Liquid-fluorine tank construction.

Figure 4–3 shows the general construction features of fluorine transport trailers at Lewis. Major design specifications used in construction of some existing NASA fluorine transport systems are listed in table 4-I. General information in the remainder of this chapter (on components, subsystems, etc.) will apply equally to facility storage and mobile storage systems and will cover some of the detailed design and fabrication requirements. Some construction details are shown in figure 4–4.

4.1.3.1 *Special considerations in mobile storage systems design.*—Some considerations that must be taken into account during design of any mobile liquid-fluorine storage system are as follows:

Interstate Commerce Commission regulations forbid the use of pressure-relief valves on gaseous fluorine storage cylinders (ref. 1). This ruling may also forbid inclusion of any relief device on the liquid-fluorine storage tank of the mobile storage system. Aside from the regulatory prohibitions against use of relief devices, several other considerations also argue against their use:

(1) The use of a burst diaphragm as a pressure-relief device does not seem practical for the reliability required in over-the-highway transport. This device would of necessity be thin walled, since the storage pressure of fluorine is nearly atmospheric, and possible progressive corrosion from hydrogen fluoride contamination would make the burst diaphragm subject to unpredictable failure.

(2) Other pressure-relief devices, such as pop-off relief valves, are considered undesirable since they introduce an additional potential avenue of system contamination through atmospheric leakage into the system.

(3) Fluorine trailers use city streets and state highways (in all present mobile storage systems) in transit from the manufacturer to the using site. Therefore, safety considerations forbid exposing the public to the possible venting of fluorine.

(4) Joint investigations by the U.S. Air Force and Lewis, and later operating experience, have proved that properly designed, maintained, and operated mobile storage systems can be used to transport fluorine safely under no-loss conditions in sealed containers (ref. 4). (Maintenance and operating procedures are included in chapter 8.)

4.1.3.2 *Supporting structures considerations.*—In three-shell fluorine-FLOX storage tanks, the nitrogen-jacketed fluorine or FLOX container must be supported to minimize the rate of heat leak into the liquid. This is a particular requirement for cryogenic fluids. The supports should be designed to furnish maximum resistance to heat conductance; the three general types of tensile supports are rods, cables, and chains.

The suspension system must be designed to provide for appropriate load distribution in the suspension for all load conditions, such as motion and vibration, as well as for loads from thermal contractions. Some support also must be provided for the outer shell or vacuum jacket. This shell is usually at ambient temperature and there is no reason to provide an effective heat barrier between it and the surroundings. Therefore, the outer shell can be supported by a conventional structural means.

When the support structures for the various shells of the mobile storage tank are designed, consideration must be given to mobile shock loads that are not present in static facility storage systems. The criteria selected for these loadings (for present Lewis systems) were 3 g's vertically downward, 2 g's longitudinally, and 1 g laterally.

The maximum permissible loading for highway vehicles ranges for various states and is presented in reference 1. While even contemplated 20 000-pound-capacity mobile storage trailers would not exceed the limitations, specific investigation must be made for the particular routes to be used to assure that federal, state, or municipal weight limitations would not be violated by the total design load.

4.2 INSULATION

Most techniques for insulation of cryogenic storage tanks for storage of liquid hydrogen, liquid oxygen, and liquid nitrogen are applicable to liquid fluorine or FLOX. The National Bureau of Standards, Cryogenic Engineering Laboratory, has been continually investigating insulation, support systems, and tank design parameters as they affect the storage of liquid hydrogen and helium. Much of the work done by NBS, while directed toward these two cryogenics, would also be applicable to the storage tank design problem for liquid fluorine or FLOX.

Normally only two types of large containers would be used for the storage of liquid fluorine or FLOX: (1) conventional two-shell cryogenic storage vessels composed of a central containment vessel surrounded by a reflective (metal) insulation-plus-vacuum annulus; and (2) the three-shell system, made up of a central container, surrounded by a bath of liquid nitrogen (−320° F) in the first annulus and by powder insulation plus vacuum in the outer shell. While the latter is the most attractive from the standpoint of reliability, cost considerations may dictate the use of the former.

Effective insulating media have been developed for cryogenic fluid storage systems such as (1) vacuum, (2) high vacuum plus metallic radiation shields, (3) "super insulation," which consists of high vacuum plus a series of metal foils separated by low-conductivity materials, (4) high vacuum plus powders such as Perlite, and (5) standard nonvacuum powder, blanket, or foamed plastic insulations. The first two provide an insulation that is compatible with a fluorine system should leakage occur, since only metals are used in the insulating annulus. The others vary in their reactivity but can combust in contact with fluorine or FLOX.

In general, powder insulations in a vacuum jacket are suitable for use with three-shell containers because there is a liquid-nitrogen barrier between the fluorine or FLOX and the insulation. In the conventional two-shell cryogenic container, the use of powder insulations is less desirable since a minor fluorine leak could cause ignition of the insulation. For the two-shell container, the efficiency of the outer vacuum jacket as the thermal barrier could be increased by installing radiation shields (by using a corrugated or "waffle" material to minimize conduction); however, the installation technique would be a problem. The use of super insulations is more feasible for three-shell storage vessels, since the middle of the insulation "sandwich" and its binding agents are reactive with fluorine; in the three-shell case, this insulation would be isolated from the fluorine or FLOX by the liquid-nitrogen jacket. For very large storage tanks (about 28 000 gal and larger), three-shell vessels may prove high in cost—perhaps prohibitively so. In this event, the two-shell storage tank (with appropriate insulation) plus a recondensing system must be considered.

4.3 LINES, JOINTS, AND FITTINGS

Fluorine or FLOX systems must meet design objectives for a leakproof, cleanly designed, crevice-free system that can be easily cleaned and kept free from contamination. For gaseous service, the preferred materials for lines, fittings, and flanges are stainless steel, aluminum, copper, brass, or mild steel (low pressure). For liquid service, 300-series stainless steel, aluminum 6061, Monel, Inconel, or copper (low pressure) are preferred. Piping used to contain fluorine or FLOX should be X-ray inspected for flaws, cracks, or discontinuities; these imperfections should be removed by cutting away the pipe section that contains them. Welding, soldering, and brazing techniques for assembling a zero-leak system are discussed in section 4.9.

4.3.1 Flared Tube and Compression Fittings

Compression fittings and flared-tube fittings have been used successfully at Lewis for both liquid- and gaseous-fluorine systems at pressures up to 1500 pounds per square inch gage. Some types of compression fittings and flared-tube connectors larger than $\frac{3}{4}$ inch are more difficult to seat properly than smaller sizes, which increases the possibility for high-pressure leaks.

Compression fittings larger than $\frac{3}{4}$ inch are not recommended for use at high pressures because they are more subject to failure than other fittings (i.e., $\frac{3}{4}$-in. AN-type fittings have been satisfactory to 1500 psig. Sizes larger than $\frac{3}{4}$ in. should be limited to appropriately reduced pressures). Causes of failures at Lewis were traced to high-pressure inadequacy of the fitting design, to mechanical failure from overtightening to achieve zero-leak seals, and to other causes of overstress failure (e.g., tubing pulls out of compression fitting). In all fluorine or FLOX installations where these fittings are used, torque values should be specified as a function of fitting size, type, and material. Of course, lubricants *may* be used on the threaded portion of the fitting because the threads are external to the fluorine system and therefore are not exposed; however, a subsequent leak in the fitting *may* result in ignition and line failure.

4.3.2 **Flange Fittings**

Flange fittings have been used quite extensively in gaseous- and liquid-fluorine installations and portable equipment. They are recommended fittings where connections must be frequently made and broken. Flange fittings are also applicable for semipermanent connections and are particularly suitable for high-pressure systems. The preferred facing

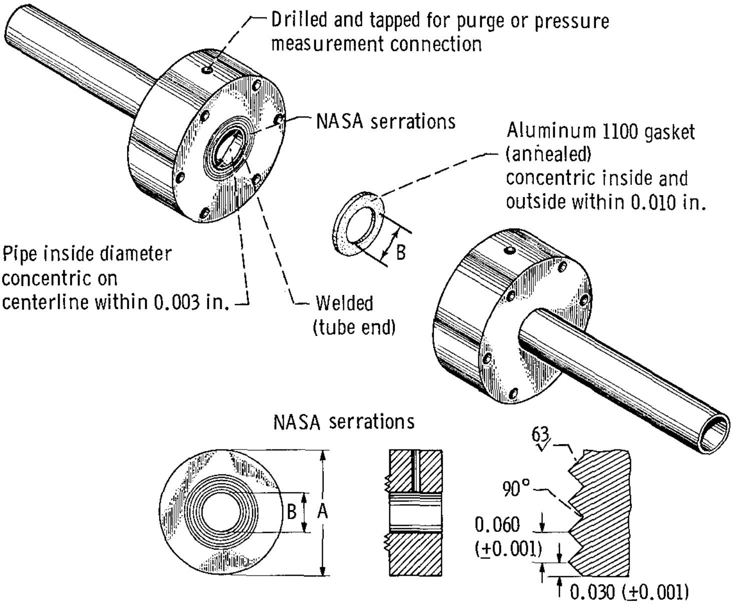


FIGURE 4–5.—Flange-type connectors for fluorine service. (Flange connector bolts must be periodically retorqued since they tend to loosen under cryogenic-ambient temperature cycling.)

on flanged fittings is concentrically serrated with a raised face; the seal is provided by soft annealed aluminum (or soft copper) gaskets (fig. 4–5). In this fitting, all surfaces, where not otherwise specified, should have a number 125 finish.

In addition to meeting the general design criteria, which apply to the selection of flange types for any service (size, working pressure, and temperature), flanged connections for fluorine service should offer a minimum of pockets, cracks, or restrictions where residue or contaminants could accumulate. Cryogenic cycling tends to loosen bolted connections; therefore, *flange bolt tensions must be checked frequently to correct tension,* especially after several extreme temperature cycles. Metallic confined ring gaskets (O-rings, U-rings, crush gaskets, etc.) have been used successfully in bolted flange fittings to provide zero-leak seals.

Nonmetals, such as polytetrafluoroethylene (TFE), have been successfully applied in fluorine systems but are normally used in applications where metals are not feasible (e.g., valve-stem packing). Nonmetals have been tested under severe exposure conditions (see section 3.3) that define the extreme limits within which they can be applied; their use would probably be normally restricted to zero-leak-seal applications in gaseous service. In any application, care should be taken to protect nonmetals from direct contact with liquid fluorine, and direct contact with the fluorine or FLOX flow stream should be avoided. Studies described in section 3.3.4 indicate the feasibility of the use of soft-seal materials in exposed-seal liquid-fluorine or FLOX applications, although the reliability of seals directly exposed to the liquid or to flow conditions is reduced.

Many compression-type fittings and mechanical clamping techniques to hold the fitting together are commercially available. The design and choice of sealing materials in many of these fittings are suitable for use in fluorine systems. The choice of using these fittings must be made on the basis of criteria in this text on the specific application.

4.3.3 Threaded Fittings

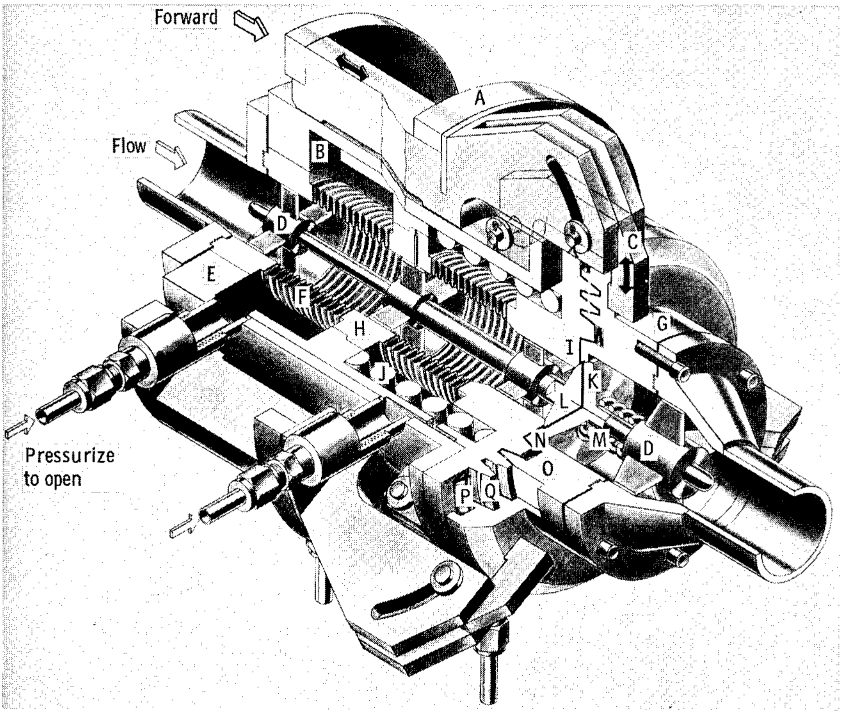
Threaded pipe fittings should normally be avoided in fluorine or FLOX service. When it is necessary to use pipe fittings because of size considerations, they should be installed (by welding, silver soldering, or brazing, as described in section 4.9.3) so that the threads are removed or completely isolated from the fluorine or FLOX.

Threaded fittings and thread compounds and/or lubricants should be used only where risk of possible reaction and line or component failure is acceptable.

4.3.4 Quick-Disconnect Couplings

Requirements for quick-disconnect couplings for fluorine or FLOX service differ from those for other cryogenic fluids mainly in the consideration that must be given to the toxic and reactive nature of fluorine and the corrosive nature of its reaction by-product. For this reason, fluorine or FLOX couplings should be designed for minimum leakage and for minimum spillage of fluorine or FLOX during disengagement of the coupling halves.

A prototype quick-disconnect coupling (see cutaway view in fig. 4–6) for ground-to-vehicle transfer of liquid fluorine or FLOX was designed,



A, Driver
B, Chamber
C, Locking finger
D, Valve stem guide
E, Ground-half housing
F, Bellows flow passage
G, Vehicle-half housing
H, Slider ring with internal spider
I, Ground-half valve seat
J, Ground-half loading spring
K, Vehicle-half valve stem and trim
L, Ground-half valve trim and stem
M, Vehicle-half loading spring
N, Vehicle-half valve seat
O, Inner V-ring seal
P, Outer V-ring seal
Q, Labyrinth face (plane of disconnection)

FIGURE 4–6.—Sectional view (connected phase) of liquid-fluorine quick-disconnect coupling (ref. 5).

fabricated, and successfully demonstrated at Lewis in 1963 (ref. 5). The coupling operation is shown schematically in figure 4–7. The primary features of this disconnect coupling include the capability for liquid-fluorine or FLOX flow during transfer operations, remote connection and separation capabilities, negligible fluorine spillage on disconnection, and remote reconnection. A pneumatic cylinder was used to release the coupling lock and to separate the coupling halves. The locking mechanism in this device was designed for the specific convenience of test-cell operations and is not necessarily optimum for general use. Operation of the coupling (figs. 4–6 and 4–7) is as follows:

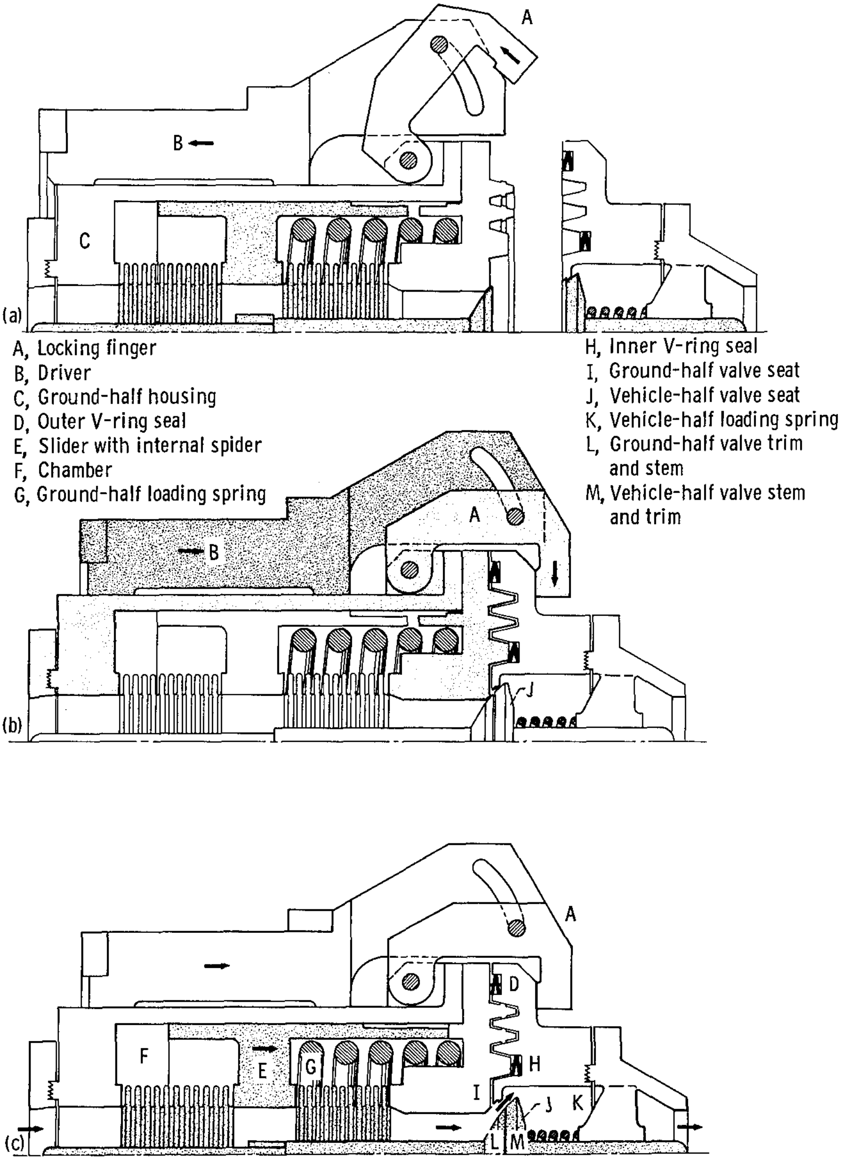
(1) To commence the connection phase, a rearward movement of the driver B (fig. 4–6) relative to the ground-half housing C spreads the locking fingers A. Both halves of the coupling are then alined and mated. Finally, a forward movement of the driver arrangement (fig. 4–7(b)) closes the fingers around the vehicle half. To maintain positive contact between the halves, the driver must be kept in this forward position.

(2) The coupling valving is opened by introducing pressurized gas into the chamber F of the ground half, which moves the concentric slider ring E downstream and raises the ground-half trim L from its seat I. As the ground-half trim continues its movement, it bears against the trim M of the vehicle half of the coupling and forces it from its seat J. Both the ground-half and the vehicle-half loading springs G and K, respectively, are compressed by the operation to provide fail-closed operation on loss of pressurant gas. The coupling open for flow is shown in figure 4–7(c).

(3) During liquid-fluorine transfer through the coupling, external leakage is prevented by a combination of the static labyrinth grip (formed by the intermeshing faces of the two halves) and the inner and outer V-ring seals D and H, respectively. Any cryogenic liquid leakage past the inner seal gasifies in the cavity between the labyrinth faces and the outer V-ring seal from normal heat transfer. Because of the orientation of the V-ring seals (see fig. 4–7), any pressure buildup in the cavity could not exceed that of the liquid-fluorine transfer pressure within the flow passage. An excess of the cavity pressure over the transfer pressure would cause leakage through the inner V-ring seal in a reverse direction (i.e., back into the fluorine flow passage).

(4) The coupling valving is closed by venting the chamber F of the ground half and allowing the loading springs in both halves to seal their respective trims (fig. 4–7(b)). Separation of the two halves of the coupling is accomplished by a rearward movement of the entire ground half, as shown in figure 4–7(a).

An indication of the external sealing efficiency of the coupling design was obtained by recording a time history of pressure buildup in the



(a) Disconnected phase.

(b) Halves mated and locked.

(c) Valving open for flow.

FIGURE 4-7.—Schematic diagrams of operation of liquid-fluorine quick-disconnect coupling (ref. 5).

static labyrinth seal cavity. No pressure rise was measured over an entire series of liquid-fluorine transfers, which indicated that the inner seal was completely effective; in addition, no external leakage was observed at the plane of separation of the coupling during the steady-state flow periods (ref. 5).

4.4 VALVES

Most of the standard globe, plug, or needle valves can be adapted for gaseous fluorine (or FLOX) service by using polytetrafluoroethylene valve-stem packing. In most cases, liquid fluorine or FLOX applications would require diaphragm or bellows-seal valves to ensure that the liquid does not contact the stem-seal material. Packed-stem valves are subject to leakage because of thermal shrinkage when they are exposed to cryogenic fluids, but they have been applied in liquid-fluorine service by using extended stem bonnets. Vertically mounted valve-bonnet extensions reduce the possibility that liquid fluorine or FLOX will contact the stem packing, since heat transfer into the valve maintains a gas pocket in the area of the packing, provides relatively higher packing temperatures, and thus prevents leaks that might cause spontaneous ignition. Preferred valve materials are shown in table 4-III.

Packless valves use a flexible metallic seal to isolate the valve-operating mechanism. Bellows seals permit greater motion of the valve stem and plug. Diaphragm seals have been used successfully in the smaller valve sizes.

Packless valves are inherently more reliable in both liquid and gaseous fluorine service; consequently, they are often used in fluorine installations and handling equipment. It is highly recommended that valves used in high-pressure liquid-fluorine service be restricted to packless bellows or diaphragm sealed. Valves should be completely disassembled for thorough cleaning prior to use, and while the valve is apart, it is a good practice to lap the valve plug into its mating seat to ensure perfect mating.

All bolted connections on valves, flanges, etc., should be retightened periodically to ensure proper torque for sealing. Temperature cycling from ambient to cryogenic temperature tends to loosen bolted connections. In most cases, valve failures at Lewis were traced to high-pressure leaks from loosened bolt connections or from extreme pressure surges (such as might result from a reaction and failure elsewhere in the system). It should be pointed out that leaks can occur without ignition or catastrophic failure; however, loosened connections or points of leakage are particularly susceptible to contamination and subsequent high-pressure ignition and failure.

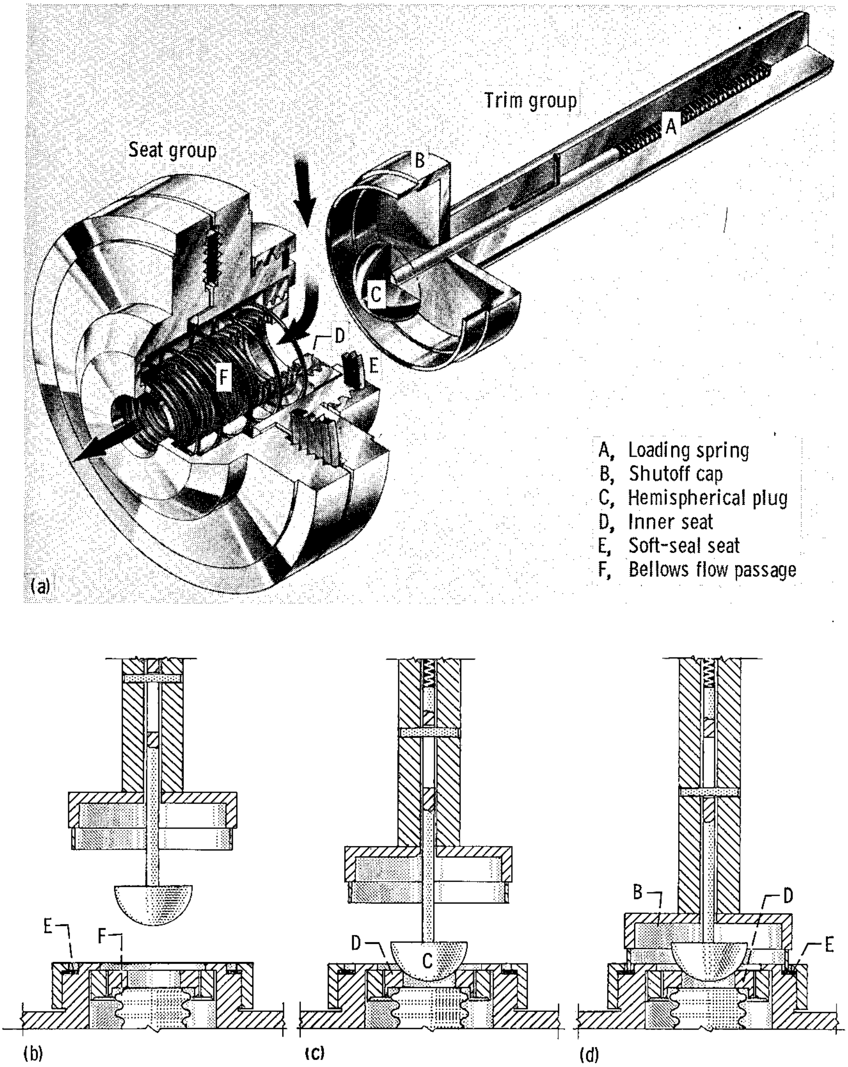
TABLE 4-III.—PREFERRED MATERIALS FOR VALVE COMPONENTS

Valve component	Service	
	Gaseous	Liquid
Bodies	Nickel (300 series) Stainless steel Monel Aluminum Inconel Brass	Copper (low pressure) Monel Nickel Aluminum Stainless steel (300 series) Inconel
Plugs	Stainless steel (300 series) Monel Aluminum	Stainless steel (300 series) Monel
Bellows	Monel Stainless steel 347	Monel Stainless steel 347
Diaphragms	Stainless steel 347	Stainless steel 347
Gaskets	Soft aluminum Soft copper Polytetrafluoroethylene (TFE) Lead	Soft aluminum Soft copper
Seats [a]	Nickel Copper Aluminum Brass	Nickel Copper Aluminum Brass
Chevron packing	Polytetrafluoroethylene (TFE) Copper braid and TFE	Not recommended
O-rings, V-rings, etc., (refer to section 4.3.2)	Aluminum Polytetrafluoroethylene (TFE) Stainless steel	Copper Aluminum Stainless steel

[a] All-stainless-steel valves have been used, but they have a tendency to gall and bind under high closure forces; therefore, stainless-steel valve seats are usually avoided for fluorine or FLOX service.

4.4.1 Soft-Seal Valve Design

The use of soft seals to permit adaption of standard valves to a zero-leak application is often desirable. However, exposure of the seals to the fluorine environment, to the rubbing friction of closure conditions, and to the flow of fluorine (all of which present ignition hazards) has made



(a) Cutaway of soft-seal valve in opening position.

(b) Valve open. (c) Bulk flow stopped. (d) Valve closed.

FIGURE 4-8.—Soft-seal valve developed at Lewis.

the use of soft seals generally unreliable.

As part of a testing program to develop and evaluate liquid-fluorine components (ref. 5), a zero-leak valve employing a soft-seal material at the flow shutoff interface was developed (fig. 4–8). It was successfully tested with liquid fluorine at flow rates up to 2 pounds per second and inlet pressure up to 97 pounds per square inch absolute. This valve was tested under dynamic liquid-fluorine conditions with soft-seal materials, including glass-filled and metal-filled tetrafluoroethylene, and nitroso rubber. (The metal- and glass-filled polymers were chosen arbitrarily, but in support of compatibility studies; the nitroso rubber was purposely selected as a normally noncompatible material.) By designing the valve for minimum exposure to fluorine and by surrounding the seal with metal to provide good thermal conductivity for heat transfer, it was expected that material compatibility could be enhanced. The test results confirmed this assumption.

A sectional view and schematic drawing of the soft-seal valve in its open position are shown in figure 4–8. A standard commercial valve actuator and housing was used for the testing. In operation, liquid-fluorine flow was directed past valve plug C, through the bellows flow passage F to the housing exhaust port. As the trim group was lowered, the spring-loaded hemispherical plug C contacted the floating spring-loaded inner metal seat D, which shut off the bulk of fluorine flow (fig. 4–8(c)). Continued downward movement of the trim group allowed the shutoff cap B to contact the soft seal E and completely seal the valve to fluorine flow (fig. 4–8(d)). Any of the cryogenic liquid trapped between the shutoff cap and the hemispherical plug vented itself to the downstream side of the valve assembly through the spring-loaded seal formed between the hemispherical plug and the inner seat D.

The design was tested at flow rates up to 2.06 pounds per second and a valve inlet pressure of 97.7 pounds per square inch absolute. At the conclusion of the testing, the valve soft-seal material was inspected for signs of erosion or chemical action. Results of the tests with various seal materials with respect to compatibility are discussed in section 3.3.4.

Principles demonstrated by this valve design indicated that limited application could be made by using soft-seal materials to achieve a zero-leak valve. Extensive testing would be required to assure adequate reliability, however.

4.4.2 All-Metal Conical Valve Design

Some limited work has been done to explore the possibility of an all-metal zero-leak valve design (ref. 6). This investigation was based on meeting the following specifications:

(1) The valve configuration must be all metal in order to have maximum compatibility with fluorine.

(2) The valve design must feature zero-leak capability under extreme conditions of environment and must not be affected by repeated open-close cycling.

(3) The valve design must permit the use of a wide range of valve actuator forces to permit easy adaption to flight-weight hardware.

A valve was designed based on the concept that the elasticity of metal could be used in the same fashion as the elasticity of soft seals to achieve zero-leak capability in a valve.

The general, physical characteristics of the design which evolved (fig. 4–9) are that (1) the cone is tapered so that (for circular cross sections) a constant total rim area is present from the lip back to the cone apex (the valve plug has a constant-thickness center section where the actuator stem is attached and the stem force is applied) and (2) the valve seat has a spherical seating surface.

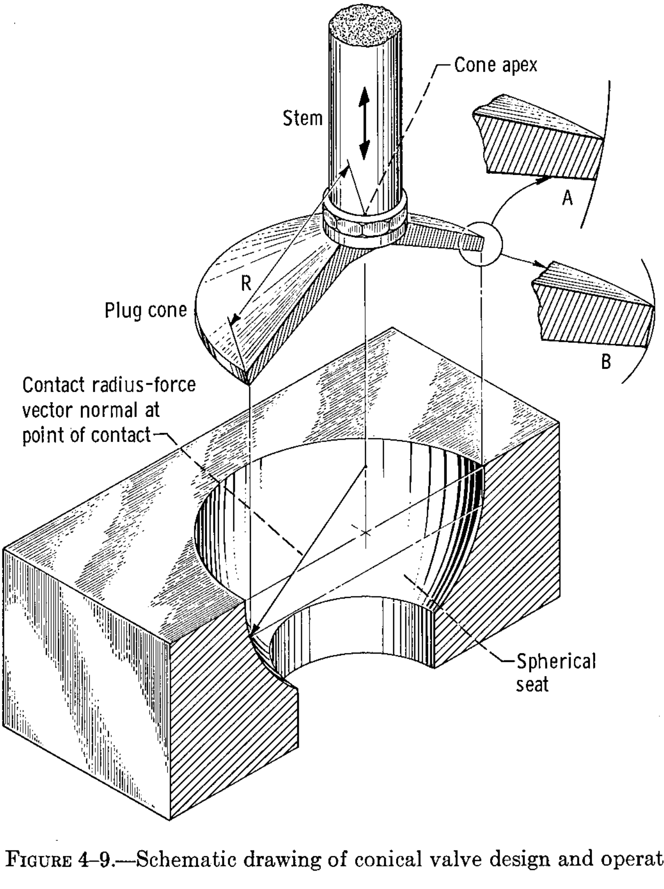


Figure 4–9.—Schematic drawing of conical valve design and operation.

For this type of valve, any desired mechanical advantage can be obtained for plugstem force applied by selecting an angle α from 0° (a cylinder) to an angle approaching 90° (fig. 4–9). (The sealing force is equal to the plugstem force divided by cosine α.) Since the distance R (fig. 4–9) is the same for the plug cone and the valve seat, this sealing force is applied normal to the valve seat and eliminates the sliding contact found in most valve plug-seat combinations. The mechanical advantage permits use of light plugstem pressures to achieve zero-leak seals.

Major design parameters for this valve can be widely varied. As one approach, after selecting the materials to be used, the cross-sectional area of the cone lip, and the force to be applied, the designer can choose the optimum cone angle so that the elastic limits of the cone material are not exceeded. In general, a minimum lip width is desirable to avoid stress concentration on sharp corners (see inset B in fig. 4–9) with resultant strain-hardening of the material. If thicker cross sections are used, the cone lip should be ground and lapped to provide a spherical surface to mate with the spherical valve seat (inset A, fig. 4–9).

Contact faces between the valve plug and seat must be smooth and round with 100 percent contact. For this reason, machining must be held to close tolerances to maintain roundness of plug rim and seat and proper plug taper, since underloading an out-of-round protrusion on either the rim or seat could cause local strain beyond the elastic limit of the material. A #4 finish (American Standard B46) was used for the contacting surface of the plug and seat to reduce the possibility of localized work hardening of hills and valleys on the contacting surfaces.

The design shows a number of attractive features:

(1) It can be used in fluorine (or other reagent) environments.

(2) The elastic properties of the conical plug afford zero-leak seals under repeated cycling.

(3) A slight angular misalinement or rotation of the valve plug in the seat will not affect the sealing properties of the valve.

(4) Normal passivation film does not affect the sealing properties of the valve.

(5) The conical plug characteristic is adaptable to a wide range of sealing forces (from valve operators) because of the inherent mechanical advantage supplied by the plug shape.

Leak tests were performed with aluminum, magnesium, and stainless-steel plugs in stainless-steel seats (seat material should be as hard as, or harder than, the plug material). The test fluids were helium and fluorine gas at ambient temperatures (fig. 4–10). Zero leakage was obtained with both fluids at pressures up to 200 pounds per square inch gage during and after 100 operating cycles (open-close). This capability is a result of another important feature of this valve; open-close cycling does

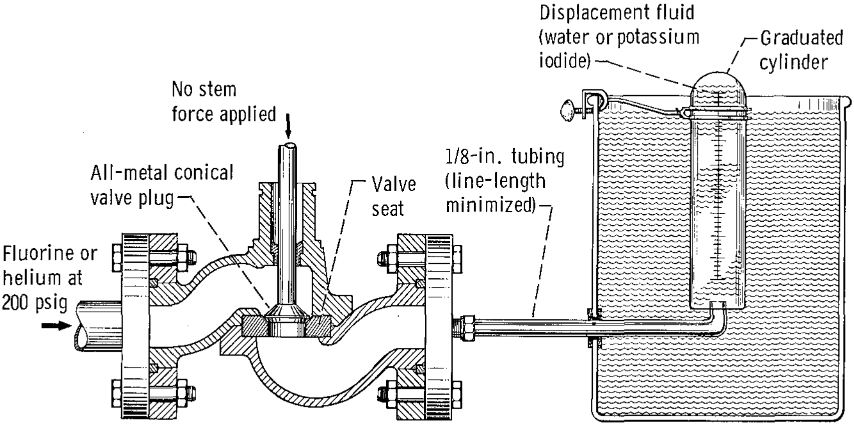


FIGURE 4–10.—Schematic drawing of apparatus used to verify zero-leak capability (24 hr) with no plugstem pressure applied.

not cause plug-seal material deformation or wear of contacting surfaces. All materials used were capable of achieving zero leakage as long as the elastic load limits were not exceeded.

Zero leakage was measured for periods up to 24 hours by using a water displacement method for helium and a potassium iodide solution for fluorine detection. This development effort was limited to demonstrating the design concept. No effort was made to optimize the design for minimum pressure drop across the valve or to develop a specific hardware item.

4.4.3 Pressure Regulating Valves

Pressure regulating valves as such have not been used for fluorine because of the nonmetallic parts normally included in these valves. Where automatic flow control is required, fluorine-compatible valves with flow- or pressure-sensing actuator-controllers have been used. If gaseous fluorine is used, pressure is reduced and throttled with throttling valves. (The gas cylinder shutoff valves should *never* be used for throttling fluorine gas flow, because this results in undue wear and stress of the primary shutoff valve.)

4.4.4 Pressure Relief

The fluorine containment system in mobile storage operations does not use pressure-relief devices (refer to section 4.1.3). In fixed tank facility storage applications, both burst diaphragms and pressure-relief valves have been used for pressure relief in fluorine containment systems. Burst diaphragms are preferred for pressure-relief devices, since they are generally more reliable and less prone to leakage than relief valves. This is important both in subcooled fluorine containment systems (vapor pressure is below atmospheric) and during any evaluation procedures, since an inward leak of moist air can occur. Monel diaphragms, sized to relieve at the desired overpressure in the particular system, are commonly used at Lewis. If repressurization following burst disk failure would be a requirement (e.g., to transfer fluorine from a containment vessel), two burst disks can be hooked up to the outlets of a three-way valve or a normally open automatically actuated valve can be installed upstream of the burst disk. Outlets from the burst diaphragms should be connected to the disposal system to prevent any release of fluorine contaminant to the atmosphere.

Automatic valves, modified to open on sensing an upstream overpressure, have been used as pressure-relief valves at Lewis. Since the possibility of inward air leakage through the seat exists in this device, however, its use is usually avoided. Whichever relief device is selected, the practice of regular inspection should be followed to ensure reliability.

4.4.5 Check Valves

Most commercial all-metal check valves are suitable for either gaseous or liquid fluorine. Selection should be based on the general criteria discussed in chapter 3 and in this section. Check valves that tend to "chatter" should not be used.

4.4.6 Valve Operators

4.4.6.1 *Manually operated valves.*—For safety considerations in handling gaseous fluorine under pressure, manual valves should be used with a protective barrier separating the operator from the valve. Valve handle extensions are generally used, and, where necessary, a bevel gear arrangement is included to change the direction of valve closure force.

4.4.6.2 *Pneumatic, hydraulic, and motor-operated valves.*—There is a great variety of actuators applicable to valve operation in fluorine systems. The only special requirements would be design considerations for possible exposure to fluorine or hydrogen fluoride vapors.

4.4.6.3 *Solenoid operators.*—In general, solenoid operators are restricted to smaller valves and to pilot-valve applications. Most solenoid valves cannot be used with fluorine or FLOX because the materials used for sealing solenoid windings are not compatible with fluorine. If solenoid valves are used in a fluorine line, the solenoid must be hermetically sealed with a compatible (preferably metal) sealing system to prevent contact with the fluorine. Also, precautions should be taken to ensure that the connecting wiring is protected from the effects of fluorine or hydrogen fluoride vapors (refer to section 5.2.5.3).

4.5 FLUORINE PUMPS

Although design data for liquid-fluorine pumps are limited, the extensive development of liquid-oxygen pumps (and recent work with seals for fluorine and FLOX pumps) has indirectly provided information for most areas of a liquid-fluorine-pump design.

The most difficult barrier in using existing conventional cryogenic pump designs for FLOX or fluorine lies in the lack of a compatible and reliable shaft seal that will operate for extended periods in the reactive fluorine or FLOX environment. Development testing of a fluorine pump at Bell Aircraft Corporation demonstrated that such seals were feasible. One seal accumulated over 27 minutes running time in liquid fluorine, and another seal operated well through three 300-second runs in a single 2-hour period (ref. 7). Work performed at Lewis and by Rocketdyne Division of North American Aviation and by the Florida Research and Development Center of Pratt & Whitney Aircraft has contributed to resolution of the seal problem (refer to section 4.5.2). Other major problem areas in pump design are the seal configuration and the impeller-inducer design.

4.5.1 Dynamic Seals

The most critical problem in designing a seal for a liquid-fluorine pump is controlling the leakage of fluorine to prevent contact of fluorine or FLOX with noncompatible elements of the pump (particularly the bearing lubricant, since no known lubricants are compatible with liquid fluorine). Leakage control can be maintained (1) by providing a more compatible environment for the seal by a backpressure inerting technique, bleeding an inert pressurant through the seal cavity and past the seal into the impeller cavity, or (2) by venting and purging the seal cavity overboard with or without use of a purge gas sweep. Both these methods, discussed subsequently, have been successfully demonstrated in pump tests (ref. 7).

Mechanical seals, bellows or spring-loaded, appear to be the better choice to incorporate in a positive shaft-seal design. This type of seal has been used successfully in liquid–oxygen pumps (ref. 8). In the following discussion it is assumed that the bellows seal is used, but if spring-loaded seals were considered, the discussion would still generally apply.

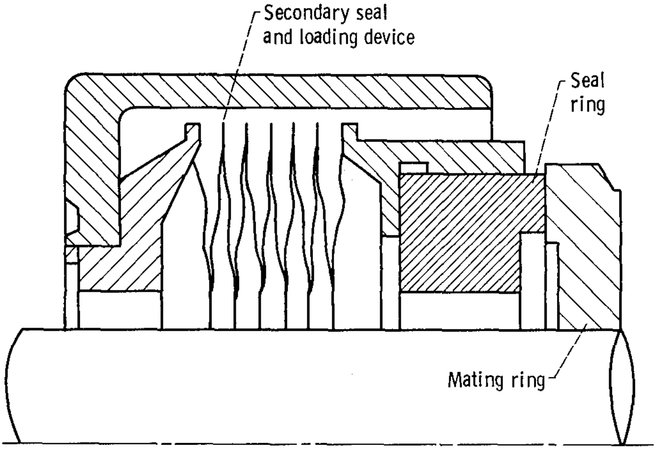
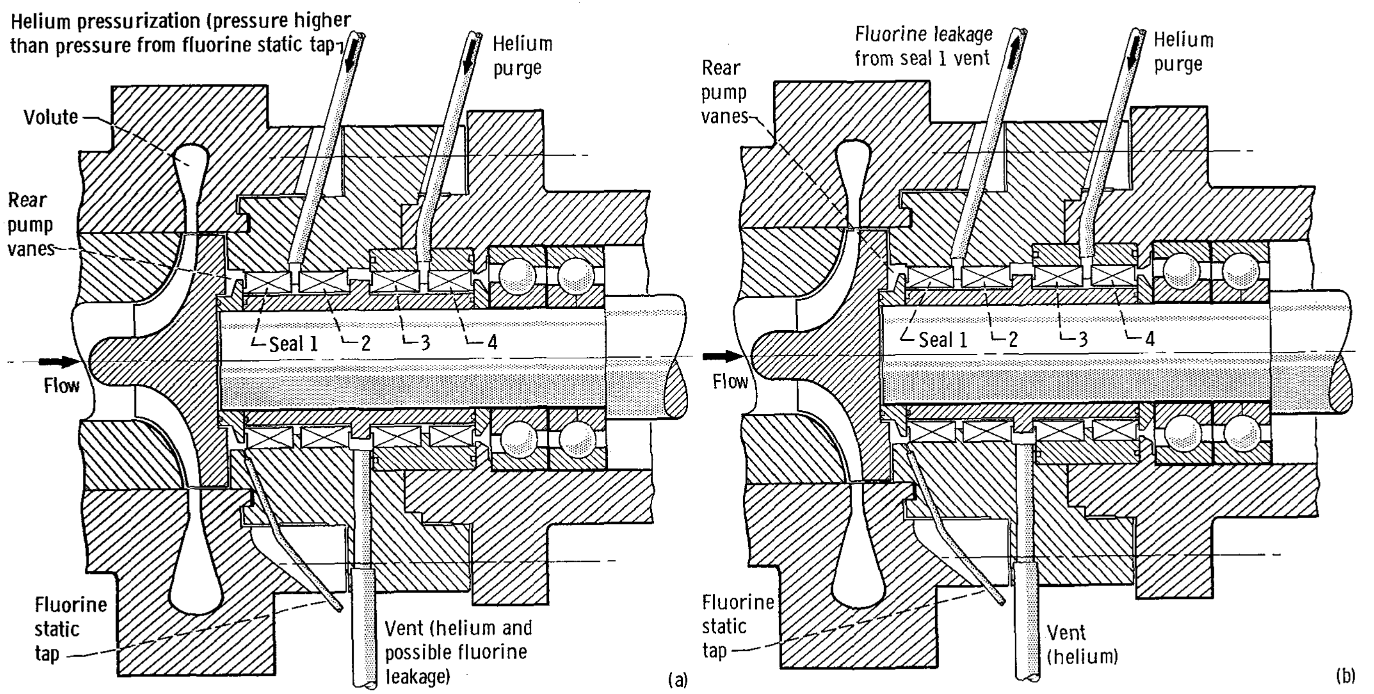


FIGURE 4–11.—Bellows and dynamic seal.

The dynamic seal (fig. 4–11) consists of a stationary seal ring, attached to a secondary seal and loading device (bellows), rubbing against a rotating mating ring attached to the pump shaft. The selection of the rubbing materials is important since they must both perform adequately as seals and dissipate the frictional energy generated without reacting with the fluorine. (Seal materials are discussed in section 4.5.2.)

Early liquid-fluorine pump tests (ref. 8) used a graphite carbon seal ring rubbing against a rotating nitralloy mating ring· The inside of the seal was pressurized with helium gas to a value slightly higher than the pressure of the fluorine being sealed. Thus, the seals operated with a small flow of inert gas across the rubbing surface (see section 3.3.3.6). Such a seal configuration is shown in figure 4–12(a). Seal 1 is the primary fluorine seal. Also shown in figure 4–12(a) is a second set of seals (seals 3 and 4) purged with helium to prevent contact between the bearing lubricant and any possible fluorine leakage. Pump tests with this seal configuration were successful because of the helium protection. However, helium leakage into the liquid fluorine sometimes causes problems with pump priming. Therefore, for rocket-engine applications, it is desirable to have a seal configuration similar to that shown in figure 4–12(b) in which fluorine leakage is accepted across seal 1 and is then vented overboard. Pump tests with graphitic carbon seals in which fluorine leakage was accepted across the seal generally resulted in burnouts due to the reaction of the fluorine and carbon (refer to section 3·3.3.6). Thus, graphitic carbon seals are not recommended for liquid-fluorine pumps.



(a) Helium purge and sweep gas across seal 1.

(b) Helium backpressure with overboard venting of fluorine leakage past seal 1.

FIGURE 4-12.—Liquid-fluorine pump assembly.

4.5.2 Seal Materials

Considerable work has been done in the selection and testing of materials for use as dynamic pump shaft seals for a liquid-fluorine environment (refs. 8 to 10). These studies can be divided into two parts: (1) preliminary friction and wear studies to determine lubricating characteristics of fluoride films in sliding friction, and (2) simulated and actual dynamic-pump-seal tests to examine realistically the best materials determined from the earlier friction studies.

Evaluation of all the testing reported indicates that a combination of titanium carbide cermet with a nickel binder (K-162B) and aluminum oxide (solid or flame sprayed) or a K-126B seal ring with a K-162B mating ring both have good friction and wear qualities when submerged in liquid fluorine. While both the K-162B and aluminum oxide have proved suitable for application as seals in liquid fluorine, the latter combination (K-162B used for both the seal and mating rings) is probably the best. Solid aluminum oxide is very fragile and subject to breakage, and the flame-sprayed aluminum oxide is susceptible to chipping, with subsequent high wear rates and loss of the film coating. It appears then that these materials are the best offered by the state of the art but are limited in long-term exposure to seal environments. For realistic evaluation of this type of seal for application in ground-support equipment pumping (from storage to launch of the test vehicle) considerably more testing is required. However, the testing to date indicates that such seals could provide reliable short-term operation, such as that required in launch-vehicle systems.

4.5.2.1 *Friction and wear studies at Lewis.*—Four material combinations were submerged in liquid oxygen and in liquid fluorine to determine their potentials as dynamic seal components for fluorine turbopump applications (ref. 8). Data were obtained in liquid oxygen and liquid fluorine with aluminum oxide riders sliding on four disk compositions: (1) titanium carbide cermet with nickel binder, (2) solid aluminum oxide, (3) fused coating (76 percent calcium fluoride+23 percent lithium fluoride+1 percent nickel fluoride) on aluminum oxide, and (4) coating (62 percent barium fluoride+38 percent calcium fluoride) on a nickel-chromium alloy. The tests were conducted with a $\frac{3}{16}$-inch-radius hemispherically tipped rider sliding in a circumferential path on a $2\frac{1}{2}$-inch-diameter disk.

Results (shown in table 4-IV) indicated that the presence of a fluoride film, either as an applied fused coating—calcium fluoride+lithium fluoride+nickel fluoride (CaF_2+LiF+NiF_2)—or as a film formed during sliding contact (titanium fluoride or nickel fluoride on the titanium carbide cermet, or possible aluminum fluoride on aluminum oxide) in liquid fluorine, was beneficial in reducing the friction and wear of the aluminum oxide riders.

TABLE 4-IV.—EXPERIMENTAL DATA FOR FRICTION AND WEAR OF MATERIALS IN LIQUID OXYGEN AND LIQUID FLUORINE (REF. 8)

[Riders, aluminum oxide; sliding velocity, 2300 ft/min; load, 1000 g.]

Disk material composition	Coating composition, percent	Coating thickness, in.	Test liquid	Total run time, min	Rider wear rate, cu in./ft of sliding	Disk substrate wear rate, cu in./ft of sliding	Friction coefficient	Remarks
Titanium carbide cermet[a] (52 Ti–5 Mo–25 Ni–4.5 Cb–13.2 C–0.3 Ta)	None	------	Oxygen	60	0.015×10^{-9}	1.180×10^{-9}	0.37	Friction erratic; polished wear scars
			Fluorine	[b]23	0.012×10^{-9}	0.120×10^{-9}	<0.10	Friction steady; surface reaction film nickel fluoride identified
Aluminum oxide--	None	------	Oxygen	60	0.140×10^{-9}	Negligible	0.50	Friction erratic; polished wear scars
			Fluorine	60	0.028×10^{-9}	Negligible	0.12	Friction steady; polished wear scars
	76 CaF_2–23 LiF–1 NiF_2	0.0025	Oxygen	62.5	0.015×10^{-9}	Negligible	[c]0.29	Friction steady; film failed at approximately 61.5 min
		0.003	Fluorine	[b]45	0.033×10^{-9}	Negligible	0.17	Friction steady

Nickel-chromium alloy (53 Ni–3.2 Ti–19 Cr–2.2 Fe–11 Co–1.6 Al–10 Mo)	62 BaF_2–38 CaF_2	0.0025	Oxygen	59	8.300×10^{-9}	Excessive	0.66	Film failed immediately
		0.002	Fluorine	[b]20	0.076×10^{-9}	0.011×10^{-9}	0.24	Friction steady

[a] Kentanium K-162B.

[b] Test terminated because of low liquid-fluorine level.

[c] Coefficient of friction after film failure, 0.50.

TABLE 4-V.—EXPERIMENTAL SEAL DATA IN LIQUID FLUORINE (REF. 8)

[Nosepiece, flame-sprayed aluminum oxide; sliding velocity, 2300 ft/min; pressure difference 2 psi.]

Disk material	Coating composition, percent	Coating thickness, in.	Face load,[a] lb	Total run time, min	Nosepiece wear, cu in./ft of sliding	Disk substrate wear rate, cu in./ft of sliding	Coefficient of friction	Remarks
Titanium carbide cermet	None	------	15	40	6.85×10^{-9}	0.152×10^{-9}	<0.10	Surface reaction; film nickel fluoride identified
Aluminum oxide..	76 CaF_2–23 LiF–1 NiF_2	0.0015	15	60	$<0.80 \times 10^{-9}$	Negligible	0.12	Trace amounts of applied fluoride film detected on wear track

[a] Calculated load at cryogenic temperature taking into account differential thermal contraction of assembly.

4.5.2.2 *Dynamic seal studies.*—The two best materials determined in friction and wear tests were tested as dynamic seals (ref. 8) under conditions representative of an actual pump application. This follow-on investigation used a flame-sprayed aluminum oxide nosepiece (0.006 to 0.008 in. thick) run against a mating disk of titanium carbide cermet or a fused coating (calcium fluoride+lithium fluoride+nickel fluoride) on aluminum oxide.

The stationary nosepiece, attached to a machined beryllium-copper bellows with a spring constant of 1000 pounds per square inch, was run against the mating disk while submerged in liquid fluorine. Experimental test conditions included a sliding velocity of 2300 feet per minute, a seal face load of 15 pounds, and a pressure differential across the seal of 2 pounds per square inch. In these seal experiments, the low pressure differential did not prevent the sealing surfaces from being wetted down by liquid fluorine.

The results of these seal experiments (ref. 8), given in table 4-V, indicated that aluminum oxide sliding against either the fused fluoride film on aluminum oxide or the titanium carbide cermet are acceptable material combinations for fluorine seal applications. Proper pressure balancing of the seal is required, however, to prevent excessive or uneven face loading, which can cause catastrophic seal wear and local fragmentation of aluminum oxide (discussed further in the following paragraphs).

Material combinations selected from these earlier tests (ref. 8) were also run in later tests of RL-10 (Centaur) engines with fluorine and hydrogen (ref. 10) and in tests of Atlas sustainer engines with FLOX–RP-1 propellant. In these tests, fluorine leakage was accepted across seal 1 (fig. 4–12(a)) and was vented overboard.

Results from the RL-10 engine testing program confirmed some of the conclusions drawn in the dynamic tests at Lewis. Material combinations (seal ring and mating ring), which included aluminum oxide (flame-sprayed film), displayed good wear characteristics; however, aluminum oxide introduces the possibility of failure due to poor bonding, from wearthrough of the flame-deposited film or from chipping of the film. Tests in the program (ref. 9) also indicated that a seal ring of beryllium oxide sliding on a titanium carbide cermet mating ring provided good wear characteristics. After $\frac{1}{2}$ hour, the mating ring indicated a 0.0006-inch wear and the seal ring a 0.0001-inch wear. (This compares with earlier tests that gave a 0.0002-in. wear and a 0.0002-in. growth, respectively.) However, two later tests with these materials at Lewis indicated excessive wear rates, so that further evaluation would be required before using the combination in a fluorine pump.

Testing during FLOX studies of the Atlas sustainer engine and components included tests to define seal materials performance. This was followed by engine firing tests. Seal materials testing involved use of a titanium carbide cermet (K-162B) mating ring with two types of aluminum oxide nosepieces (flame sprayed and in ceramic form) and a solid K-162B nosepiece. While all the material configurations were tested without failure, the aluminum oxide materials were highly subject to chipping and breakage. Seal components made of solid K-162B accumulated about 150 minutes of operating exposure time during the seal tests. As a result of materials evaluation from these tests, and from previous dynamic tests at Lewis, the combination of a K-162B seal ring and K-162B mating ring was chosen for use in the oxidizer pump during sustainer-engine-firing tests. The seals accumulated several hundred seconds of exposure time during these tests, with no seal problems traceable to seal materials. It is concluded that this combination is the best of presently available materials.

4.5.3 Housing and Impeller

Both liquid fluorine and FLOX can be considered incompressible fluids. Consequently, the impeller discharge configuration and pump housing volute design can be determined by using normal pump design parameters, which are usually obtained from water data. The impeller or inducer inlet configuration can be based on liquid-oxygen or liquid-nitrogen-pump data, or determined by methods listed in reference 11 when high-suction-specific-speed pumps are needed to meet low-suction-pressure requirements.

The pump impeller design should include a method of reducing the fluorine pressure at the rear of the impeller near the shaft (e.g., by the use of vanes or labyrinths) to lessen the dynamic seal problems.

Data for a liquid-fluorine inducer and main-stage pump combination designed for a suction specific speed of 20 000 were obtained in three runs with a total operating time of 16.7 minutes in liquid fluorine (ref. 10). The following results were realized from the investigation:

(1) At a net positive suction head of 100.5 feet, a maximum pressure rise of 547 pounds per square inch, a maximum flow rate of 302 gallons per minute, and a maximum efficiency of 0.635 were obtained.

(2) At a net positive suction head of 29 feet, a maximum pressure rise of 547 pounds per square inch, a maximum flow rate of 225 gallons per minute, and a maximum efficiency of 0.62 were obtained.

(3) An increase of 41.5 percent in maximum flow rate was obtained for the performance of the pump with an inducer compared with the performance of the pump without an inducer at approximately the same inlet total pressure (14 psi).

(4) It is probable that cavitation damage will not be a problem in liquid-fluorine pumps for rocket applications. Inspection of the rotors

used in this investigation revealed no damage from approximately 12 minutes of operation under cavitating flow conditions with suction specific speeds as high as 22 358.

(5) The titanium carbide and aluminum oxide materials used for the rotating shaft seals in this investigation showed no reaction with liquid fluorine and adequately performed their functions as seal materials.

4.5.4 **Pump Materials Selection**

Table 4-VI gives pump components and the various materials of construction most suitable for each component.

TABLE 4-VI.—PREFERRED MATERIALS OF CONSTRUCTION FOR LIQUID-FLUORINE OR FLOX PUMPS

Component	Material
Housing	Monel "K" and "S" Stainless steel 304, 347 Aluminum 356
Impeller	Monel Stainless steel 304, 347 Aluminum 356
Shaft	Monel Stainless steel 304, 347
Seals (wear surfaces), nosepiece and mating ring	Titanium carbide cermet with nickel binder (see table 5-IV for composition)
Bellows	Monel Stainless steel 347
Gaskets	Aluminum (annealed) Copper (annealed)
Lines and fittings	Monel Stainless steel (300 series) Aluminum 2017, 2024, 6061, and 500 series
Orifice	Monel Stainless steel Copper Aluminum Brass
Bearings	Stainless steel on stainless steel (400 series)

4.6 INSTRUMENTATION

4.6.1 General Considerations

The considerations involved in instrumenting a fluorine or FLOX facility include the same criteria that apply to hardware in general:

(1) Component materials must be fluorine-compatible and preferably of all-metal construction.

(2) Where they are used, nonmetals must be applied within the usage limits defined in chapter 3.

(3) Assembling, cleaning, and installation of all components should meet the same requirements previously defined for other hardware, as well as those specified in section 4.9.

With application of these major principles, most off-the-shelf hardware can be adapted for fluorine or FLOX use with minimal modification (e.g., replacing seal materials or making connection modifications). The fluorine or FLOX should only be in contact with materials suitable to the operating environment, that is, those materials with the highest degree of material compatibility possible in the particular application. The inner flow surfaces through which the fluorine or FLOX passes should form, as much as possible, a smooth-walled enclosure, free of unnecessary protrusions or cavities. Systems should be simplified to include minimum instrumentation to perform tasks required (penetration of the fluorine containment system should be minimized). Overly complex assemblies should be avoided.

4.6.2 Flow Measurement

In liquid-fluorine or FLOX systems, flow can best be measured by two methods. Rotating-vane (turbine type) flowmeters can be used, or the differential pressure from a venturi or an orifice can be measured.

4.6.2.1 *Turbine flowmeters.*—The metered fluid spins a magnetized rotor that is suspended by bearings in the flow passage. Magnetic flux induces a current in an external field, which results in an output signal that is an index of flow. This type of instrument, which must be all-metal (preferably 300- or 400-series stainless steel), has proved accurate to within 0.75 percent in operations at Lewis. Ball-bearing shaft supports are preferred for this application, since bushing-type bearings have proved to be unreliable (ref. 12).

Turbine type flowmeters (ball bearing) have been in intermittent use with sustained operations for about 5 years without incidents or loss of accuracy. As with other components in fluorine or FLOX systems, however, it is important to maintain the system free of hydrogen-fluoride contaminants in order to prevent bearing deterioration.

4.6.2.2 *Differential pressure flowmeters.*—The determination of fluid flow by the ΔP method involves measurement of the pressure drop across either an orifice (normally installed between two line flanges) or a venturi. Stainless steel, Monel, or nickel are the preferred metals for fabrication of either orifices or venturi tubes, although aluminum and copper alloys may be used in reasonably contaminant-free systems. Modifications and installation requirements for differential pressure transducers used in this application are included in section 4.6.3.1.

4.6.2.3 *Rotameters.*—The rotameter may be modified for fluorine service by replacing the standard tube packing with polytetrafluoroethylene; the use of aluminum floats with stainless steel or Monel guide wires is also recommended. Standard Pyrex glass tubes may be used, but because hydrogen fluoride will etch the glass and coat or corrode the floats this, as well as moisture contaminants, should be minimized in the system. Trace quantities of these contaminants will usually be present in gaseous fluorine; thus, the flowmeter should be calibrated frequently with dry nitrogen. This instrument is most suitable for laboratory use.

Rotameters should be shielded for direct reading (e.g., by surrounding the tube with a Pyrex glass shield for protection in case of tube rupture). The rotameter can also be adapted for liquid service by adding a liquid-nitrogen jacket around the tube; other required modifications are substantially the same as those for gaseous fluorine.

4.6.3 Pressure Measurement

4.6.3.1 *Pressure transducers.*—Standard commercial instruments normally can be used for measuring pressure if they meet compatibility requirements. Since the only surface presented to fluorine or FLOX contact is a metal sensing diaphragm, no modification would be required, although the instrument should be thoroughly cleaned and passivated. All-metal instruments that are commercially available can be mounted directly into the cryogenic tank wall (pipe, etc.). When the instrument being used cannot tolerate direct exposure to the cryogenic, it can be attached by a short tube, which is helium bubble purged (refer to section 5.2.6.1) to prevent percolation of the cryogenic at the sensing diaphragm and resultant fluctuation in the pressure sensed.

The type of transducer used for ΔP measurement usually has an oil-filled pressure-sensing chamber between the sensing diaphragms. This chamber should be drained, cleaned, and refilled with a fluoropolymer oil.

When this ΔP transducer for level measurement is installed, the liquid leg should be connected to a bubbler system (refer to section 4.6.5.1) to ensure that the cryogenic liquid does not contact the transducer (percolation would cause pressure fluctuation and/or the cryogenic would freeze the oil in the sensing chamber).

When the differential pressure transducer is mounted in a flow line, the instrument should be located above the flow line, or mounted so that the cryogenic fluid will not contact the sensing diaphragm, since most ΔP transducers cannot tolerate low temperatures. The connecting pressure-sensing lines must be of the proper size and length (1) to protect the instrument from direct contact with the cryogenic fluid, and (2) to provide maximum sensitivity to changes in flow rates by minimizing the volume of the gas pocket near the instrument. In Lewis operations, the optimum length has generally been about 1 foot with ¼-inch tubing. To prevent excessive radiant heat transfer from the body of the transducer to the flow line, a layer of insulation should be used to shield the instrument.

4.6.3.2 *Bourdon gages.*—The Bourdon tube has been used extensively in test-cell applications. There are several types of commercially available Bourdon gages with sensing tubes made of stainless steel or K-Monel. Lewis has made use of these gages in fluorine service to measure pressures up to 1500 pounds per square inch gage.

Special care must be taken to clean the Bourdon tube because it is quite small and has a relatively long cavity. First, it should be evacuated to permit the cleaning fluid (trichloroethylene or trichlorotrifluoroethane) to be drawn into the tube. Then, after it is cleaned, the tube must again be evacuated to remove the cleaning fluid. This same procedure should be used for final passivation and cleaning before the component is used in fluorine or FLOX service.

4.6.4 Temperature Measurement

4.6.4.1 *Thermocouples.*—Stainless-steel-shielded thermocouples are commercially available and are particularly suitable for use in a fluorine environment. The thermocouple wires are installed in an insulating medium (e.g., alumina) inside a protective tubing, sealed at the same end as the thermocouple junction. This entire assembly is then swaged to immobilize the thermocouple wires. The thermocouple is generally inserted through a compression fitting welded into the side of the fluorine line or container, or the unit may be silver-soldered or nicro-brazed into place.

This arrangement offers the advantage of presenting only metal surfaces to the fluorine or FLOX without critically affecting response time. In some installations, instrumentation wiring from the thermocouple may be run through metallic conduit, hermetically sealed at the point of junction with the thermocouple, to ensure that no contact would be made between the wiring and fluorine or FLOX.

4.6.4.2 *Thermistors.*—These are used like thermocouples in low-temperature systems; they provide a more measurable signal (voltage) for given temperature changes than thermocouples. Basically, thermistors are either wire-wound coils (around an insulator) or crystals (e.g., gallium arsenide) through which a known current is passed. The thermistor resistance varies with the temperature changes and is measured as an indication of temperature.

Both basic types of thermistors are commercially available in metal casings (that have AN-fittings, etc.) and may be used in fluorine systems if the general precautions given in section 4.6.1 are followed. Wiring should be hermetically sealed to prevent exposure to a fluorine or FLOX environment.

4.6.5 Liquid-Level or Quantity Measurement

There are many techniques for measuring levels in cryogenic liquids that can be divided into two groups: (1) continuous-level sensors and (2) point-level sensors. These techniques employ measurements of thermal conductivity, density, weight, magnetic susceptibility, ultrasonic attenuation, and optical refraction as parameters to indicate level or quantity. Detailed discussion of all the possible techniques is beyond the scope of this report (see refs. 13 to 15); however, instruments that use these techniques can be applied to fluorine or FLOX measurement if they can be adapted to meet the fluorine-peculiar criteria discussed in section 4.6.1. Methods that have been successfully applied to measurement in fluorine systems are discussed in sections 4.6.5.1 and 4.6.5.2.

4.6.5.1 *Continuous-level sensing.*—While continuous-level detection is generally less accurate than point-level sensing, several methods have been successfully applied:

(1) Direct weighing of the fluorine container (immersed in liquid nitrogen as shown in fig. 4–2) has proved accurate to about 1.0 to 2.0 percent in test-cell operations at Lewis. Some fluorine trailers include provisions for load cells to measure the total weight of the three-shell storage vessel; however, since the weight change involved from a slight change in quantity in the fluorine container is small compared with the total weight, the accuracy is reduced. Use of weighing systems would be restricted to ground-support systems.

(2) Differential pressure (ΔP) level meters can provide a more accurate method of determining the liquid level in a tank and consequently the quantity of fluorine or FLOX in the container. This method uses a transducer to measure the differential head of the liquid. The liquid sensing leg can be connected either directly into the bottom of the storage tank or through a dip tube that extends to the bottom of the tank. Either method requires use of a standard "bubbler" system, in which

pressure-regulated helium is admitted so that only a few bubbles per minute escape at the bottom of the storage tank. The hazard involved with use of this method is that, even with extremely pure helium, contaminants (primarily moisture) in the helium will tend to accumulate in the fluorine or FLOX containers. This type of freezeout occurred in an actual facility, with ice forming in the tank ullage at a vent outlet. A resulting reaction occurred between the fluorine and the ice and the containment tank was badly damaged.

(3) The capacitance probe level sensor employs the principle that the capacitance of a condenser is a function of the mean dielectric constant between the capacitor plates, where two mediums (gas and liquid) exist between the plates. The measured capacitance of the probe is an index of the level of the liquid fluorine or FLOX within the storage vessel.

Figure 4–13 shows the major construction of a probe that has been in intermittent service for level measurement at the Lewis Plum Brook Facility through 19 test runs. The probe was modified from a standard commercial instrument to make it compatible with fluorine or FLOX.

The probe is composed of two concentric tubes spaced and held rigidly within the tank by aluminum oxide spacers and holders. This is actually a liquid-gas interface detector in which the level, as it raises and lowers, varies the capacitance of the probe, which is detected on a bridge balance circuit.

Modification consisted of replacing the original seals with two sets of aluminum oxide spacers and chevron polytetrafluoroethylene (TFE) packing. In this arrangement, the TFE is exposed only to a static gaseous fluorine atmosphere, and the second set of seals ensures against any further leakage up the shaft.

(4) Flowmetering is the fourth method for determining a changing quantity in a tank by measurement of outflow (section 4.6.2).

4.6.5.2 *Point-level sensing.*—This method can be highly accurate and is particularly useful where a critical measurement is involved (e.g., launch vehicle maximum fill). The following methods have been applied for this purpose:

(1) Temperature sensing involves the use of a thermocouple or thermistor to detect the temperature change across the vapor-liquid interface (refer to section 4.6.4).

(2) Capacitance probes can be used for point-level sensing.

(3) Instruments that use vibrating crystals are commercially available and can be adapted for fluorine service (see section 4.6.1 for general modifications). All wiring should be hermetically sealed to prevent exposure to fluorine or FLOX atmospheres. (AN adapters are available on commercial instruments). In application, the crystal is contained in a metal casing; a current passed through the crystal causes vibration due

to the piezoelectric effect. When the metal casing (to which the crystal is bonded) touches an incompressible medium (liquid), vibrations are damped; to maintain the vibration, more energy is required. This provides a pronounced indication of liquid level.

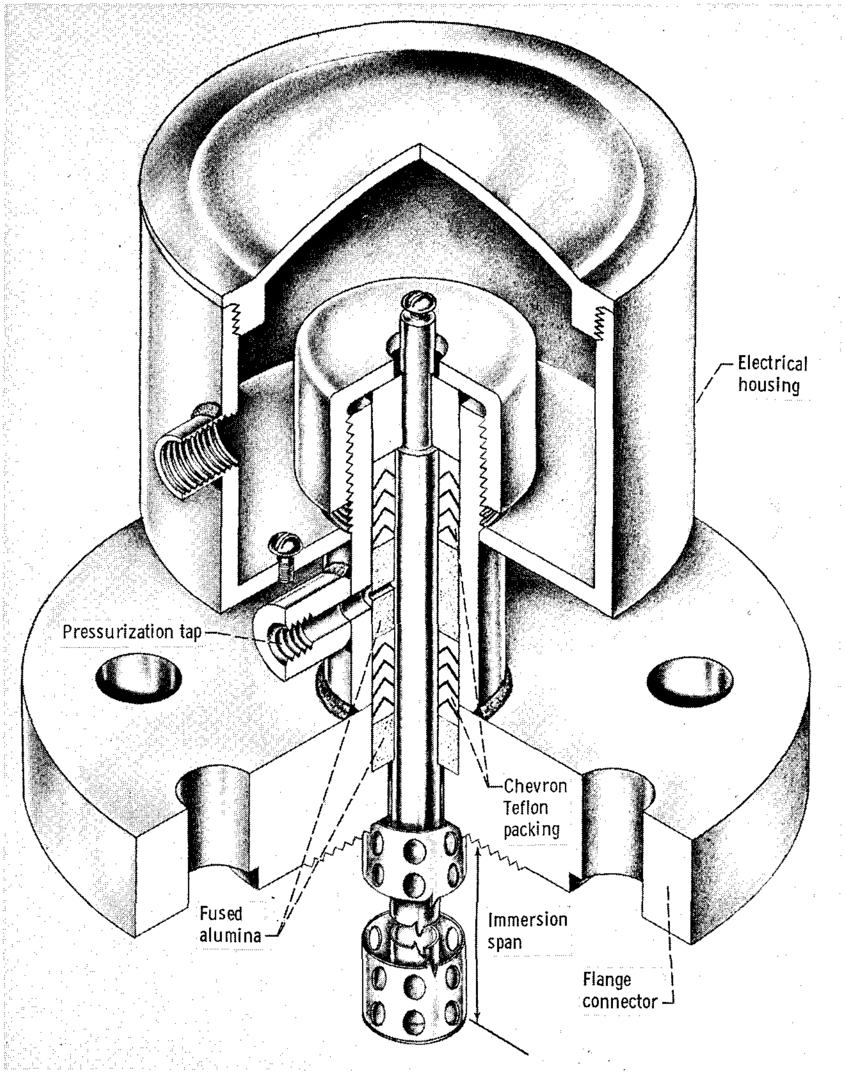


FIGURE 4-13.—Capacitance probe level sensor. All parts except electrical housing are Monel metal.

4.7 REFRIGERATION SYSTEMS

4.7.1 General

The most commonly used refrigeration system for fluorine and FLOX storage has been a liquid-nitrogen jacket around the storage tank. Larger storage tanks (without liquid-nitrogen jackets) would require the use of condensers to liquefy boiloff or subcoolers to maintain the temperature of the stored fluid. Condensers might also be used for boiloff recovery systems, and cryogenic propellant loading systems often include a subcooler in the propellant loading line to the vehicle.

For storage tanks with jacketing, the coolant fluid can be liquid nitrogen (b.p., −320° F), liquid air (b.p., −312° F), or liquid oxygen (b.p., −298° F). The coolant would be selected to give the desired storage temperature and vapor pressure. Liquid nitrogen would be used as the coolant in subcoolers and recondensers to obtain the highest ΔT.

4.7.2 Condensers

Condenser design should be kept simple to provide a system that is easy to clean and maintain. The simplest heat exchanger would be a liquid-nitrogen-jacketed tank, or a conventional tube and shell system with liquid nitrogen in the shell and the fluorine or FLOX contained in the tubes. The use of an exchanger with vertical tubes provides maximum efficiency since this results in maximum condensate velocity and minimum film thickness on the tube walls.

Figure 4–14 is a plot of the condenser load as a function of the condensing heat-transfer coefficient for fluorine (ref. 1). The condensing heat-transfer coefficient is a function of unit tube length only, so that for a given tube length, the condensation rate per tube is a linear function of the tube diameter (total surface area).

Figure 4–15 shows a plot of fluorine condensation rate per tube as a function of tube length for a 1-inch-diameter tube (ref. 1). In this way,

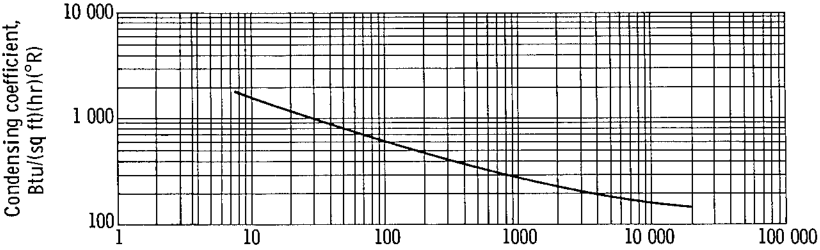


FIGURE 4–14.—Fluorine condenser load as function of condensing heat-transfer coefficient (ref. 1).

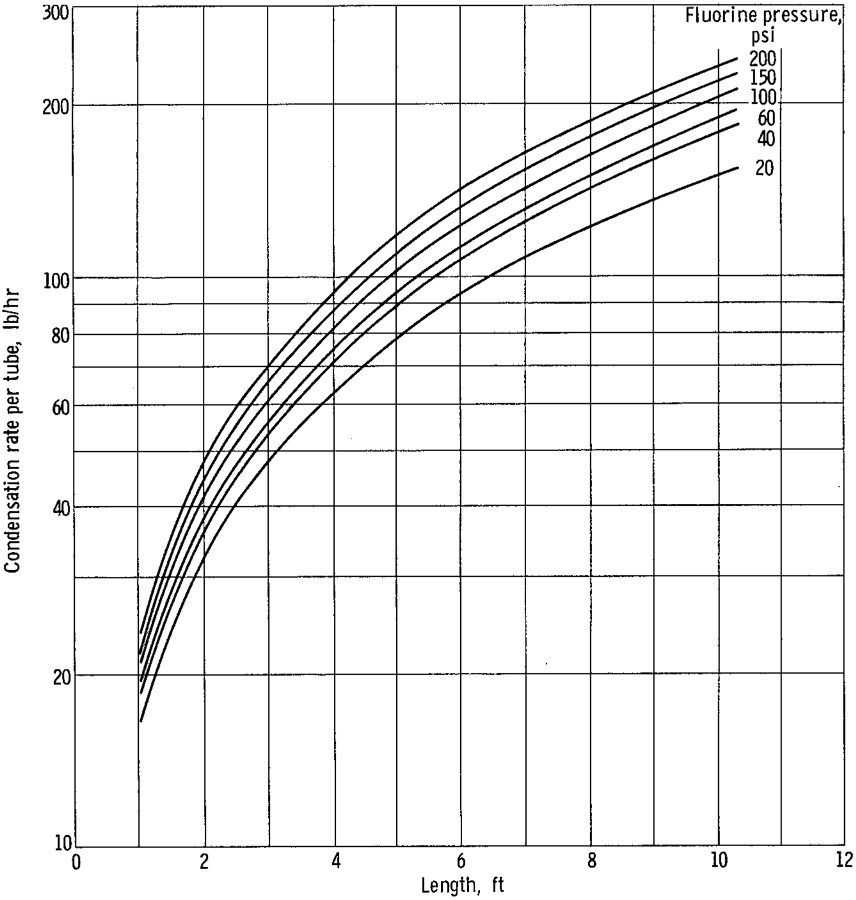


FIGURE 4–15.—Fluorine condensation rate per tube as function of tube length for vertical tube and shell heat exchanger (ref. 1). Nitrogen boiling at pressure of 1 atmosphere in 1-inch-diameter shell tube. Condensation rate is directly proportional to tube diameter and number of tubes in exchanger.

for any given condenser of this design, the total condensation rate is given by

$$W = wN_t\frac{d}{d'}$$

where

W	condensation rate, lb/hr
w	condensation rate per tube (fig. 4–15), lb/hr
N_t	number of tubes
d	diameter of tubes, in.
d'	1-in.-diam tube

For example, assume a storage tank of 28 000-gallon capacity with a heat leak rate that will result in a fluorine boiloff rate of 2 percent or 560 gallons per day. The desired storage pressure in the system is 20 pounds per square inch absolute, and the equilibrium temperature and density at this pressure are 158.69° R and 92.54 pounds per cubic foot, respectively. This boiloff rate therefore amounts to 289 pounds per hour. From the curve for 20 pounds per square inch gage in figure 4–15, the various combinations of tube lengths and numbers of tubes that will satisfy this requirement may be determined.

4.7.3 Subcoolers

The need for subcoolers in a fluorine or FLOX (vehicle) loading system (at a rocket installation) would largely be a function of

(1) The mode of facility storage (whether subcooled by liquid nitrogen, etc.)
(2) The heat gain during transfer operations from storage to launch vehicle
(3) The propellant-topping requirements and net-positive-suction-head (pump) requirements

The simplest exchanger for this system is similar to that considered in section 4.7.2. Since the fluorine will be in forced convection through the tubes and will be entirely in the liquid state, the tubes may be either vertical or horizontal.

The heat-transfer coefficient in the tubes is given by reference 1:

$$h_c = \frac{0.023\, C_p G \left[1 + \left(\frac{D}{L}\right)^{0.7}\right]}{\left(\frac{C_p \mu}{k}\right)_f^{2/3} \left(\frac{DG}{\mu}\right)_f^{0.2}}$$

where

h_c	condensing heat-transfer coefficient
C_p	specific heat
G	mass velocity
D	diameter of tube
L	length of tube
μ	viscosity
k	thermal conductivity
f	film conditions

4.8 FLUORINE DISPOSAL METHODS AND DESIGN

The toxicity of fluorine and FLOX makes direct venting to the atmosphere inadvisable in most locations. There are several methods that can be used to provide inert reaction products:

(1) Reaction of fluorine with charcoal to produce primarily inert carbon tetrafluoride gas has the advantage of reacting almost all the elemental fluorine to a nontoxic state and is recommended by Lewis for use whenever practical (refer to sections 3.1.2.2. and 4.8.1).

(2) Direct burning of gaseous fluorine and/or FLOX mixtures (gaseous) with fuels such as methane or propane in burners on top of exhaust stacks can be used by sizing the number of burners and the fuel flow to the expected rate and quantity of elemental fluorine to be reacted (refer to section 4.8.1).

(3) Reactions of fluorine with alkaline solutions (lime, sodium hydroxide, or sodium bicarbonate) to neutralize reaction products are most suitable for laboratory quantities of fluorine but are generally more cumbersome to use than the charcoal reactor method (refer to section 4.8.2).

(4) Recovery systems, where system design and operating conditions permit, should be considered, since fluorine is expensive and no-loss storage is preferable (refer to section 5.2.2).

4.8.1 Disposal System Design

4.8.1.1 *Charcoal reactor design.*—In order to equip operational facilities at Lewis with immediate disposal equipment, a carbon-fluorine combustion method was developed (refs. 16 and 17) and a number of reactors were made, as shown in figure 4–16. To build these reactors, standard ring-clamp 50-gallon drums (6.7 cu ft) were lined with 2 inches of castable refractory cement. A 3-inch layer of the cement was used on the underside of the lids, but the bottoms were not protected. The fluorine inlet tubes passed through the lid and ended flush on the inside at the refractory cement surface. *The top inlet feed system allows the high-temperature reaction zone to be supported by the charcoal;* in a furnace-grating support with bottom inlet feed, the reaction process tends to consume the grating. The use of two or more of these drums connected in parallel is preferred to one large unit because the parallel-drum system provides continued disposal capability in the event of burnout in one of the units. The capacity fluorine-disposal rate per drum was approximately 100 pounds per hour, but in one test the equipment was operated at a rate higher than 600 pounds per hour for approximately 3 minutes (30 lb fluorine) with a possibility of liquid-fluorine entrainment without damage to the reactor.

The maximum rate of fluorine disposal for an effluent containing less than 100 parts per million of fluorine was approximately four times greater for the 3/8-inch charcoal material than for the 1½-inch material.

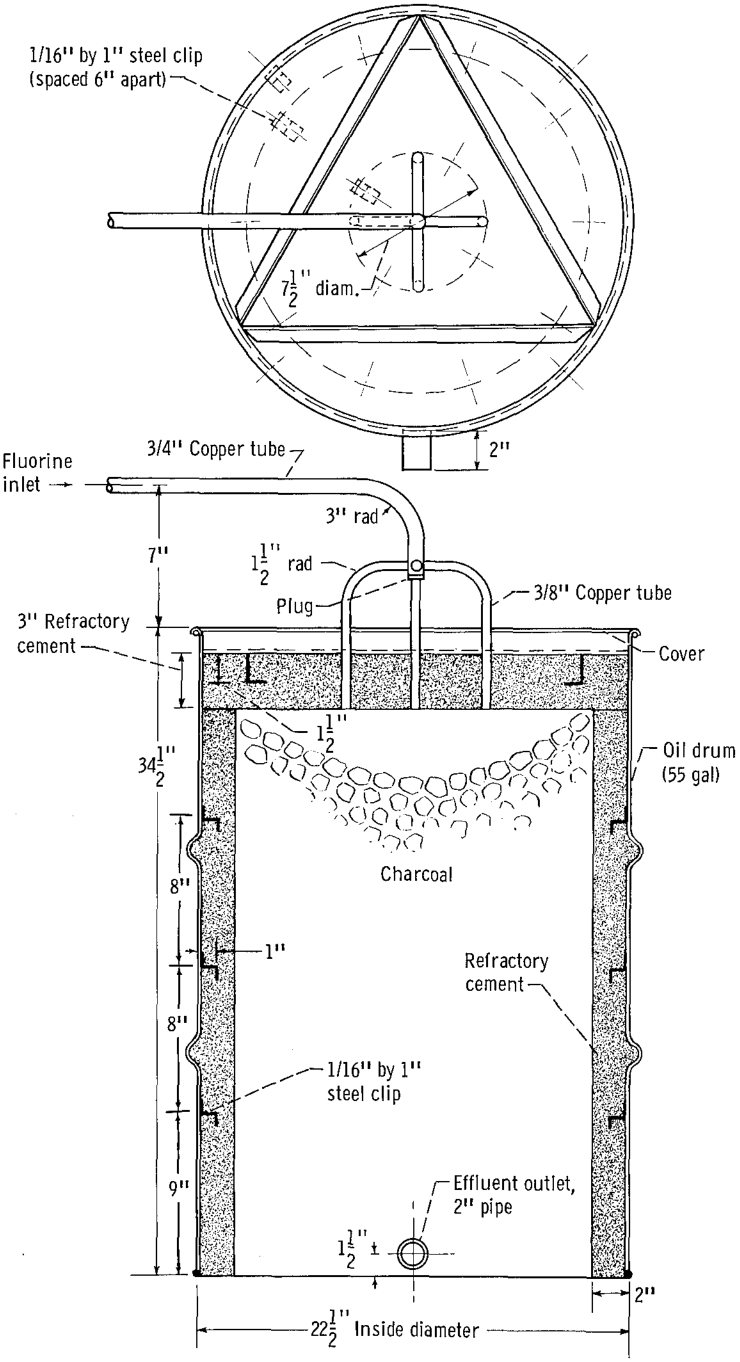


FIGURE 4–16.—Uncooled fluorine reactor.

Thus, the rate of fluorine disposal is inversely proportional to the nominal particle diameter. Since the ratio of the total external surface area per unit volume of charcoal is also 4 to 1 for the $\frac{3}{8}$- and $1\frac{1}{2}$-inch particles, only the external surfaces of the charcoal particles are active in the reaction.

The data (table 4-VII) show that the maximum disposal rate for optimum efficiency for $1\frac{1}{2}$-inch-diameter charcoal particles was about 8 pounds per hour for the 0.18 cubic foot of effective charcoal volume; the limit for $\frac{3}{8}$-inch-diameter charcoal particles was approximately 30 pounds per hour. Since the fluorine flow rate per unit volume of charcoal is inversely proportional to the particle diameter

$$R/V=K/D$$

where

R	fluorine flow rate, lb/hr
V	charcoal volume, cu ft
D	nominal charcoal particle diameter, in.
K	proportionality constant

Using the maximum allowable rate values gives

$$K(\tfrac{3}{8}\text{ in.})=\frac{30\text{ lb}}{\text{hr}}\ \frac{1}{0.18\text{ cu ft}}\ \tfrac{3}{8}\text{ in.}=62.5\,\frac{(\text{lb})\,(\text{in.})}{(\text{cu ft})\,(\text{hr})}$$

and

$$K(1\tfrac{1}{2}\text{ in.})=\frac{8\text{ lb}}{\text{hr}}\ \frac{1}{0.18\text{ cu ft}}\ \tfrac{3}{2}\text{ in.}=66.6\,\frac{(\text{lb})\,(\text{in.})}{(\text{cu ft})\,(\text{hr})}$$

Therefore, for engineering design approximations, an average maximum allowable disposal rate R may be expressed as

$$R=\frac{65V}{D}\ (\text{lb fluorine/hr})$$

The volume term in the preceding equation represents the maximum requirements for maximum rate and does not allow for the fact that charcoal is consumed in the process. Therefore, additional volume is required equivalent to the volume of charcoal to be consumed. The stoichiometric charcoal requirement for fluorine consumption is assumed to be 17.5 pounds of charcoal per 100 pounds of fluorine plus the minimum amount of charcoal for maintaining reaction efficiency toward the end of the burning period.

The length of time a given reactor may be used continuously is limited by the high-temperature resistance of the reactor structure to fluorine attack, the heat capacity of the system, and the rate of fluorine input. The number of nozzles required for any given bed area is arbitrary; however, one to three nozzles per square foot have given satisfactory distribution.

TABLE 4-VII.—DATA FROM LEWIS FLUORINE-DISPOSAL EXPERIMENTS USING A CHARCOAL REACTOR

Fluorine in nitrogen, percent	Flow rate, lb/hr	Nominal charcoal particle diameter, in.	Moisture in charcoal, percent	Run time, min	Ratio of fluorine to effluent, $\frac{g}{\text{std cu ft}}$ [a]	Fluorine in effluent, ppm [a]
Effect of fluorine dilution with nitrogen						
54.4	<7	3/8	<6	-----	2.4×10^{-3}	30
50.0				-----	2.5	29
31.4				-----	2.1	31
22.2				-----	.5	9
18.5				-----	1.5	29
15.5				-----	1.7	34
15.4				-----	.9	17
14.0				-----	4.9	98
10.0				-----	4.8	105
2.5				-----	4.2	111
.3				-----	6.1	171
.3				-----	4.9	137
Effect of flow rate and charcoal particle size						
100	2.1	3/8	<6	-----	4.7×10^{-3}	37
	2.4			-----	5.1	41
	4.0			-----	8.3	66
	4.0			-----	4.1	32
	4.0			-----	.8	6
	4.4			-----	3.9	31
	4.5			-----	2.5	20
	4.5			-----	5.2	41
	9.0			-----	2.1	16
	42.3			-----	14.7	117
	61.0			-----	31.2	247
Effect of flow rate and charcoal particle size						
100	2.2	1½	<6	-----	12.1×10^{-3}	96
	2.3			-----	8.0	63
	4.0			-----	8.5	67
	4.5			-----	11.1	87
	8.0			-----	5.5	43
	10.2			-----	24.7	195
	48.4			-----	104	825

[a] The parts per million of fluorine in effluent are not proportional to grams of fluorine ($\times10^{-3}$) per standard cubic foot of effluent when dilute feed is used; the nitrogen content in the effluent reduces the average molecular weight of a given sample volume thereby increasing the parts per million value, whereas the grams per standard cubic foot are not affected.

TABLE 4-VII.—DATA FROM LEWIS FLUORINE-DISPOSAL EXPERIMENTS USING A CHARCOAL REACTOR—Concluded

Fluorine in nitrogen, percent	Flow rate, lb/hr	Nominal charcoal particle diameter, in.	Moisture in charcoal, percent	Run time, min	Ratio of fluorine to effluent, $\frac{\text{g}}{\text{std cu ft}}$ [a]	Fluorine in effluent, ppm [a]
Effect of moisture; saturation maintained						
100	<6	3/8	24	3.25	0.7×10^{-3}	5
			↓	5.25	2.9	23
			↓	8.85	6.3	50
			↓	10.25	17.7	140
			↓	14.75	8.1	64
			29	18.45	9.0	71
Effect of moisture; high initial water allowed to diminish						
100	<6	3/8	30	2.0	1.72×10^{-3}	14
			↓	3.1	4.82	38
			↓	5.0	4.4	35
			↓	6.0	15.3	121
			↓	8.0	10.9	86
			↓	8.5	14.9	118
			19.8	11.0	2.9	23
			-----	12.0	7.9	63
			-----	18.2	3.8	30

[a] The parts per million of fluorine in effluent are not proportional to grams of fluorine ($\times 10^{-3}$) per standard cubic foot of effluent when dilute feed is used; the nitrogen content in the effluent reduces the average molecular weight of a given sample volume thereby increasing the parts per million value, whereas the grams per standard cubic foot are not affected.

Reactor-bed depth is also arbitrary and may be subject to design convenience since the reaction is dependent on charcoal surface areas, provided, however, that the fluorine is impinged onto the charcoal surface and not into a nearby void space, as could occur with a single layer of particles.

In summary, the Lewis investigation showed generally that the carbon-fluorine disposal system may be operated effectively over a wide range of conditions. The following results were obtained:

(1) 100-percent fluorine or fluorine diluted with nitrogen to concentrations as low as 0.3-percent fluorine may be disposed of efficiently.

(2) The maximum fluorine flow-rate capacity increases with a decrease in the charcoal-particle size.

(3) Moisture content as high as 30 percent in charcoal had no appreciable effect on reactor efficiency after the reaction zone was established and the moisture was driven off by the heat of reaction.

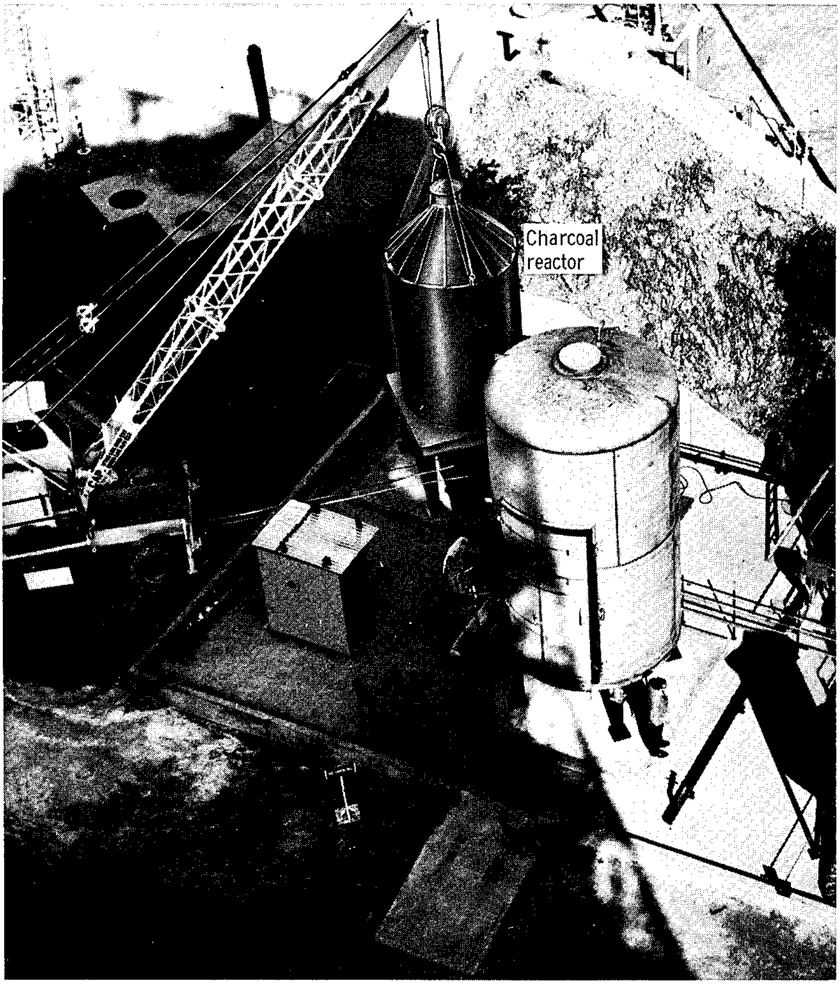


FIGURE 4–17.—Charcoal reactor installation at General Dynamics/Convair test facility, San Diego, California.

(4) No evidence of charcoal-bed poisoning was indicated during this investigation.

These design criteria have been applied in constructing a 500-cubic-foot reactor (fig. 4–17) at a Sycamore Canyon (San Diego) location and two reactors at Plum Brook; all have been in successful operation.

4.8.1.2 *Stack burner design.*—Where local conditions permit and where large quantities of fluorine are not involved, an exhaust stack burner may be used for fluorine disposal instead of a charcoal reactor. This

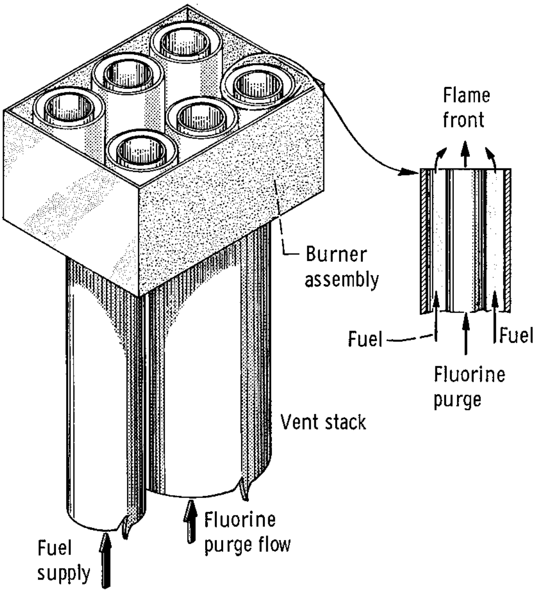


FIGURE 4–18.—Typical vent stack burner.

method (fig. 4–18) involves the use of a methane, propane, or natural gas burner mounted in a vent stack to produce lighter-than-air hydrogen fluoride, which (while still toxic) will disperse readily in the atmosphere.

A series of tests was conducted at the Lewis Plum Brook facility to determine an optimum fluorine-methane burner. Of the types tested, only one burner proved feasible. It consists of two concentric tubes; the inner tube carries fluorine, and the outer tube carries fuel. When the stack burner is not in use as a reactor, the fuel is burned with atmospheric oxygen. The tips of the fuel and fluorine tubes are flush (fig. 4–18), and the relative sizes are such that more than stoichiometric quantities of fuel are always available to react with the fluorine. Fluorine flow rates must be kept high enough to keep the flame front away from the tip of the tube. The Plum Brook tests indicated that this could be done by keeping the fluorine vent gas pressure above 20 to 25 pounds per square inch gage. The use of this type of disposal facility is primarily rate-limited by the permissible rate-of-release for hydrogen fluoride in a given locale.

4.8.2 Laboratory Disposal Methods

Although test-tube quantities of fluorine may be vented directly into hoods connected to vent stacks, the preferred method is to use the charcoal reactor system that reacts the fluorine to nontoxic carbon tetrafluoride gas, which can be safely vented through the vent stack. The construction of the size of the reactor may be scaled to the particular application and can be test-tube size if desired.

A second method for routine disposal of laboratory-size quantities of fluorine is to bubble the fluorine, diluted with a minimum of 200 percent excess air or nitrogen, through a 5- to 10-percent solution of lime. If the reaction proceeds too vigorously, the dilution of the fluorine should be increased. A solution of sodium hydroxide, sodium carbonate, or sodium bicarbonate may be used instead of the lime solution.

Still a third method involves passage of the fluorine over a bed of sodium chloride or calcium chloride, with subsequent reaction of the liberated chlorine by a soda-lime slurry.

The obvious advantage of the charcoal reactor can be seen by a comparison of these methods, since the reactor can be stored ready for use and requires no secondary treatment of the effluent, except that it should be vented to a hood or directly outdoors.

The requirement for emergency disposal of tank-size (6 lb) quantities of fluorine should be taken into account when building or setting up a laboratory. Since burnout, a broken or galled fluorine cylinder valve stem, or similar failure in the supply to the laboratory can occur, a charcoal reactor can be manifolded to the cylinder supply. If damage to a cylinder valve is suspected, or if other malfunctions occur that require use of the reactor, the fluorine may be dumped through the reactor, where it will react to form inert carbon tetrafluoride. Construction details for the reactor are included in section 4.8.1.

4.9 SYSTEM FABRICATION AND COMPONENT INSTALLATION

4.9.1 Prefabrication X-ray Inspection

Experience at Lewis has shown that, even in the best quality materials (such as sheet stock for tank fabrication, piping, tubing, and fittings), discontinuities, cracks, or inclusions in the metal may be found by X-ray and visual inspection. These must be cut away or removed to make the material homogeneous and suitable for use in the fluorine or FLOX system before fabrication or installation.

Both components and systems for handling liquid fluorine must be chemically cleaned before assembly or installation. Fabrication, assembly, and installation procedures should be such as to eliminate the possibility of having weld slag, weld beads, dirt, grease, or other foreign material in the completed system. Before the assembled system is passivated, it should be chemically cleaned by using the detailed cleaning procedures given in chapter 6.

4.9.2 General Precautions in Installation of Fittings and Components

The installation of fittings should be conducted in such a manner as to prevent the introduction of contaminants. If the reaction of a contaminant with fluorine or FLOX generates sufficient heat, it can trigger a reaction between fluorine and the metal line or fittings, even though the line has been properly passivated, since passivation may not totally remove pockets of contaminants.

4.9.3 Welding, Soldering, and Brazing Procedures

Pipe ends to be welded should be beveled suitable for full-penetration V-notch butt welding with minimum bead on the inside of the pipe. Sleeve joints should be avoided unless the overlap joint can be brazed or isolated by welding. Welding should be performed by a qualified welder. A shielded arc (Heliarc) that has an inert gas backup should be used to prevent the pipe from being contaminated with slag, etc., that cannot be removed by normal cleaning procedures. The weld should be protected by a purge with argon or helium gas before welding is started. The purge may be reduced during welding to prevent blowout of the weld. Gas-protective devices should be in place throughout the welding process. An appropriate filler rod should be added on the first pass. The remaining passes may be metal-arced to minimize distortion and carbon precipitation in susceptible alloys and to increase welding speed. The weld penetration or depth of fusion must be to the bottom of the V-groove (excess penetration of a bead $1/16$ in. high on the inside of the pipe is acceptable if the bead is smooth and well rounded, refs. 12 and 17).

There must be no cracks, crater defects, pinholes, or slag. After the first pass, the weld should be carefully inspected for defects. Craters, cracks, and rough spots must be ground out before continuing the weld. The arc should not be broken at the centerline of the weld. The welding rate should be accelerated until the weld pool becomes small, then moved off to the side of the groove before being broken. The bead, where it is broken, should have a tapered end. It is recommended that the work be turned to allow downhand welding wherever possible. However, the most important thing is individual technique and skill of the welder.

Welded joints should be stress relieved, if necessary, by heat treating. Welded seams and connections used in fluorine-FLOX installations require X-ray inspection of all welded joints. Welds with poor penetration, flux or slag inclusion, pockets, bubbles or surface flaking cannot be permitted. Welded connections must be cleaned and passivated prior to being placed in fluorine service according to the procedures described in chapter 6.

4.9.3.1 *Soldering and brazing.*—Precautions for these joining methods are the same as those for welding, since the objective is to obtain a clean crevice-free joint without pockets or inclusions. Flux should *never* be used for soldering or brazing in a fluorine system. Silver solder and Nicro-braze (or their equivalents) are the preferred soldering and brazing compounds.

4.9.3.2 *Castings, forgings, and purchased parts.*—All purchased parts, fittings, and hardware, such as castings, forgings, and heat-treated or welded parts coated with heavy scales or oxides produced in manufacture, should be cleaned and/or acid pickled (refer to section 6.2). Castings should be nonporous and free of sand and other foreign materials. Porous castings, particularly bronze, should not be used, since they are difficult to clean, and solutions may be absorbed (making them unreliable for fluorine service).

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Chapter 5. Facility Design Criteria

The future application of fluorine or FLOX (fluorine-oxygen mixtures) in rockets or test facilities should take advantage of past experience with smaller scale handling and test facilities. Design planning problems for fluorine or FLOX application will probably involve the modification of an existing facility to accommodate either a fluorine-oxidized upper-stage vehicle or a FLOX-oxidized booster. The design or modification of oxidizer systems or facilities to handle liquid fluorine or FLOX should follow the current practices for cryogenic oxidizers used in the rocket industry, but there are several considerations peculiar to fluorine and FLOX that require emphasis. Both fluorine and FLOX can be characterized as cryogenic, toxic, and hypergolic. However, most of the problems associated with using fluorine as a propellant are not unique to fluorine or FLOX; other more commonly used propellants or propellant combinations also exhibit these characteristics. Fluorine and FLOX are unique because they combine all these characteristics into a single propellant, and because their primary combustion product (hydrogen fluoride) is toxic and corrosive. To cope with the properties of fluorine and FLOX, facility design effort should be directed toward obtaining a system that will (1) *completely contain the fluorine or FLOX with minimum release to the atmosphere,* (2) *react as much released fluorine as possible to an inert nontoxic state* and (3) *provide for maximum diffusion of toxic products.*

5.1 GENERAL CONSIDERATIONS IN FACILITY DESIGN

Fluorine-peculiar areas of facility design can be summarized as

(1) Achieving a fluorine-compatible system:
Compatibility aspects of design are discussed in chapters 3 and 4, and the importance of compatibility in facility operations is stressed in chapter 6.

(2) Proper ratio control of fluorine to oxygen in FLOX facilities:
Various combinations of storage, transfer, and disposal systems can be selected to meet the requirements for no-loss containment, reaction or diffusion of any fluorine releases, and for providing ratio control of FLOX. Evaluation of these systems for a given facility must equate the relative economy of construction and operation, and utility provided by each combination. Storage systems, for instance, could use a single tank for fluorine or FLOX storage, or two tanks for FLOX systems (contain-

ing liquid oxygen and fluorine) with ratio control of the FLOX achieved either in a third mixing tank or by a ratio-feed-control system. Similarly, transfer can be achieved by pressurizing the storage tank with helium or by self-pressurizing with FLOX (or fluorine). Present equipment available for fluorine or FLOX service does not include a reliable off-the-shelf pump for *sustained* service; however, studies indicate that such a pump could be built (section 4.5).

(3) Control of pollution caused by the toxic and corrosive effluents from these facilities:

To meet the general criteria outlined in the introductory paragraph to this chapter, planning for the fluorine or FLOX facility should emphasize failure control (i.e., making the system fail-safe). *Failure-mode analysis should anticipate all possible failures, and the engineering design must permit effective fluid-handling procedures to minimize inadvertent fluorine releases. Generally, a failure should only be unpredictable from the standpoint of time of occurrence, but not type of failure* (see section 5.2.1). Site selection and evaluation would then include a study of atmospheric diffusion characteristics and downwind concentration predictions (see section 5.2.4) to determine if available weather windows permit specific fluorine or FLOX operations at the site. (Weather windows are weather conditions that will allow a given operation to be performed within the limits and restrictions of local pollution-control requirements and the worst credible release determined by failure-mode analysis.)

5.1.1 Atmospheric Pollution Sources

Unless a system is capable of maintaining a cryogenic fluid at or below its saturation temperature *at the storage pressure,* boiloff gases must be vented. In those cases where vented gases create a hazard, the facility should be designed to eliminate or reduce the hazard to an acceptable level.

Several sources of potential release of toxic fluorine and hydrogen fluoride must be considered in facility design. These sources include (1) vent gases and residuals of fluorine in lines, tanks, etc., following passivation operations (unless they can be recondensed or held without venting), (2) line contents (fluorine or FLOX) in the event of line failure during transfer operations, (3) exhaust products from a launch vehicle during launch, (4) catastrophic failure involving the launch vehicle, and (5) catastrophic failure involving facility-storage-tank contents. Consideration of these five principal sources and the requirements of the 1963 Federal Clean Air Act (ref. 1) illustrate why the general design philosophies in section 5.1 are important in facilities where fluorine and FLOX are used.

The first effluent source, vent gases, can be coped with by using appropriately designed disposal systems. While these systems probably would be charcoal reactors, other methods could also be used. Disposal methods and design are discussed in section 4.8.

The second effluent source, transfer line contents, may involve a somewhat larger release of fluorine or FLOX, since flow rates in excess of 2000 gallons per minute are not uncommon during propellant loading operations. For example, a rupture in the flow line would result in the release of about 167 gallons of fluorine or FLOX in 5 seconds, in addition to the contents of the transfer line (5 sec would be a conservative estimate for the time required for an automatic shutdown system to sense a line failure and to close appropriate automatic shutdown valves). Proper engineering design and selection of operating procedures will provide considerable control in minimizing the quantities of fluorine or FLOX released in the event of a line failure.

In the third source of release, which involves the exhaust products of the launch vehicle, fluorides (mainly hydrogen fluoride) would be released only infrequently and for short periods during actual launch or test operations. Compared with the daily release of thousands of pounds of fluorides per day (in larger operations) from superphosphate plants, cement processing factories, aluminum reduction plants, and open hearth furnaces, it is logical to assume that relative ecological effects would be insignificant (refer to section 5.2.4.2). Launchings would, however, be made during proper weather windows to permit maximum diffusion of all toxic releases.

The fourth type of release, catastrophic release of launch vehicle contents, can occur during launch operations and might involve a lift-off and fall-back, tipover, etc. Pollution control can be obtained by selection of proper weather windows for the anticipated magnitude of the failure. Since the fluorine (or FLOX) and the fuel would mix as the propellant tanks rupture during this type of failure, a large fireball could be expected to form, lifting the reaction products high off the ground to become an elevated source of release. Launch sites and launch weather windows should be selected to provide diffusion characteristics needed for this type of occurrence.

The fifth case, involving release of facility storage tank contents, is considered extremely unlikely. The probability of failure of FLOX (or fluorine) storage tanks is essentially zero and may be considered a noncredible failure mode. However, a measure of protection against failures such as storm or rocket-destruct debris damage to storage tanks, etc., can be provided by applying the facility design practices discussed in section 5.2.

5.1.2 Release Modes

Regardless of the source of effluent release, it will be one of two types: a hot release or a cold release. The hot release would include all spills where sufficient heat of reaction occurred to lift the cloud of reaction products well above the ground. (A rocket engine exhaust during test or ascent can also be considered as a hot spill.) Both liquid fluorine and FLOX are extremely hypergolic with most materials including such substances as charcoal, tars, greases, vegetation, and soil with a high humus content; some limited reactions can even occur when fluorine contacts sand, gravel, and limestone (see section 3.4). Thus, any major spill would probably become a moderately hot (or at least warm) release of effluent containing fluorine, hydrogen fluoride, and other fluorides.

Review of motion pictures of fluorine and FLOX spills and of large rocket conflagrations involving combustion of other propellants reveals that, following the initial reaction, a fireball forms and rises. As it does, a strong scavenging effect occurs along and near the ground at the base of the fireball, which necks down into a stem as the fireball rises. Maximum influx wind velocities (estimated from Atlas failures involving liquid-oxygen–RP-1 propellant reactions) are of the order of 75 feet per second, and the initial velocities at the narrow part of the fireball stem are estimated at 300 feet per second. After the initial rapid gas rise, the smoke color (of the ground fire) turns from the characteristic white of an oxygen-rich fire to the black of atmospheric-fed combustion. Thus, it is indicated that practically all the oxidizer has been consumed or swept upward into the top portion of the column. In a major conflagration involving fluorine or FLOX, the same characteristics could be expected, with the oxidizer spread by the initial reaction being swept into the rising hot gas cloud by the scavenging effect and lifted high into the air. Residual fluorine in the cloud would then react with atmospheric water vapor to form hydrogen fluoride, and the warm hydrogen fluoride would rise and diffuse rapidly. Spill studies (refs. 2 and 3) support these conclusions on hot-spill behavior.

An aspect of hot-spill behavior of concern has been whether reaction clouds will penetrate or pierce temperature inversions. Temperature inversions, which may extend upward for hundreds of feet, are characterized by an increase in temperature with an increase in height. This means that a warm rising cloud would be trapped beneath the inversion unless the cloud energy is sufficient to lift it well into the inversion layer. Inversion penetration is more important when low-lying temperature inversions are present, since the reaction cloud will then diffuse while trapped within the layer, reducing the ground-level pollution downwind.

Tests in reference 3 involved spills of from 200 to 3000 pounds of

30-percent FLOX on JP-4 fuel and on charcoal. The spills were made on a flat pad that provided combustion efficiencies up to 40 percent. The minimum energy required for inversion penetration determined from these tests was approximately 5×10^6 Btu, or about the energy produced by the 3000-pound spills of FLOX at 30-percent efficiency. Figure 5–1 (from ref. 3) interrelates the oxidizer source strength with the approximate reaction cloud volume and temperature difference (from ambient) to be expected at an elevation of 200 feet.

Reaction clouds penetrated low inversions (starting at about 800 to 1300 ft above ground level) and rose to about 1000 to 2000 feet in tests reported in reference 3. The 3000-pound quantities in these tests were considerably less than those available in most launch vehicles and, further, the reaction efficiency would probably be greater in a large conflagration. For instance, the heat releases in 2500- to 3000-pound spills in the FLOX tests (ref. 3) were determined to provide a temperature difference 16 to 23 F° between the reaction cloud and ambient at an elevation of 200 feet. As shown in figure 5–1, extrapolation of the test data to a Saturn S-IV size fire (with about 90 000 lb of hydrogen and

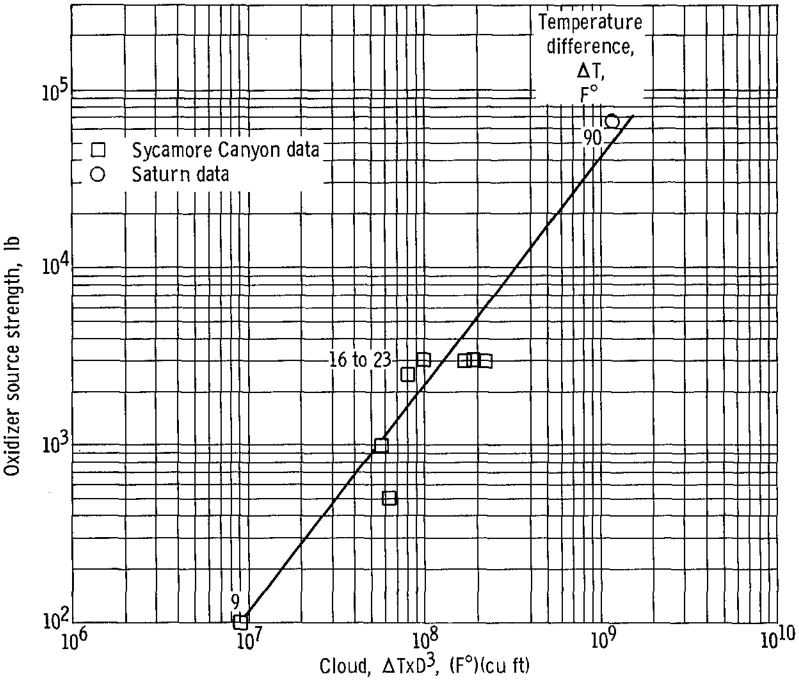


FIGURE 5–1.—Effect of source strength on cloud parameters at elevation of 200 feet (ref. 3).

oxygen) indicated a cloud ΔT of 90 F°. Obviously a reaction cloud from this larger energy source would permit penetration of even stronger inversions. For the Saturn S-IV case, the reaction cloud would still possess a ΔT of 10 F° at 1800 feet. Even without an inversion, the cloud would be an elevated release source, and downwind pollution at ground level should not be a serious problem (refer to section 5.2.4.1). An inflight abort (fire or hot release at altitude) would result in lower concentrations of ground-level pollution, because of the elevation of the release source, than a fire of comparable magnitude on the launch pad.

A cold release produces gas products that tend to hug the ground and would be the most hazardous case to consider in evaluating facility location, design, and operations. Unlike nitrogen tetroxide and red fuming nitric acid (also toxic propellants), both fluorine and FLOX are cryogenics, and the temperature difference between them and the surroundings on which they would spill is probably in excess of 300 F°. Thus they will "flash" and boil off at high initial rates from nonreacting materials on which they might spill. This is particularly probable when an appreciable wind exists and the spill is both shallow and dispersed. Cold spills may occur (ref. 2) when fluorine or FLOX falls on concrete, structural steel, or in the case of FLOX of low concentration, sand and various other inorganic materials. Because of the hypergolic nature of both fluorine and FLOX with most other materials, cold spills are considered unlikely where large spill amounts are involved.

Cold spills are complicated by the fact that boiloff rates from the spill depend on the type of accident, thermal capacities, and heat conductivities of materials on which the spill impinges, wind velocity, amount of reaction, and, to a minor extent, variations in ambient temperature. Also the contour as well as other characteristics of the surface on which the fluorine or FLOX falls is important in determining whether or not puddling occurs. The boiloff rate is highest initially when the surface on which the spill occurs has not yet chilled to cryogenic temperatures. Initial flash-vaporization will vary, depending on whether the cryogenic falls on ordinary terrain, into a pit, or if it is channeled into a runoff ditch. While puddling will reduce boiloff rates, the boiloff process continues over a longer period so that the integrated pollution over a given area is about the same regardless of the degree of fluorine or FLOX puddling. However, containment could be important in reducing the peak dosage at a given location. As the wind velocity approaches zero, however, the slight advantage of containment and controlled boiloff is reduced (refer to section 5.2.3.3).

In the studies described in reference 3, the cold-spill FLOX clouds absorbed heat from the sunwarmed hillsides as they were blown up the slope. This energy addition was sufficient to lift them above the top of the hill, so that the spills become, in effect, "warm" releases, with diffusion of pollutants toward ground level beginning from a slightly elevated source. In addition, hydrolysis with atmospheric moisture occurred, converting the fluorine in the FLOX to hydrogen fluoride and thus reducing cloud toxicity.

5.2 FACILITY DESIGN

5.2.1 Failure-Mode Analysis

A study should be made of all vehicle ground-support equipment and facility operating modes to identify and establish all credible failures that could occur and present a hazard to surrounding populace, personnel, or equipment. Operating sequences should be analyzed from start to end of each operation to define effects on the system from sequence initiation (e.g., filling liquid-nitrogen shields, opening valves, etc.). The results of this study can be used to improve facility operating procedures, to assure a contaminant-free system at all times, and to minimize the possibility of failures during all operating sequences. Failure-mode analysis should take into account fluorine exposure factors such as compatibility of materials, temperature, pressure, flow velocity, phase of fluorine or FLOX (gaseous or liquid), and the concentration of fluorine involved. This type of analysis permits separate consideration of the fluorine-peculiar effects of system conditions on each subsystem, component, or connection.

Identification of potentially hazardous conditions should not be confined to the mode of failure (e.g., burnout) but should identify the results of the potential failure and provide a preplanned course of action if the failure should occur. In addition, the study should define weather-window limitations within which the worst-case failure in the operating mode could occur without undue hazard to the facility or the surrounding area. By this means, the limiting conditions are defined under which given operations (e.g., maintenance, propellant loading, launch, or test firing) would be permissible at the fluorine or FLOX facility.

5.2.2 Boiloff Recovery or Disposal Systems

During launch or test operations, large quantities of fluorine or FLOX are removed from the passive, confined environment of facility storage through the flow transfer of the oxidizer into the launch or test vehicle where design considerations do not permit no-loss storage. Since both fluorine and FLOX are cryogenic, the high rate of heat leak into the launch or test vehicle will cause an appreciable amount of boiloff and attendant problems in handling the toxic vapors. A theoretical evaluation of the Atlas launch vehicle with 30-percent FLOX, for instance, indicated that a boiloff rate of the order of 145 to 605 pounds per minute

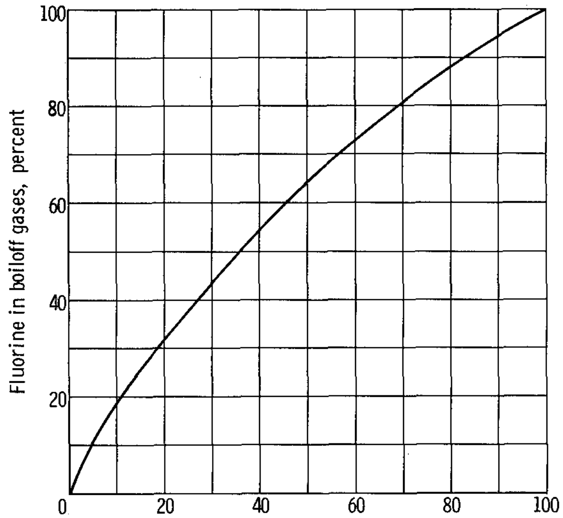


FIGURE 5–2.—Fluorine concentration in boiloff gases from FLOX mixtures.

could be expected(the boiloff rate from a fluorine-oxidized upper stage would be less, probably 15 to 20 lb/min). In FLOX systems, boiloff presents an additional problem because the boiloff vapors are fluorine rich (see fig. 5–2) with a resulting decay of the desired FLOX mixture ratio. However, the rate of release of fluorine would be less for a given vehicle that uses FLOX rather than fluorine. For instance, in the Atlas case cited, the fluorine content of the FLOX boiloff would be 60 to 254 pounds per minute. (Feasibility studies on the use of FLOX in present-generation boosters used the Atlas as a "typical" example, and excerpts from these studies are used in this discussion.)

There are three basic approaches that can be applied in handling the problem of boiloff from fluorine or FLOX systems. The first and probably most feasible method would be to reliquefy the boiloff and either recycle it to the launch or test vehicle or return it to facility storage. The second method would involve suppressing the boiloff inside the launch or test vehicle by keeping the storage temperature below the oxidizer boiling point. The third method would involve free venting of the boiloff gases, with the effluent either vented directly to atmosphere or through a charcoal disposal system.

Recovery or disposal system design should also provide for recovery of the liquid contents of the launch or test vehicle if it is necessary to detank part or all of the oxidizer contents. In normal situations, recovery is achieved by reverse flow through the transfer system to facility storage. Provision should be made, however, for the operating conditions that do not permit this type of transfer (e.g., burnout of the transfer-system piping).

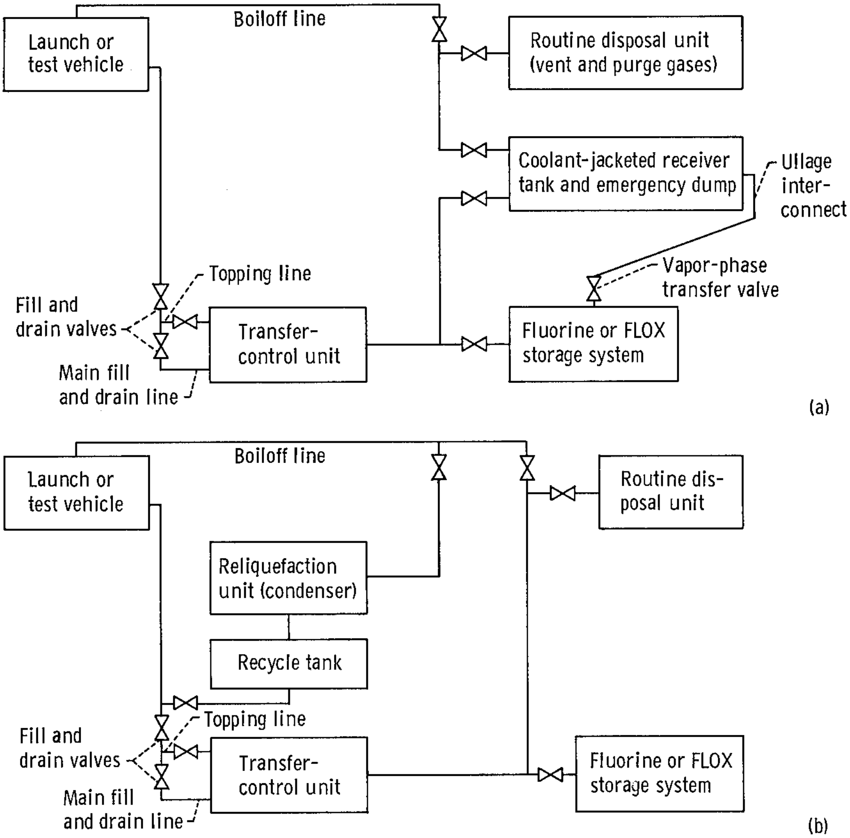
During the transfer of cryogenic propellant to the vehicle, there will be high initial boiloff rates of fluorine or FLOX until system piping and the launch or test vehicle tanks reach equilibrium temperature. Also, the need to maintain a pressure differential between the facility storage and launch or test vehicle tanks (constant ullage pressure) will require venting of pressurant gases through the disposal system or to a recovery system. The selection of size for the routine disposal system should then include (as a minimum) sufficient capacity to react this amount of fluorine release. Additionally, if detanking of the launch or test vehicle is required, venting of the facility storage tank may be required. Any residuals in the launch or test vehicle and transfer lines must be vented and purged through the routine disposal system. Capacity must be provided for these conditions.

5.2.2.1 *Application of boiloff reliquefaction and recycling systems.*— Boiloff reliquefaction systems can be considered in two basic configurations that can be used separately or in combination. Reliquefaction methods prevent a shift of the fluorine-oxygen ratio, due to preferential boiloff of the fluorine (fig. 5–2) in FLOX mixtures in the launch or test vehicles. The two basic configurations are receiver tanks and boiloff recondensers and recycle systems.

Receiver tanks (fig. 5–3(a)) involve the use of an extra (or redundant) liquid-nitrogen-jacketed storage tank to reliquefy and store boiloff gases from the launch or test vehicle; this stored fluid is then periodically recycled. The dual tank system permits maximum total system flexibility and redundancy because it provides the capability for recovering facility storage tank contents (in case of emergency requirements) or launch vehicle contents, if required by an abort or extended hold during operations. Use of this system would eliminate the need for large emergency disposal dump systems because the redundant storage could be used for this purpose. This system is also attractive because it requires no special design of the launch vehicle other than the boiloff disconnect. In summary, the advantages of this system include a high safety factor, reduction of the possibility of oxidizer waste, no limiting of oxidizer tanking rates, provision of redundant storage to ease maintenance problems, and provision for an efficient and effective fluorine and FLOX handling system. The principal disadvantages of this system are requirements for long return lines (boiloff return) and requirements for large volumes of pressurant to recycle the liquefied boiloff. This last disadvantage would not be present, of course, with development of a reliable fluorine or FLOX pump for sustained service, or if self-pressurization techniques are used.

Boiloff recondensers and recycle systems (fig. 5–3(b)) would utilize a ground heat exchanger to recondense boiloff gases, coupled with a relatively small storage (slug) tank to collect the condensate, which would be periodically recycled to the launch vehicle. While this method affords many of the advantages included in use of a receiver tank, the size of the recycle tank would not provide for storage of the entire launch vehicle contents, and the large emergency dump disposal system may become a facility requirement. However, this method permits sustained holds during launch or test operations without loss of oxidizer or degeneration of FLOX ratios.

In practice, a combination of the condenser-slug tank, located close to the launch pad and a more remotely located condenser-receiver tank



(a) Receiver tank method.

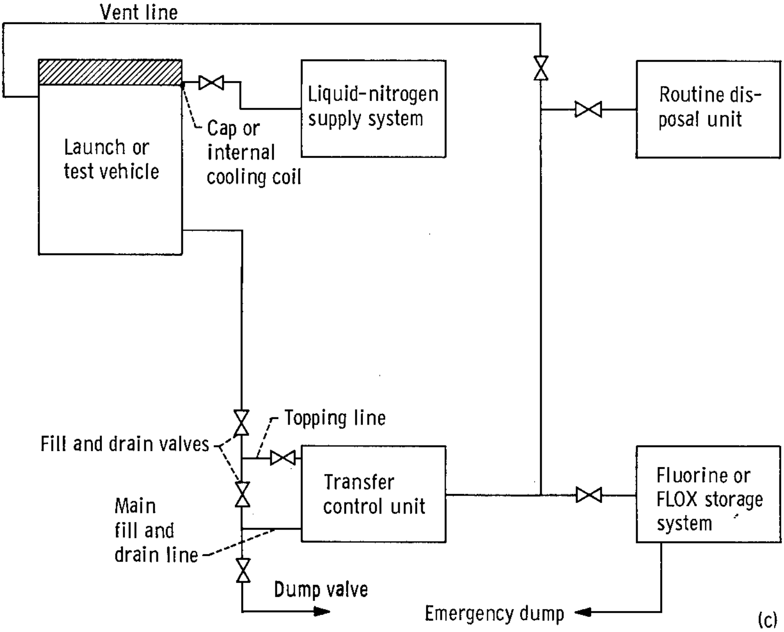
(b) Recycle tank method.

FIGURE 5–3.—Oxidizer transfer and boiloff recovery.

may be required or desired. Use of the receiver tank would overcome the disadvantage of limited storage capacity for emergencies or sustained holds; the use of the condenser-slug tank would limit requirements for pressurant gases for recycle transfer by appropriate use of the recycle condenser.

A third method for reliquefying boiloff is the use of a condenser mounted above the oxidizer liquid level in the launch or test vehicle. Boiloff gases could be liquefied and returned by gravity into the oxidizer tank. This method offers a major advantage because it would eliminate the need for periodic recycling of fluorine-rich FLOX into the vehicle. The disadvantage lies in the fact that it would require a bulky structure on the umbilical tower (e.g., a condenser of the order of 7 by 6 by 15 ft, containing about 3500 gal of liquid nitrogen and consuming about 600 gal/min, was estimated in the Lewis feasibility studies as a requirement to reliquefy 605 gal/min of 30-percent FLOX).

5.2.2.2 *Boiloff suppression techniques.*—The vapor pressure of fluorine or FLOX in the launch or test vehicle is maintained at subatmospheric values by subcooling (fig. 5–3(c)). The most feasible means for achieving this, according to the Lewis feasibility study, appeared to be either a liquid-nitrogen-filled cap on the launch vehicle or upper stage, or a



(c) Boiloff suppression method.

FIGURE 5–3.—Concluded.

coolant coil inside the oxidizer tank. Both these methods impose weight penalties on the flight vehicle, but both would be effective in controlling ratio shifts in FLOX mixtures. The use of either would minimize requirements for modification of ground-support equipment, since the oxidizer would be kept in a subcooled state and boiloff disposal would thus not be a problem. Venting of the tank ullage (through a disposal system) would still be required during the fill cycle, however.

Of these two methods, the use of a coolant-filled cap or jacket is probably the best because it can provide the required heat-transfer surface between fluorine or FLOX and the liquid nitrogen with less weight penalty, in most cases, than with the use of internal cooling coils.

5.2.2.3 *Venting boiloff gases.*—The system involving direct venting of boiloff gases from the launch vehicle represents the most simple configuration from the standpoint of required vehicle or ground-support-equipment modifications. However, this system would only be feasible where site evaluation and weather-window criteria permit (refer to section 5.2.4). When this is not the case, boiloff gases should be treated to render them chemically inert, preferably by using a charcoal reactor sized to react the total contents of the vehicle. This technique would require minimal addition to vehicle weight, probably only a disconnect for routing boiloff gases into the disposal system or into a duct to carry them away from the launch vehicle. The major disadvantage in using this type of system is cost, both in unrecovered fluorine that is reacted and vented to the atmosphere, and in the charcoal reactor system used to effect the reaction. This method, in the case of FLOX-oxidized vehicles, also introduces the problem of maintaining the desired fluorine-oxygen ratio in the FLOX, due to the preferential boiloff of fluorine from the mixture (see fig. 5-2).

5.2.3 Disposal Considerations

The toxic nature of fluorine and FLOX makes a properly designed disposal (or recovery) system a major facility design consideration. A fluorine or FLOX facility ideally should include a disposal system that can render the total fluorine or FLOX contents safe under all conditions where dumping, transferring, or overpressure venting is required.

Basically, there are two approaches to the disposal problem: reacting as much of the fluorine as possible to a nontoxic state and allowing diffusion into the atmosphere, or designing the facility to permit recovery of most of the fluorine and FLOX in the ground-support equipment and the launch vehicle. Either of these approaches is consistent with the basic facility design philosophies outlined at the beginning of this chapter.

In facility design, three major categories of fluorine or FLOX disposal should be considered:

(1) Routine disposal of small quantities of fluorine or FLOX
(2) Emergency disposal of large quantities of fluorine or FLOX in situations that permit controlled transfer to recovery or disposal areas
(3) Emergency release of quantities of fluorine or FLOX in situations in which no control can be exercised over the rate of release or the time of release

5.2.3.1 *Charcoal reactor applications in facility disposal.*—The main function of a routine disposal system would be disposal of transfer-line contents during test operations, and disposal of residual expendable quantities of fluorine or FLOX, or vent gases, following test operations. For all these conditions, transfer-line and storage facilities should be constructed so that they can be purged through the routine fluorine disposal system. The routine disposal system may also require additional capacity to handle part or all the oxidizer contents of the launch or test vehicle, the extra capacity required depending on the method selected for handling boiloff. (Boiloff handling problems are discussed in section 5.2.2.) When these larger quantities must be processed, use of the charcoal reactor is probably the most feasible disposal method. Specifically, this method provides for disposal by reacting the fluorine to an inert and nontoxic product, mainly carbon tetrafluoride (refer to section 3.1.2.2). The reactors (described in section 4.8.1.1) can be scaled up to meet facility needs; one such existing reactor has a capacity of 500 cubic feet. Because large reactors can be expensive to build and maintain, several small reactors manifolded through valves to the disposal line would be preferable to a single large reactor. The size of the disposal system will depend, of course, on the effectiveness of the facility design and operations in holding production of fluorine waste products to minimum quantities and release rates.

5.2.3.2 *Emergency controlled disposal of large quantities of fluorine or FLOX.*—Disposal requirements include providing for emergency disposal of large quantities of fluorine or FLOX during facility operations. This could, for instance, include the contents of a launch vehicle during a protracted hold (from boiloff) or in a situation where the contents cannot be returned to facility storage. While large charcoal reactors can be designed that could cope with this disposal problem, this involves cost factors in construction and maintenance, as well as the additional cost of the fluorine lost by using this method of disposal. For sustained operations at a large facility, these cost factors might be large enough so that recovery systems (sec. 5.2.2.1) would be preferable for all except routine disposal (of purge gases, line residuals, etc.).

The use of an open dump area containing charcoal fuel is also feasible for this purpose. Tests discussed in reference 3, which involved spills of up to 3000 pounds of 30-percent FLOX on charcoal on a flat surface, produced reaction efficiencies of the order of 40 percent and also indicated that atmospheric hydrolysis will occur to react the remaining fluorine to lighter-than-air hydrogen fluoride. Had this spill been made into a pit of charcoal, or had the fluorine or FLOX release been made through a flow line into a confined area, better contact would have been achieved between the fluorine and charcoal. Considerably higher reaction efficiency would be expected in these cases. The reaction efficiency in an enclosed charcoal reactor approaches 100 percent. The heat of reaction in this type of open disposal system will lift the cloud of reaction products well off the ground (in ref. 3 tests, an inversion was penetrated), and the carbon tetrafluoride formed from the carbon-fluorine reaction will act as a diluent to reduce the toxicity of the cloud. Results obtainable from this type of reaction are discussed in section 5.2.4.1.

5.2.3.3 *Emergency spills or releases at uncontrollable rates.*—A survey of problems involved in spills (ref. 2) led to some conclusions that may be useful when uncontrollable rates of release during facility operations are considered:

(1) Cold releases (the most undesirable type of fluorine or FLOX release) can be prevented by providing a reactant, such as charcoal, in the area of a possible spill. The value in using charcoal cannot be overemphasized because most of the fluorine that reacts will be converted to carbon tetrafluoride, which is chemically inert and nontoxic. The pollutant is reduced by the amount of fluorine reacted, the heat of reaction enhances the removal and diffusion of reaction products, and the carbon tetrafluoride acts as a diluent to reduce the pollutant concentration.

(2) Containment of the fluorine or FLOX spill in pits or behind dikes, but particularly in a basin with minimum "wetted-surface to volume" ratio, can be effective in decreasing high boiloff rates (ref. 3). The tests with liquid fluorine and liquid oxygen demonstrating this feasibility indicated that boiloff rates drop off sharply after the initial chilldown of the bottom of the spill basin. By contrast, almost instantaneous evaporation was observed when no containment was used (ref. 3). Problem areas for consideration with this method include channeling the fluorine or FLOX into a spill basin and the high flashing rates that occur during channel and pit cooldown (see section 5.1.2 for a discussion of cold spills). Data from reference 3 indicate that, in a cold release of fluorine, hydrolysis occurs with the atmospheric moisture to produce hydrogen fluoride, which is less toxic than fluorine (see section 5.2.4.1 and table 9-I, p. 246). Water sprays could also be used in combination to

improve the pollution control provided by the containment method (see discussion in items 3(a) and 3(b)).

(3) Tests (refs. 3 and 4) indicate that water sprays could be used to capture fluorine and reduce total downwind pollution from both fluorine and FLOX cold spills. However, the use of water requires consideration of several problem areas:

(a) When water sprays are used on puddled cryogenic FLOX, the high heat content of the water causes flash vaporization of the FLOX and results in a higher peak pollution concentration downwind. However, the *30-percent-FLOX–water* reaction is noncombustive and if *sufficient* water can be supplied, downwind contamination can be greatly reduced (ref. 3) by the reaction of fluorine to hydrogen fluoride and the subsequent capture of the hydrogen fluoride by the excess water.

(b) The *water-fluorine* reaction, by contrast, is hypergolic and when liquid fluorine is involved, becomes explosive (see section 3.1.2.1). When fog spray water is used, however, the liquid-fluorine–water reaction becomes combustive and behaves like the hot spill described in section 5.1.2. The main problem in using water sprays as a fluorine capture agent with liquid-fluorine spills is getting sufficient water to the reaction zone quickly enough to capture the fluorine before it is lifted into the reaction cloud.

(c) When water is used as a capture agent for fluorine or FLOX, the water then contains hydrofluoric acid. However, the water can be collected in a catch basin and then neutralized with caustic or lime before it is released.

The use of water sprays to capture pure fluorine was investigated in tests conducted inside a building (ref. 4). Soda ash was also tested as an inerting agent. The amount of fluorine captured by deluge agents in the confined tests varied between 30 and 43 percent for gaseous-fluorine–water, 34 to 43 percent for liquid-fluorine–water, and 33 percent for liquid-fluorine–soda-ash (ref. 4). In the confined gaseous-fluorine–water tests, the amount of fluorine captured increased with the time of flow for deluge water (the only variable). This was expected, since the structure limited the loss of fluorine to the atmosphere and permitted extended contact time with the water spray. For the liquid-fluorine–water tests, conventional spray nozzles were used in one test and fog-spray nozzles, flowing half as much water, were used in the other test. (The water deluge lagged the fluorine release by 20 sec compared with the normal 2-sec lag.) The fog spray captured a greater percent of released fluorine despite the lower flow rate, which indicates that the smaller water-particle size-increased the reaction efficiency (ref. 4).

5.2.4 Site Evaluation

In determining whether a particular site is suitable for operations with fluorine or FLOX, studies must be performed to provide assurance that fluorine, FLOX, or hydrogen fluoride spills or releases would not create unacceptable levels of pollution for the surrounding populace and countryside (refer to section 9.2.2). Site evaluation should take into account the meteorological variables (i.e., wind velocities and direction, temperature lapse rates, etc.) affecting the diffusion of the gaseous products. Standard equations relating these variables are given in section 5.2.4.1 together with sample calculations.

Conditions that limit fluorine or FLOX operations are dependent on terrain, direction and distance to populated areas, type of fluorine operation or accidental release, and the existing meteorological variables. A complete and thorough failure-mode analysis should be made to determine all possible and credible failures including (1) rate and quantity of release, (2) whether a hot or cold spill will result or is planned, (3) boiloff rates for cold spills, (4) probable amount and rate of heat release for hot spills, and (5) method of ensuring combustion and convective removal of toxic gases. In further defining the problem of determining safe weather conditions for fluorine or FLOX operations, it is necessary to specify maximum allowable concentrations at specified distances from the site of operations, boundaries beyond which these concentrations may not be exceeded (refer to section 9.2.2).

In evaluating a site for possible fluorine or FLOX facilities, the worst case for each type of release mode (cold or hot, refer to section 5.1.2) is considered. Precautions must always be taken to ensure that no unacceptable hazard exists for possible worst case failures.

In the event of a spill, it is probable that sufficient reaction will occur to produce a fire and resultant rising hot gas cloud (hot spill). In a hot spill of fluorine or FLOX, the resulting heat release would cause the combustion gases to rise and ensure dissipation at an atmosphere where ground-level hazard would be minimized.

5.2.4.1 *Diffusion prediction.*—To investigate pollution effects from uncontrolled releases of fluorine, two release modes must be considered: hot spill and cold spill. The characteristics of hot and cold fluorine or FLOX releases are discussed in sections 5.1.1 and 5.1.2.

COLD SPILLS: The diffusion and transport equation (ref. 5) may be used to approximate the expected concentration of gaseous pollutant downwind along the axis of contamination. The equation is valid for relatively flat terrain and was developed empirically by fitting data from more than 200 different diffusion tests. Both sulfur dioxide and zinc sulfide (particulate) were used in the tests by applying the same formula. The most significant meteorological parameters and their effects are included in the Weather Information Network Display (WIND) system equation (ref. 5):

$$\frac{P_c}{S_t}0.00211\,(x^{-1.96})\,(\sigma\theta)^{-0.506}(\Delta T+10)^{4.33} \tag{1}$$

where

P_c	concentration of pollutant at distance x, lb/ cu m
S_t	source strength of effluent, lb/sec
P_cS_t	normalized peak concentration, sec/cu m
$\sigma\theta$	standard deviation of wind at 12-ft level in degrees of azimuth (15-sec smoothing interval, one wind data sampling per second)
x	distance downwind, m
ΔT	temperature at 54 ft minus temperature at 6 ft above ground (measure of air stability at low levels); $\Delta T+10$ applied to avoid necessity of raising negative numbers to a power

It can be seen from equation (1) that conditions for fluorine or FLOX operations are most favorable when winds are strong and variable in direction and the lower atmosphere is unstable, that is, when ΔT has a large negative value. As an example of the use of the WIND equation, if $S_t=10\,000$ pounds of 30-percent FLOX that flashes from a spill in 5 minutes, $\Delta T=-0.126°$ F, $\sigma\theta=10°$, and $x=3000$ meters ($\cong 1.864$ miles), the pollutant concentration is

$$P_c=\left[\frac{(0.3\times 10\,000)}{300}\right][0.00211(3000)^{-1.96}]\;[10^{-0.506}]\;[(9.874)^{4.33}]$$
$$=2.05\times 10^{-5}\text{ lb/cu m}$$

But the air density is 0.0765 pound per cubic foot or 2.705 pound per cubic meter at standard temperature and pressure, so that

$$P_c=\frac{20.5\times 10^{-6}\text{ lb/cu m}}{2.705\text{ lb/cu m}}\times 10^{-6}=7.6\text{ ppm (by weight)}$$

Concentration downwind is approximately inversely proportional to the square of the distance (note the exponent -1.96 in the equation) from the release point. The lateral extent of the cloud is not predicted. The pollutant concentration P_c is nearly inversely proportional to the square root of $\sigma\theta$. (Note the exponent -0.506 in the equation; $\sigma\theta$ is measured every second and is smoothed over 15-sec intervals.) The preceding analysis is valid only for a cold spill of fluorine or FLOX, as the WIND system is based on horizontal gas travel only.

In cold-spill studies (ref. 3) effects from wind and slope heating appeared to enhance diffusion rates by a factor of 10 over predicted rates. The effects from wind and strong sunlight in a facility situated in rolling or hilly terrain would probably produce similar effects. There-

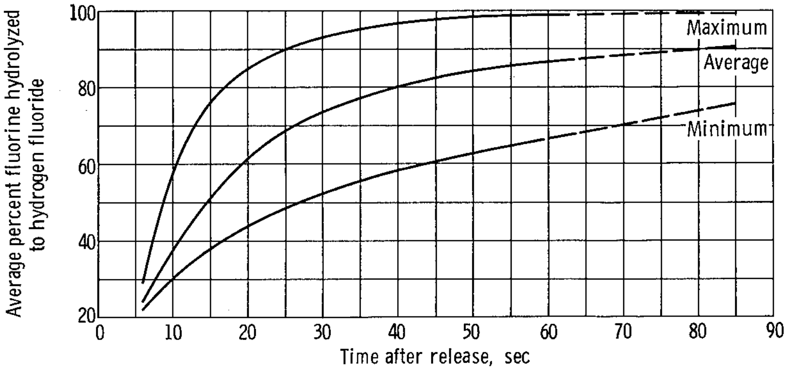


FIGURE 5-4.—Reaction of fluorine with atmospheric moisture to form hydrogen fluoride (data from ref. 3).

fore, the conservative value normally obtained from this equation may be in part a result of the energy input from solar heating and similar factors of weather.

In almost any facility location, there will be sufficient moisture present as water vapor to react with a cold release of elemental fluorine and produce a reaction cloud of hydrogen fluoride. Tests described in reference 3, for instance, were conducted at an inland facility located north of San Diego, in a climate which can be classified as arid and semi-desert. The water present for fluorine reaction on the driest day was about 20 grams of moisture per pound of dry air. With a test cloud of 27×10^6 cubic feet after 14 seconds, about 5000 pounds of water (far in excess of stoichiometric) were thus available for reaction with the 1000 pounds (maximum) of fluorine in the reaction cloud (ref. 3). This atmospheric hydrolysis is a particularly important consideration in defining the possible effects from a cold spill or release of fluorine or FLOX, since the reaction product, hydrogen fluoride, is both lighter than air and less toxic than elemental fluorine. In effect this would raise the permissible parts-per-million pollution level, enlarge the exclusion area boundary, or make possible a smaller exclusion area around the operations area. The expected rate of hydrolysis of fluorine release is shown in figure 5–4, based on data from reference 3.

HOT SPILLS: Sutton (ref. 6) developed a series of equations that can be applied to hot spills or releases of fluorine or FLOX. Equation (2a) relates the height of hot-gas-cloud rise to the reaction energy release and the temperature lapse rate in the atmosphere for a heating period of approximately 15 seconds:

$$H=\left[\frac{2(3m+2p)Q}{9C_p\rho\pi^{3/2}C^3a}\right]^{\frac{1}{p+(3m/2)}} \qquad (2a)$$

where

H	maximum height of cloud rise
m	$2-n$
n	air stability parameter (see table 5-I)
p	1
Q	heat release, g-cal
C_p	specific heat at constant pressure of cloud gases
ρ	air density (1225 g/cu m at standard temperature, 59° F, and pressure 14.7 psia)
C	generalized coefficient of diffusion, function of elevation above ground and air stability (table 5-I)

TABLE 5-I.—VALUES OF STABILITY FACTOR AND SUTTON'S GENERALIZED DIFFUSION COEFFICIENT FOR VARIOUS TEMPERATURE LAPSE RATES

Air stability factor, n	Lapse rate, C°/100 m	Generalized diffusion coefficient, C
0.15	—0.9	0.60
.17	—0.8	.59
.20	—0.5	585
.23	0.0	.57
.26	0.5	.55
.30	1.0	.525
.35	1.5	.48
.40	2.0	.42
.50	3.0	.30
.60	4.0	.18

For the graphical solution of a, a pseudo-adiabatic diagram is used:

$$a=\frac{\theta-\theta_0}{\rho z} \qquad (\mathrm{C}^\circ/\mathrm{m})$$

where

θ	potential temperature at height z of air reduced adiabatically to pressure of height $z=0$
θ_0	potential temperature at height where $z=0$
z	arbitrary height

For the mathematical determination of a, the following equation is used:

$$a=\frac{T_0}{T}\left(\frac{dt}{dz}+k\right)$$

where

T_0	absolute ambient temperature at ground level or reference height
T	absolute ambient temperature at arbitrary height z
dt/dz	measured lapse rate, C°/m
k	dry adiabatic lapse rate, 0.0099 C°/m

Equation (2b) can be used to determine the maximum ground-level pollution χ_{max} as a function of cloud height and atmospheric stability (instantaneous point source) to be expected from the hot release if ground reflection[1] of the pollutant is assumed:

$$\chi_{max}=\frac{2S}{\left(\frac{2}{3}e\pi\right)^{3/2}H^3} \tag{2b}$$

where

χ_{max}	pollutant concentration at ground level $\left(\text{conversion to ppm by weight of dry air is obtained by multiplying } \chi \text{ by } \frac{\text{g/cu m pollutant}}{\text{1225 g/cu m dry air}}\times 10^6=816\right)$
S	source strength, *grams*
H	height of point source, m

Equation (2c) can be used to determine the distance downwind at which maximum pollution concentration will be experienced:

$$d\chi_{max}=\left(\frac{2H^2}{3C^{*2}}\right)^{1/(2-n)} \tag{2c}$$

where

$d\chi_{max}$	distance from instantaneous point source to point of maximum ground-level pollution, m
n	air stability parameter (see table 5-I)
H	height of point source, m
C^*	vertical diffusion coefficient (see fig. 5–5)

A limitation in the use of the equations results from the uncertainties involved in predicting combustion efficiencies and attendant heat release. However, since the height of cloud rise is proportional to some value between the quartic and the cubic roots of the heat release Q, the situation is not as serious as it might seem on first consideration.

Two examples are given here for illustration of the use of hot-spill equations (see eqs. (2)). In Example I, a spill of 10 000 pounds of

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[1] If no reflection is assumed (pollutant reacting with ground surface), the factor $2S$ is replaced by S.

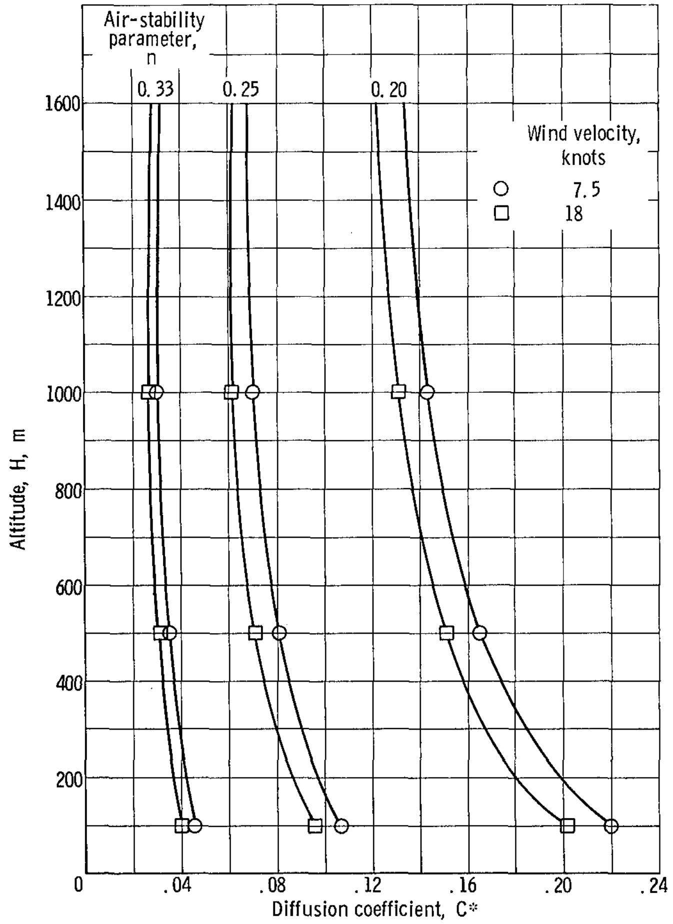

FIGURE 5-5.—Vertical diffusion coefficient for hot-spill diffusion-analysis equation from equation (26) (ref. 6).

30-percent FLOX (the same quantity used in the cold-spill discussion) on RP-1 fuel is considered, and in Example II, a similar spill on charcoal is discussed. In *each* case a combustion efficiency of 50 percent was assumed, and the following representative values were selected for variables in the equations:

Air stability parameter, n	0.20
Vertical diffusion coefficient, C^*	0.585
Lapse rate, k, °C/100 m	−0.5
Constant, p	1
Air density at standard temperature and pressure, ρ, g/ cu m	1255
Wind speed, knots	7.5

In an actual evaluation, the meteorological constants would be determined from weather data for the site being evaluated.

In Example I (nominal oxidant-fuel ratio, 2.4), which might result from a vehicle fallback and rupture on the launch pad, the heat release Q would be about 1.159×10^{10} calories (approximately) and the specific heat at constant pressure would be 0.25, where Q is the sensible heat remaining after the reaction has gone to completion, all the cryogenic fluid has been vaporized, and the reaction products (total) have been raised to 15° C. To determine the height of reaction-cloud rise, substitution is first made into equation (2a):

$$H = \left\{ \frac{2[3(1.8)+2]1.16 \times 10^{10}}{(9)(0.25)(1225)(3.14)^{1.5}(0.585)^{3}a} \right\}^{1+\frac{1/(3)(1.8)}{2}} \tag{3a}$$

By iteration, solve for a with an assumed H of 600 meters:[2]

$$\left.\begin{aligned} a &= \frac{T_0}{T}\left(\frac{dt}{dz}+k\right) \\ &= \frac{288.16\ ^\circ\mathrm{K}}{285.16\ ^\circ\mathrm{K}}(-0.005+0.0099) \\ &= 1.012(0.0049) = 0.00495\ ^\circ\mathrm{C/m} \end{aligned}\right\} \tag{3b}$$

Applying this value for a in equation (3a) gives

$$H \cong 518 \text{ meters } (\cong 1700 \text{ ft})^{2} \tag{3c}$$

This height of cloud rise can now be applied in equation (2b) to determine the maximum pollution level χ_{max} expected from the hot spill. The source strength S (which is 1.388×10^6 g) used for the RP-1 propellant example includes the unreacted fluorine and the hydrogen fluoride portion of the reaction products, since these are the only toxic pollutants:

$$\left.\begin{aligned} \chi_{max} &= \frac{2S}{\left(\frac{2}{3}e\pi\right)^{3/2} H^3} \\ &= \frac{2(1.388 \times 10^6)}{\left[\frac{2}{3}(2.718)(3.1416)\right]^{3/2}(518)^3} \\ &= 1.474 \times 10^{-3} \text{ g/cu m} \\ &= \frac{1.474 \times 10^{-3}}{1.225 \times 10^{3}} \times 10^6 = 1.2 \text{ ppm} \end{aligned}\right\} \tag{4}$$

The equation for the height of reaction-cloud rise (eq. (2c)) may now be applied to determine the distance from the release point at which the

---

[2] If the value selected for H (e.g., 600 m) in defining a value for a differs greatly from the final H determination, estimated a new H value to determine a new a, and repeat the calculation process until the selected H and computed H are satisfactorily close values.

maximum ground pollution level χ_{max} will occur (wind velocity, 7.5 knots):

$$
\begin{aligned}
d\chi_{max} &= \left(\frac{2H^2}{3C^{*2}}\right)^{1/(2-n)} && \text{(5a)}\\
&= \left[\frac{2(2.72\times 10^5)}{3(0.163)^2}\right]^{1/1.8} && \text{(5b)}\\
&\cong 6200 \text{ m} && \text{(5c)}
\end{aligned}
$$

(The values for the diffusion coefficient C^* are given in fig. 5–5.)

In Example II (50 percent reaction efficiency assumed), the heat release Q would be about 6.36×10^9 calories. (No effects of reaction between the unreacted fluorine and atmospheric water vapor are included. Additional reaction has been observed in FLOX spill tests (ref. 3) as providing significant heat to the reaction cloud.) Equation (2a) then becomes

$$
H = \left\{\frac{2[3(1.8)+2](6.36\times 10^9)}{(9)(0.25)(1225)(3.14)^{1.5}(0.585)^3 a}\right\}^{1/(1+2.7)} \tag{6a}
$$

By iteration, solve for a by assuming a ground-level ambient temperature T_0 of 15° C, a height of 500 meters, and a lapse rate of -0.05:

$$
\begin{aligned}
a &= \frac{T_0}{T}\left(\frac{dt}{dz}+k\right)\\
&= \frac{288.16}{285.66}(-0.005+0.0099) && \text{(6b)}\\
&= 0.004943 \text{ °C/m}
\end{aligned}
$$

Substituting this value for a in equation (6a) gives

$$
H \cong 443 \text{ m} (= 1455 \text{ ft}) \tag{6c}
$$

Applying the height of cloud rise to equation (2b) gives the maximum pollution level. The source strength in this case will be the remaining 50 percent of unreacted fluorine (or 6.82×10^5 g), since the carbon reaction products are nontoxic. This reduced source strength explains the low ppm (χ_{max}) from this reaction.

$$
\left.
\begin{aligned}
\chi_{max} &= \frac{2S}{\left(\frac{2}{3}e\pi\right)^{3/2} H^3}\\
&= \frac{2(6.82\times 10^5)}{\left[\frac{2}{3}(2718)(3.1416)\right]^{3/2}(443)^3}\\
&= \frac{13.64\times 10^5}{13.55(443)^3} = 1.16\times 10^{-3} \text{ g/cu m}\\
&= \frac{1.16\times 10^{-3}}{1.225\times 10^3}\times 10^6 = 0.94 \text{ ppm (by weight)}
\end{aligned}
\right\} \tag{7}
$$

Applying the same height of cloud rise to determine the distance at which maximum pollution will occur (for an assumed wind velocity of 7.5 knots) gives

$$\left.\begin{aligned} d_{\chi_{max}} &= \left(\frac{2H^2}{3C^{*2}}\right)^{1/(2-n)} \\ &= \frac{2(1.975\times10^5)^{1/1.8}}{3(0.17)^2} \\ &\cong 5000\text{ m} \end{aligned}\right\} \tag{8}$$

5.2.4.2 *Ecological effects from launch operations.*—A study was performed in 1964 to define the risk to areas surrounding Cape Kennedy from operations with Atlas vehicles using FLOX as the oxidizer (ref. 7). This study was concerned with possible effects from worst-case fluorine releases on surrounding agriculture, orchards, fishing, and wildlife and was based on a fluorine release of 8748 to 64 140 pounds over a 1-year period in the area of three Eastern Test Range launch complexes. Distances to areas of potential hazard used were as follows:

(1) To adjacent launch complexes, 1500 to 2000 feet
(2) To industrial area, 10 000 feet
(3) To the river, 14 000 feet
(4) To Port Canaveral, 29 000 feet
(5) To East Merritt Island (orange groves), 33 000 feet
(6) To Central Merritt Island (orange groves), 46 000 feet

The indications (ref. 7) are that the probability of maximum failure mode occurrence is small, since low level (Atlas) abort failures have occurred only rarely. The anticipated airborne release would then constitute a vertical line source in a normal launch, or (in event of a failure) most probably an elevated volume source in the spill or abort case.

Conclusions from the study considering worst-case failures were that some effects on ecology are possible, but this effect would probably be restricted to vegetation and marine life in the immediate area of the launch site. According to previous studies at the AFETR (ref. 7), toxic contaminants in soil, vegetation, and water more than 1000 feet from a launch site were not measurable.

These conclusions are confirmed by some field tests. Examination of areas where fluorides would concentrate, following two FLOX test programs (ref. 3), revealed that the increase in fluoride content in soil and water samples was negligible.

The probability that FLOX operations at Cape Kennedy would cause fluorosis in cattle, which are highly susceptible, on the mainland is considered negligible (ref. 7), as is possible damage to citrus groves. Chronic effects or accumulation of fluorides in plants and animals around the launch area is unlikely considering the instantaneous nature of pollutant sources and time duration between launch operations. The amount of fluorine released in launch operations would be small on a time-integrated basis when compared with the release from commercial sources (superphosphates, plants, etc.) of thousands of pounds of fluorides daily. However, to assure safety to marine life in surrounding waters, reference 7 recommends treatment of all waste water effluent from launch operations to reduce the fluoride content to less than 11 parts per million with a pH of 6.0 to 8.0.

5.2.5 Miscellaneous Considerations in Facility Design

5.2.5.1 *Storage tank placement.*—Within the limits of practicality, the fluorine or FLOX storage tank should be isolated from the rest of the facility. Generally, this would be accomplished by distance, in combination with the use of shielding earthwork, concrete bunkers, or revetments, etc. The storage-tank location should be selected for reasonable safety from other occurrences (e.g., vehicle fallback, windblown debris, etc.) that are credible for the particular facility.

5.2.5.2 *Water systems.*—Requirements for emergency personnel water deluge facilities are discussed in chapter 9. Other areas for consideration in designing the facility water and drainage systems include the following:

(1) A fire-control system that includes fire hoses spotted throughout the facility should be provided for control of secondary fires (water would not have any appreciable quenching effect on fires involving fluorine during reaction), or for protection of critical equipment in proximity to a potential source of burnout in lines or components. During spill tests (ref. 3) with 30-percent FLOX, however, no significant fire damage occurred to the facility, because the time duration of high temperature was short. Fire equipment could also be used for washing hardware and equipment periodically to remove residual hydrofluoric acid and other fluorides from equipment surfaces. Fire systems should also include quenching systems for use when charcoal reactants which are open to the atmosphere are used (to extinguish air-fed fires in the charcoal).

(2) If a system of fog nozzles for spill control, which involves the use of a ring of fog nozzles around storage tank facilities, is used, consideration must be given to its usage in the overall water and drainage design. It is required that water be supplied in excess of stoichiometric quantities at a rate equal to the release of oxidant vapor. For FLOX systems, the use of fog nozzles to obtain a hot hydrogen fluoride reaction product is impractical, since tests at Lewis and Rocketdyne have indicated (section 3.4) that, with the lower percentage FLOX mixtures, a marked inhibition to the reaction of FLOX with water exists (refer to section 5.2.3.3 for further discussion).

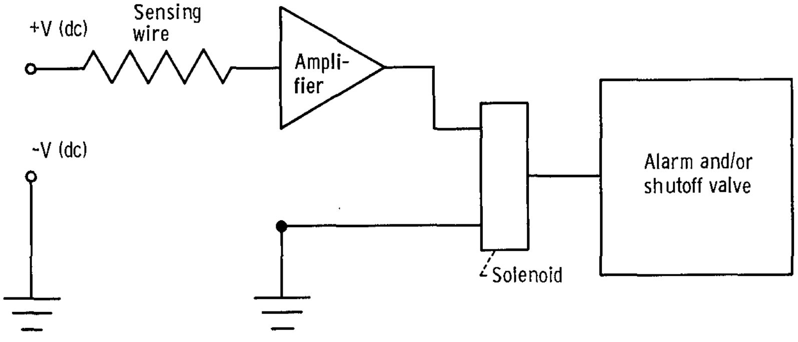

FIGURE 5-6.—Schematic drawing of burglar-alarm system.

5.2.5.3 *Electrical systems.*—Insulating materials around electrical wiring react readily with fluorine. Therefore, particular attention should be given to making all electrical wiring in the fluorine or FLOX facility safe from exposure to fluorine or fluorine-oxygen. Explosion-proof fixtures that have been made vapor-tight or are purged with inert gas are preferable for use throughout the installation. All control-system wiring should be run through sealed conduit, with connection points (to instruments, through walls, etc.) made in a gas-tight manner. If exposure to fluorine or FLOX atmosphere is slight, or of low concentration, wire sealed in polytetrafluoroethylene sheathing is acceptable (refer to section 3.3). All entrance points into equipment, through walls, etc., should be hermetically sealed. Motors and solenoids should be of the enclosed type to prevent exposure of windings to fluorine or FLOX vapors.

A useful automatic failure detection and system shutdown device for application in fluorine or FLOX systems is the "burglar alarm." In this system (fig. 5-6), the sensing wire is wrapped around the area where burnout could occur, and a circuit is established through the wire. Any significant fluorine or FLOX leak would then burn through the sensing wire and interrupt the circuit. The sensing wire can be made relatively resistant to minor leaks of low concentration FLOX by using a polytetrafluoroethylene dielectric coating on the wire. This type of circuit can be used to shut down the system operation and prevent further fluorine-FLOX flow through the area of burnout and/or to actuate a warning alarm. The burglar-alarm circuit was used during the Lewis compatibility studies and in recent test operations to achieve rapid system shutdown on failure of the sample under test.

5.2.5.4 *Structures and buildings.*—Buildings containing fluorine or FLOX systems should be constructed of a fireproof material, such as aluminum, structural steel, etc., to keep damage to a minimum in the event of fluorine gas release. No wood, roofing paper, or similar air-combustible materials should be used. Appropriate ventilation should be provided for closed buildings; if the climate permits, open-type construction is preferred to eliminate the necessity for forced ventilation.

5.2.5.5 *Blockhouse requirements.*—The principal requirement is that the blockhouse should be sealed so that a slight positive pressure can be maintained inside during operations. The air-conditioning system should be provided with positive seals to prevent intake of fluorine-contaminated air. The building should have a self-contained air supply that can meet requirements of a full complement of control-room personnel for at least 2 hours. In addition, each of the blockhouse personnel should be provided with a portable air supply to enable control-room evacuation.

Devices to detect fluorine contamination of the test or launch-stand area should provide remote indication inside the blockhouse (refer to section 5.2.5.6). As a minimum, there should be detectors (1) downwind from the launch or test site, (2) outside the entrance to the blockhouse, and (3) in at least two other areas of probable exposure (in event of area contamination).

5.2.5.6 *Atmospheric pollution detection.*—A number of different techniques have been developed that can be applied to detection of trace quantities of fluorine or hydrogen fluoride. Most methods rely on detection of the fluoride ion or some species that has been oxidized by fluorine. These methods have been more suitable for qualitative than for quantitative measurement. Early instruments (detectors) proved to be subject to interference due to their sensitivity to other ions. Devices currently on the market have not accumulated sufficient operating time for complete evaluation. However, the various techniques available for detection of fluorine and hydrogen fluoride were surveyed prior to a recent series of spill tests with 30-percent FLOX, to select some methods that showed the most promise for field instruments. Four detector types were used in the spill test program for pollution detection:

(1) The electrometric detector is an electrochemical instrument operating on the oxidation-reduction principle. The sample is drawn through a sensing tube containing lithium chloride and produces an output current that is linearly proportional to the amount of fluorine sensed (ref. 3). The instrument used in these tests (developed by General Dynamics/Convair) is hand portable and has a self-contained power supply. The instrument is selective in detecting fluorine, is equipped with a recorder to measure instantaneous dosage, and provides a record from which the total integrated dosage can be determined. Good results obtained under actual field use indicate that this detector has considerable potential as a primary field instrument.

(2) The chemical detector, which was used in spill tests (ref. 3), employs a pump to draw a gas sample through an aqueous potassium iodide solution. Fluorine in the sample reacts to produce potassium fluoride and free iodine, and the hydrogen fluoride goes into solution. After the test run, the sample solution is removed from the instrument and analyzed, first by titrating with sodium thiosulfate ($Na_2S_2O_3$) to determine the fluorine content, and then by adding potassium iodate and retitrating to determine the total fluoride (hydrogen fluoride) content. While this method does not provide direct readout and does not indicate peak concentrations, the instrument tested was portable and highly accurate and was used as a standard against which performance of other instruments was evaluated. This instrument also has a self-contained power supply (developed by General Dynamics/Convair for use in monitoring FLOX spills) and is hand portable.

(3) Radiochemical exchange with clathrates involves the use of radioactive krypton 85 trapped in the crystal structure of hydroquinone. On exposure to fluorine, the hydroquinone oxidizes to quinone and releases krypton 85 in proportion to the amount of fluorine reacted. A Geiger counter is then used to monitor the count rate, which is an indication of the fluorine present. (Use of this method requires an AEC license for operation and maintenance of the instrument.) The clathrate instrument used in the spill tests was hand portable and, like the electrometric instrument, provided a recorder trace to indicate both instantaneous (peak) and integrated dosage. Early models of this instrument were humidity-sensitive, though this disadvantage was reportedly being corrected in later models. Indications in the spill tests (ref. 3) were that the hydroquinone in the clathrate might become "poisoned" and insensitive through protracted use. Despite the minor problems noted, which can be corrected by periodic maintenance, this instrument showed definite promise and has the advantage of being a commercially available, fluorine-selective detector that can be applied immediately to pollution monitoring.

Similar instruments can also be developed by using the principle of radiochemical exchange with kryptonates. Kryptonates are combinations of krypton 85 and almost any solid material that can absorb krypton. They are formed by ion bombardment or by diffusion of krypton gas into the solid under conditions of high temperature and pressure. Kryptonates may be used to detect fluorine in the same manner as clathrates, but have not yet been developed for fluorine use.

(4) The conductometric instrument, also used in the FLOX spill tests (ref. 3), measures the change in conductivity of de-ionized water after a gas sample has been passed through it. The change in conductivity is a measure of the total integrated (fluorine plus hydrogen fluoride) con-

tent of the sample. The method is sensitive to the presence of any ionizing agent in the sample (e.g., sulfur dioxide in smoke) and seems more suitable for laboratory use than for field use. The instrument does have the advantage of producing a signal that can be used for indications of both peak and integrated dosages.

5.2.5.7 *FLOX concentration measurement.*—The use of FLOX as the oxidizer requires premixing of a proper ratio of liquid fluorine and liquid oxygen. To maintain the desired FLOX concentration, the concentration must be measured and monitored. An instrument is being developed that is suitable for in-line installation to monitor FLOX concentrations during flow conditions (information received in a private communication from G. Carmichael of General Dynamics/Convair, July 1965). A breadboard version of the instrument, which is based on the principle of light absorption, has been used successfully through several flow cycles with 30-percent FLOX. The FLOX concentration monitor measures both the fluorine and oxygen components of FLOX and is equipped with a selected light source, comparator device, receiver, and a test cell (flow line insert) that includes two sapphire windows to transmit light through the FLOX stream being monitored. The light source alternately provides a beam of light through the sapphire windows and to the comparator. The measured difference in light absorption is an index of the fluorine (oxygen) present. By using a hermetically sealed instrument container and wiring channels, it seems feasible that this instrument could be adapted for use as a fluorine concentration monitor mounted inside a FLOX storage or vehicle tank.

5.2.6 **Associated Systems**

5.2.6.1 *Pressurization gas systems.*—Among the major considerations in the design of the fluorine or FLOX facility is the prevention of all foreseeable system contamination. One source of possible contamination often overlooked is in the gases used for purging the fluorine or FLOX system, or for providing transfer pressurization. Care must be taken to ensure that the helium or nitrogen used for this purpose is of the highest purity.

The best way to ensure the highest purity pressurant gases for use in fluorine systems is to obtain them in the liquid state and then vaporize the gas as needed; however, stored gas systems are most widely used for helium at the present time.

Pressurant and purge gases used for fluorine and FLOX systems should meet the following minimum specifications:

(1) Helium should meet AF stock Grade A No. 7500–156410 wetness requirements.

(2) Nitrogen should meet Specification MIL-P-27401A that specifies 99.99 percent purity with inclusions not to exceed 50 parts per million of oxygen and 5 parts per million of methane, with a gas dewpoint no higher than −90° F.

The most undesirable contaminant (and most common) that can be introduced into the fluorine or FLOX system is moisture, since any ice buildup can result in an explosive reaction and combustive ignition of the container. This is a particular problem during extended purging through components at cryogenic temperatures (refer to section 4.6.5.1). Simple pressurization processes (e.g., tank pressurization for fluid transfer) tend to permit reaction of contaminants as they are admitted rather than permit a buildup (particularly of water as ice) to hazardous levels before a reaction is initiated. Use of helium or nitrogen vaporized from a liquid source provides gas with a dewpoint low enough to prevent this problem.

5.2.6.2 *Pressurization gas dryers.*—Where stored gas systems are used, pressurant and purge gases must be processed to remove moisture and hydrocarbon contamination before use in the fluorine or FLOX system; the gas should have a maximum dewpoint of −100° F. The design specifications for pressurizing gases can be met by using a "molecular sieve" (ref. 8). Commercially available standard gas drier cartridges can provide pressurant or purge gas of high purity. In this assembly, a cartridge filled with Linde Grade 13X ($\frac{1}{16}$- to $\frac{1}{8}$-in.-diam pellets) will remove both moisture and hydrocarbons. A standard unit contains a fiber-glass mat backed by a stainless-steel screen to remove particles up to 3 microns in diameter and contains 5 pounds of desiccant (other sizes are available). The combination is reported to provide dew points to below −130° F (0.1 ppm) when newly installed, and to below −100° F (1.5 ppm) after processing 111 000 standard cubic feet of specification helium.

Dew points of cryogenic fluids in the gaseous phase can be detected by resonant frequency measurement. This technique (available in a commercial instrument) uses a tuned crystal immersed in the test sample. Since the crystal is extremely hygroscopic, any moisture present is taken up and causes a shift in the resonant frequency; the degree of shift is an index of the parts per million of moisture present in the sample. This instrument was sensitive from 0.1 to 25 000 parts per million (by scale selection) in operations at Lewis. The immersed crystal is periodically removed from contact with the gas sample, and while it is being dried by heating, it is replaced by a duplicate tuned crystal.

Further cooling of the gas to −300° F by providing the "molecular sieve" with a liquid nitrogen bath results in a further reduction of moisture content of the gas. Care must be taken in the design so that all contaminants are trapped and that none can become entrained in the high-velocity flow of pressurant and be reintroduced into the gas as a slug.

5.2.6.3 *Clean-room requirements.*—Since scrupulous cleanliness is a major requirement in the fluorine system, extreme care must be taken to prevent introduction of contaminants while new components are being installed in the system. Therefore, maximum use should be made of clean-room facilities to perform subassembly cleaning and assembly operations. An ultraclean room at the Plum Brook facility consists of a 30- by 30-foot room that includes airlock windows and doors. A positive pressure of about 0.25 inch of water is maintained in the room, with air pumped through a filter.

The room contains a sonic cleaner with water and detergent, baths of trichloroethylene, acid, acetone, and distilled water. Also included is a source for dry helium.

All personnel working in the clean room wear rubber gloves and special lint-free garments. On entering the room, a person uses a special apparatus to clean the tops and the bottoms of shoes.

A typical cleaning procedure (refer to section 6.2) involves

(1) Complete disassembling of components and immersion of parts in sonic cleaner; cycling through sonic cleaner for 10 to 15 minutes, and allowing parts to air-dry
(2) Bathing parts in trichloroethylene and drying with a stream of helium
(3) Bathing parts in a 20-percent solution of nitric acid and rinsing with distilled water
(4) Bathing parts in acetone and drying with helium
(5) Assembling component, and packaging and sealing as appropriate

Requirements for the clean room construction are detailed in reference 9.

5.2.6.4 *Passivation unit.*—All passivation procedures recommended herein involve the use of fluorine gas of high purity for system passivation (refer to section 6.2). For small systems, the standard procedure is to use bottled fluorine gas supplies. To obtain gas of the required purity and quantities for large facilities, however, it may be necessary to use a passivation trailer or in-place system to evaporate gas from a liquid-fluorine source (mobile storage or facility storage tanks).

While a separate system (trailer or in-place) can be designed for this purpose, the same result can be achieved by use of a finned-tube heat exchanger on an outlet line from a liquid-fluorine supply. Mobile storage systems (described in chapter 8) may be modified for this arrangement.

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Chapter 6. Facility Preparation and Operating Procedures

A properly designed fluorine or FLOX facility in a storage configuration (i.e., with the fluorine or FLOX stored in a no-loss vessel) is considered to be in a fail-safe condition. Before any operations, including transfer operations, are performed, which change the status of the storage configuration, an evaluation should be made to determine all possible or credible failure contingencies (refer to chapter 5 for further discussion). A review should be made of current and expected weather conditions to determine whether a worst-case failure during the operation would be an unacceptable risk (refer to section 5.2.4). Failure-mode analysis should be made for the particular operation to be performed to assure that adequate provisions are made for personnel safety for all credible emergency situations. An operations and failure-mode analysis should be performed to determine if an unacceptable risk of damage to facility equipment exists. Operations should not be started until an acceptable condition has been determined or provided for.

6.1 STANDARD OPERATING PROCEDURES

Specific operating procedures must be tailored to the particular facility, but there are a number of standard practices that should be followed in all facilities operating with fluorine or FLOX. (Safety aspects of facility operation are discussed further in chapter 9.)

6.1.1 Personal Cleanliness

Personal hygiene is particularly important in fluorine and FLOX facilities. Routine use of shower facilities and handwashing before smoking or eating should become habitual. Eating facilities should always be located well outside the area of possible contamination. Tools, protective clothing, and devices should be cleaned after use. Care should be exercised to ensure neutralization and removal of any fluoride acid or salt that might be deposited during system operations. Personnel working around FLOX or fluorine systems should treat any liquid on the skin as though it were hydrofluoric acid or a fluoride, and rinse it off with water immediately. The external surfaces of the fluorine or FLOX containment system should be kept clean. Standard cleaning agents suitable to the material may be used on the external surfaces of fluorine- or FLOX-containing systems.

6.1.2 Precautions

Maintenance operations should always be performed under observation of a remotely located observer, who can lend assistance if required, or by personnel working in locations where they can observe each other. Before any operation is performed that involves breaking into a containment or transfer system, the system must be completely *depressurized and purged* of all fluorine prior to opening to assure that all toxic residues have been flushed out of the system. No welding, or other hot work, should be done on (or adjacent to) lines or equipment containing fluorine or FLOX, since this could initiate a reaction.

Contaminated areas (where leaks or spills have occurred) should be entered only by selected and trained personnel. The approach to any area of suspected leakage should be made very cautiously; before an approach is made to any fluorine or FLOX vessels, the valves must be closed and the system must be depressurized. Further discussion is included in section 9.3.1. Before any maintenance operation is performed, the system should be rendered safely inert, and appropriate warning signs should be placed to denote that a maintenance procedure is being performed. Where valve positions are critical, valves should be locked in position (open or closed) and should be tagged to indicate the position.

6.1.3 Valve Operation

In all fluorine or FLOX systems, the principle of remote operation of all valves should be used as much as practicable. All manual valves in a pressurized fluorine or FLOX system should be operated by linkage and gear arrangements that permit actuation through a barrier. The only exception to this general rule permits operation or manipulation of master shutoff or system lock-up valves prior to system activation and after system shutdown. Manipulation of pressurized fluorine-FLOX systems for flow-control functions should be performed with automatic valves.

6.1.4 Operator Limitation

Only trained and authorized personnel should be permitted to operate any equipment in the fluorine or FLOX facility, including handling equipment such as mobile-storage and passivating equipment. Operations should never be carried out by individuals working alone. Operating personnel should be assigned individual specific responsibilities rather than general responsibilities.

6.1.5 Checklist Operations

A checklist for standard operating procedures should be set up at each facility to define exact step-by-step operations to be performed in all routine facility operations. These procedures must then be rigidly followed.

6.1.6 Training

Training courses in fluorine facility operations should be provided to ensure that all facility personnel are thoroughly familiar with the equipment of the facility and the proper procedures for operations. Whenever it is possible, liquid oxygen or liquid nitrogen should be used as the test fluid for preliminary tests, checkout, and training (refer to section 9.1 for a discussion of personnel training).

6.1.7 Alarm Systems

Alarm systems must be tested periodically to ensure that they are operational.

6.1.8 Equipment Marking

All equipment used to handle fluorine or FLOX should be identified with distinctive colors and markings.

6.1.9 System Inspection

Equipment of the system should be inspected on a scheduled basis to assure that the system is operational. All flange nuts and line connections must be tightened to appropriate torque values. This procedure is particularly important for those installations where the system undergoes cryogenic cycling (refer to section 4.3.2).

An effort must be made to isolate and repair all leaks in the system before fluorine or FLOX is admitted. When a system contains fluorine, leakage can be easily detected by smell and located by chemical detectors. Leaks, under these conditions, can be precisely located by using squirt bottles or swabs of ammonium hydroxide solution. The chemical smoke produced by the spray or swab in the presence of fluorine or FLOX is easily visible. This method should *always* be used with caution, particularly when the system is pressurized above 35 to 50 pounds per square inch gage. (Fluorine leak-test pressures should not be higher than required to detect the leak.)

When the system is empty of fluorine or FLOX, the common methods of leak detection (e.g., soap bubble solutions in combination with a pressurized system and/or helium leak detectors—mass spectrometers) can be used to test for high-pressure leaks. Flange connections can be sealed with masking tape, and a pinhole made in the tape; this pinhole can then be bubble-tested with a soap solution to detect a leak. The tape can be left in place to function as a leak detector during system operation. Any fluorine or FLOX leak would become evident if the masking tape became charred.

Another method of leak detection for fluorine- or FLOX-filled systems is the use of chemical indicator papers. Potassium iodide (or potassium iodide—starch) impregnated paper, for instance, is normally white, but turns brown to black in the presence of fluorine gas. Fluorine detector and "sniffer" methods for leak detection are discussed in section 5.2.5.6.

6.2 CLEANING AND PASSIVATION

Experience in handling fluorine and FLOX has shown that most system failures that resulted in burnout could be traced to some form of contamination. Thus, it cannot be overemphasized that after a safe fluorine system has been designed strict cleanliness is required during all assembly and maintenance operations to assure safe operation. Achieving and maintaining system cleanliness involves development of, and adherence to, proper standards and procedures for cleaning, passivation and assembly of components, passivation of the system, and maintaining the integrity of the resultant fluorine-compatible system to avoid recontamination.

Passivation of components and component parts by fluorination of the system is an integral part of the cleaning process, but it is always performed after the part, component, or system has been thoroughly cleaned, purged, and dried by other means. The main value of passivation is the inerting, by reaction and complete fluorination, of any residual contaminants after normal cleaning procedures. *The formation of a resultant fluoride film is beneficial in retarding further base-material reaction with fluorine, but this reaction is secondary to the cleaning function involved in passivation.*

Where it is possible, clean-room facilities should be used during cleaning and assembly procedures for component parts, components, and small subsystems. The following paragraphs present some general cleaning and passivation precautions, methods, and procedures for a fluorine or FLOX facility. The philosophy involved in these procedures has evolved from NASA and industrial experience with fluorine systems.

6.2.1 Elastomeric Materials Cleaning Procedure

When the fluorine or FLOX system includes polymers (normally in the form of gaskets, valve-stem packing, etc.), they should be cleaned before installation into the related components or subsystem. Elastomeric materials tend to absorb some cleaning agents in exposed surfaces during any protracted immersion or exposure. The absorbed solvents can then become system contaminants and possible ignition sources when exposed to fluorine or FLOX. When it becomes necessary to flush an assembled system with a cleaning solvent, particular care must be given to system evacuation or purging following cleaning to ensure removal of the solvent from crevices, pockets, and the surface of elastomers in the system.

All visible surface impurities must be removed. Soft brushes or clean lint-free cloths may be used with the proper solvent (table 6-I).

TABLE 6-I.—CLEANING SOLVENTS (REF. 5)

Solvent or Cleaner [a]	Material
Trichloroethylene	All metals Halon TFE Teflon TFE Teflon FEP Nickel-filled Teflon Rulon A
Acetone	Kel-F-81 Plaskon 2000 series Halon TVS
Methanol	Kel-F-82

[a] Soap and water are preferred for all materials listed since elastomers absorb solvents. When solvents are used, they must be completely removed after cleaning is complete.

Extreme care should be taken to prevent scratching or otherwise marring surfaces of nonmetallic or elastomeric materials that will come in contact with fluorine or FLOX. The part or component should also be washed or flushed, as required, with the appropriate solvent (table 6-I). The solvent should either be discarded or redistilled after use.

A stream of dry oil-free nitrogen (refer to section 5.2.6.1) or dry filtered air should be used to dry thoroughly all solvent from the part or component. Unless the part or component is to be assembled into a subassembly or into the system immediately, it should be packaged in a clean polyethylene bag and sealed to prevent contamination. The final cleaning step (as in the case of metal parts of systems) is exposure to fluorine or FLOX in system passivation, as described in section 6.2.4 or 6.2.5. A "passivation chamber" may be used to prepassivate nonmetals with fluorine gas at low pressure (ambient to 25 psig).

6.2.2 Cleaning Procedures for Metallic Components

The general precautions and procedures included in section 6.2.6 should be observed during cleaning operations. The following procedure is recommended for use in cleaning and pickling components and parts of a system prior to assembly operations:

(1) The components should be disassembled as much as possible. The seals, etc., that are incompatible with cleaning solvents must be removed.

(2) Those components that show any traces of scale, weld slag, shop dirt and soils, chips, grease or other obvious foreign matter, should be cleaned by an appropriate cleaning technique. This technique may involve abrasives, chemical solvents (nitric acid or hot caustic), or soap and water. The end result of this operation must leave the component with the bright surface of the base metal and with no visible contamination. This operation should be followed by a thorough water rinse and then drying to remove all free water.

(3) Those components that show reasonably clean surfaces (e.g., only traces of oxide film), can have the surface film removed by being dipped in a bath of 10- to 25-percent nitric acid (use short exposure times for copper and brass). This operation should be followed by a thorough water rinse and then drying to remove all free water.

(4) When it is possible, parts may be vapor degreased. Solvent bath degreasing and hand wiping may also be used, depending on the available cleaning equipment, the size, shape, and material of the part, etc. When hand-wiping is required, it should be followed by an immersion of the component in solvent to ensure thorough flushing of the surface. Clean solvents should always be used.

Where items such as volutes, valves, and manifolds contain ports and holes, each hole or port should be thoroughly flushed with solvent (trichloroethylene or trichlorotrifluoroethane) during cleaning. Special vapor-degreaser-nozzle or tubing configurations should be utilized as necessary to assure cleaning of holes or ports in complex configurations.

(5) Components should be dried (with dry nitrogen or helium) and either used or packaged after cleaning. Components that have surfaces which are difficult to inspect visually may also be heated (150° to 250° F in a vacuum oven if necessary, depending on the materials present) during the drying process to aid in liquid removal.

(6) For surfaces that are particularly hard to clean, the component or part may be immersed in an acid pickling solution to react any

residual impurities. The main value of acid pickling is removal of oxide coating, scale, or embedded impurities. This step may be omitted if it is not required for the particular part or component.

(7) As a final step in cleaning (particularly for systems that cannot be flushed with cleaning solvents), individual parts may be passivated with fluorine to assure cleanliness and to form metal fluoride films. Final passivation should be completed after system or subsystem assembly by using the applicable procedure given in section 6.2.4 or 6.2.5.

6.2.3 System Cleaning Procedure

In rocket systems test operations at Lewis, it has become standard practice to clean *assembled* systems prior to initial operations. This cleaning procedure normally consists of a trichloroethylene (or trichlorotrifluoroethane) flush, followed by system evacuation, if the system can withstand evacuation, or by purging to remove all traces of the solvent. Evacuation is an extra procedural step sometimes taken for added assurance of solvent removal. Particular care must be taken to exclude air, since chlorinated hydrocarbon solvents hydrolyze readily with atmospheric moisture to form hydrochloric acid, which, in turn, will corrode system components. When system cleaning is performed, care must be taken to prevent prolonged exposure of polymers (gaskets, etc.) to the solvent, and to selection of a solvent compatible with system materials. In general, system cleaning should be carried out to the level specified in reference 1 or 2.

If the design of the system or subsystem does not permit complete removal of solvent by purging after the preceding operation, the following procedure is performed:

(1) Ensure that all parts and components are scrupulously cleaned prior to assembly into the system and that installation is performed under conditions of carefully controlled cleanliness in accordance with the general procedures outlined in section 6.2.2.

(2) Omit flushing the system with solvent, and instead passivate the system. For the final cleaning operation, the system should be passivated as outlined in section 6.2.4 or 6.2.5, as applicable.

6.2.4 Passivating Systems That Can Tolerate Vacuums

The main advantage of using evacuation during passivation is that it requires lesser amounts of high-purity purge gases, which must be processed for extremely low (−100° F or better) dew points (refer to section 5.2.6.2).

(1) The system should be evacuated. Then the vacuum is broken by introducing dry nitrogen to scavenge any residual moisture after which the evacuation process is repeated.

(2) The vacuum is broken by slowly admitting pure fluorine gas, FLOX, or fluorine-helium mixtures into the system until a slight positive pressure is reached. The pressure is held constant a few minutes to allow any reaction to occur slowly. Fluorine flow into the system should be continued, stopping at pressure increments to allow gradual reaction of any contaminants, until the pressure increases to system operating pressure, or 50 pounds per square inch gage. This pressure should be held for a minimum of 30 minutes at room temperature (longer at low temperature or if desired).

(3) After shutdown, the system should be left with a slight positive pressure of fluorine, FLOX, or helium to ensure against inward pressure leak in case of loss of the zero-leak capability of the system.

6.2.5 Passivating Systems That Will Not Tolerate Evacuation

(1) The system should be purged thoroughly with dry nitrogen or helium (dew point equal to or less than −100° F; section 5.2.6.2) until it is free of traces of moisture or solvent vapors.

(2) Gradually, gaseous fluorine should be admitted into the system until most of the nitrogen has been displaced. The vent should be closed and the fluorine pressure increased in increments, holding at each increment to permit any reaction to occur slowly, until the system operating pressure or 50 pounds per square inch gage is reached. This pressure should be held for a minimum of 30 minutes at room temperature (longer at lower temperatures, or if desired).

(3) The system should be left with a slight positive pressure (fluorine or helium as desired) to prevent inward air leak and contamination from entrained dust and moisture.

6.2.6 General Precautions and Procedures for Use with Cleaning Procedures

General processing.—Processing of components should be continuous through cleaning, acid pickling and/or passivation, and packaging or assembly. Should an interruption occur in the processing of the component, the interrupted process should be repeated before the remaining operations are completed. Components that have been dye-penetrant inspected must be recleaned to assure removal of all dye penetrant before exposure to fluorine.

Packaging components.—All parts should be packaged in a manner that will prevent physical damage or contamination. If at any time prior to their assembly into the system this package is opened for inspection or testing, the component should be rechecked to ensure that it continues to meet cleanliness requirements before it is repackaged or installed.

Use of clean rooms.—Whenever it is feasible, operations involving component disassembly and rebuilding should be performed in clean rooms (section 5.2.6.3). Where conditions do not permit use of a clean room for maintenance operations, particular care should be taken to assure cleanliness.

Postcleaning inspection.—After cleaning and pickling operations, detail parts should be inspected for any residual moisture, rust, scale, dirt, chips, oil, grease, or any other foreign material prior to packaging or assembly. The presence of any such deposits would require recleaning of the part or component. When discolorations due to welding or passivation do not display signs of foreign substances, further cleaning is not necessary.

6.3 FLUORINE IMPURITIES

While liquid fluorine delivered from the manufacturer would normally be in a high state of purity, hydrogen fluoride and other contaminants could accumulate in storage and transport systems in the course of handling. Thus, samples should be taken periodically from fluorine or FLOX storage to assure purity or to define the degree of contamination. The usual contaminants in liquid fluorine include oxygen, nitrogen, carbon tetrafluoride, and hydrogen fluoride. In addition to these contaminants, gaseous fluorine from a cylinder has been found to contain carbon dioxide, oxygen fluoride, silicon tetrafluoride, sulfur hexafluoride, and sulfuryl fluoride. The presence of contaminants in fluorine is of interest for the following reasons:

(1) The primary source of corrosive action in liquid fluorine is the presence of contaminants. Solid hydrogen fluoride in liquid fluorine is relatively inert if the system is maintained below −117° F. At higher temperatures, hydrogen fluoride (originally in the fluorine or formed by reaction with moisture or organics) can be very corrosive in the presence of any free moisture.

(2) Dilution of fluorine by soluble contaminants may affect the performance of the fluorine as a rocket oxidizer. Oxygen and nitrogen are the only contaminants that would be expected to be present in concentrations of 1 percent or more. A small amount of oxygen might not

significantly lower the performance since oxygen itself is a powerful oxidizer, but the presence of nitrogen will reduce specific impulse. Accumulation of insoluble contaminants may seriously affect the performance of system components, such as engine injectors, valves, and flow-meters.

Data on solubility of contaminants in liquid fluorine have been experimentally obtained (refs. 3 and 4) and are given in table 6-II.

TABLE 6-II.—SOLUBILITY OF MATERIALS IN LIQUID FLUORINE

Material	Solubility at —320° F, mol percent	Reference
Carbon tetrafluoride	87.5	3
Oxygen fluoride	10.0	4
Silicon tetrafluoride	<0.05	3
Hydrogen fluoride	<0.5	4
Sulfur hexafluoride	<0.1	4
Nitrogen trifluoride	0.12	3
Krypton	28.6	|
Xenon	1.28	|
Dicarbon hexafluoride	2.87	|
Perchloryl fluoride	0.33	↓

Powdered tetrafluoroethylene (TFE), silicon tetrafluoride, boron trifluoride, and aluminum trifluoride were all less soluble than could be measured with test apparatus, according to reference 4 (<0.05 mole percent at −320° F), but low solubilities agreed generally with calculated values. Oxygen and nitrogen are soluble in fluorine in all proportions. According to reference 5, other materials that are solid at liquid-fluorine temperature (−306° F), are not expected to be appreciably soluble.

6.3.1 Wet Chemical Analysis

A number of methods may be used to determine contaminants. These generally involve evaporation of the liquid sample and analysis by standard laboratory methods. Analysis methods are discussed in reference 6.

6.3.2 Infrared Spectrophotometry and Gas Chromatography

Any good commercial infrared spectrophotometer may be used for analysis of fluorine or FLOX for impurities. All test equipment coming in contact with the sample should be of compatible material (for the condition of exposure) and should be cleaned and passivated in accordance with procedures given in section 6.2.

6.4 FLOX SYSTEM PREPARATION SUMMARY

The following paragraphs describe the principal considerations for a typical operation (test or launch with FLOX as an oxidizer). If fluorine is used as the oxidizer, most steps in the procedure would be similar except for the mixing operations. Care should be taken to develop operating procedures that will not permit condensation and freezeout of atmospheric moisture within cryogenic fluorine or FLOX systems. Experience has shown that system failure may occur when the fluorine or FLOX contacts the ice. After an unpredictable induction period, liquid fluorine and ice react violently.

Prior to exposure to fluorine or FLOX, all storage-facility equipment, the FLOX transfer lines and systems, and the test or launch vehicle FLOX tanks will require passivation to remove contamination that might remain in the system after cleaning and purging. The operation sequence includes

(1) Component cleaning and acid pickling or passivation with fluorine (refer to section 6.2)
(2) Assembly of system
(3) Dry nitrogen or helium purge of system (for moisture removal)
(4) Solvent flush (if required)
(5) Nitrogen or helium purge to remove solvent (if required)
(6) System pressure test
(7) Passivation of transfer system with fluorine gas, with or without evacuation, as appropriate
(8) Precooling and system checkout with liquid oxygen or nitrogen as required
(9) Liquid-oxygen transfer to FLOX storage tank
(10) Liquid-fluorine transfer to FLOX storage tank
(11) Cooldown of transfer line and launch or test system
(12) Transfer of FLOX to tank of launch or test system

Purging and Leak Checks

After assembly, the system should be evacuated (if possible) and/or purged by warm dry nitrogen, supplied from a vaporization and warmup coil. The evacuations and/or purges will remove moisture and other contaminant vapors that remain. System leak checks are performed with helium or nitrogen prior to passivation (section 6.1) and may be followed by a low-pressure fluorine check during passivation. Should any leakage occur, the system should be shut down and corrective action should be taken.

Passivation

The dry-nitrogen or helium purge of the system during the leak test will remove moisture from the system. This is followed by a passivation procedure (described in section 6.2.4 or 6.2.5) that will safely react the remaining contamination and also form a fluoride film on exposed metal surfaces.

Storage Tank Fill

If a liquid-nitrogen subcooler or recondenser is part of the FLOX storage system, it should be placed into operation prior to filling the storage tank. If a three-shell storage tank is used, the coolant jacket should be topped with a coolant (liquid nitrogen, liquid air, or liquid oxygen).

Standard practice for mixing FLOX is to load the liquid oxygen first to minimize exposure of the tank to high fluorine concentrations; in top loading systems this also permits loading the more dense fluorine on top of the liquid oxygen, which speeds the spontaneous mixing rate (ref. 5). If loading is performed through a dip tube, leaving the more dense fluorine on the bottom, spontaneous mixing will still occur, but at a much slower rate. To assure mixing, or to speed the mixing rate, *dry* helium can be bubbled through a dip tube in the tank to provide agitation.

FLOX Transfer

In some loading operations, it may be desirable to use a precooling operation with liquid oxygen (or liquid nitrogen) to minimize boiloff when the FLOX is introduced through the system. Use of vaporized FLOX as a pressurant for transfer would also minimize disposal requirements for pressurant vent gases; the vaporized FLOX can be recondensed following the transfer cycle. The various methods for transfer are discussed in chapter 5.

Posttest Operations

The launch or test vehicle tanks of a fluorine system, when drained of residual FLOX after testing, should be left with a slight positive pressure following deactivation. After any firing test, the concentration of the hydrogen fluoride dissolved in the blast deflector coolant water (or scrubber, if used) may be sufficient to require neutralization. The water can be collected in a catch basin and the dissolved hydrogen fluoride precipitated as insoluble fluorides by treatment with lime. The fluoride concentration in the effluent after treatment must not exceed the limits established by the local water pollution control authorities (i.e., probably from about 1 to 3 ppm).

REFERENCES

1. ANON.: Cleanliness of Components for Use in Oxygen, Fuel, and Pneumatic Systems. Spec. No. MSFC-SPEC-164, George C. Marshall Space Flight Center, July 27, 1964.
2 ANON.: Cleaning and Inspection Procedures for Ballistic Missile Systems. Tech. Manual No. T. O. 42C–1–11, USAF, September 18, 1962. (Including Tech. Manual Suppl. No. 42C–1–11C, USAF, Mar. 1, 1963.)
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Chapter 7 Vehicle Systems Requirements

Complete coverage of the requirements for launch vehicle systems is beyond the scope of this report. However, this chapter presents some of the more general considerations that must be taken into account when planning for the use of fluorine or FLOX as an oxidizer for launch or tests of rocket systems.

The primary considerations in the use of fluorine or FLOX as an oxidizer in the design of boosters are systems compatibility with fluorine or FLOX and consideration of the quantity of hydrogen fluoride and fluorine that would or could be released into the atmosphere during operations.

The use of mixtures of fluorine and oxygen (FLOX) as an oxidizer rather than liquid fluorine tends to reduce the compatibility problem. The reactivity of FLOX mixtures decreases to some extent as the percent of fluorine is decreased. Vehicle hardware may be selected or modified to meet compatibility requirements. In this way, present boosters may be modified for use with FLOX by optimizing the modification effort, cost, and mission requirements.

The second consideration for the use of a booster employing fluorine or FLOX as the oxidizer involves the amount of hydrogen fluoride released and the dispersal characteristics of the exhaust products during launch (refer to section 5.2.4).

While conversion of existing upper stages to the use of fluorine or FLOX as an oxidizer would involve the same study requirements for compatibility as for the booster, the probability is that fluorine rather than FLOX would be used as the oxidizer and that the upper stage would be specifically designed for this application. U.S. Air Force and NASA programs over the past 10 years have produced regeneratively cooled prototype flight-weight hydrogen-fluorine and hydrazine-fluorine rocket engines with promise for high operational reliability. Rocket systems that use fluorine as the oxidant have been designed, developed, and successfully demonstrated in captive tests up to the point of operational evaluation.

7.1 DESIGN CONSIDERATIONS

Whether a vehicle is being newly designed for use with fluorine or FLOX as an oxidizer or an existing vehicle is being modified to make it fluorine compatible, a design investigation must be performed to ensure compatibility. All the subsystem parts and components that will interface with the fluorine-FLOX systems should be identified. All possible fluorine or FLOX paths through the vehicle system should be determined and provision should be made for compatible materials throughout these possible paths.

(1) Possible spillage quantities from quick-disconnect operations should be determined.

(2) Leakage rates (if any) in the oxidizer system isolation valves, shaft seals, and packing should be determined. No measurable external leakage should be permitted from any fluorine containment system or system component, particularly where the leakage rate could increase with time. Permissible levels of internal leakage through system components will vary with systems and component functions.

(3) A safe relative position must exist between vent ports of the fluorine-FLOX system and other launch vehicle systems. No impingement should occur (in venting of fluorine or FLOX) with venting from other systems, such as hydraulics, lubrication, oil, etc. An evaluation of the effects of possible impingement (due to leakage) on other vehicle systems such as hydraulics, pneumatics, and control systems should be included.

All materials used in all components and subsystems that will be directly exposed to fluorine or FLOX should be identified. Parts thus identified must be evaluated for compatibility with respect to (1) maximum possible FLOX (or fluorine) concentrations, (2) exposure temperature and pressure conditions, (3) type of service to be encountered (gaseous or liquid) and whether the exposure will be direct or shielded (4) exposure to friction, (5) maximum flow rates to be encountered (particularly important for nonmetallic components), and (6) whether cavitation or impact (solid or fluid) exists in service conditions.

Materials compatibility must then be determined for the conditions of application according to the information given in chapters 3 and 4.

An evaluation of penetration of the instrumentation into the fluorine or FLOX system must be made that includes materials compatibility and methods for sealing from fluorine or FLOX penetration. All sensors exposed to, or mounted within, the fluorine or FLOX system must be considered to ensure compatibility and zero-leak sealing.

Possible environmental exposure of instrument packages, electrical and electronic systems, and vehicle wiring to hydrogen fluoride, FLOX or fluorine leaks and/or propellant venting must be determined.

A study of aerodynamic heating effects on the oxidizer tank should be made to determine whether localized heating could raise the fluorine-FLOX containment system temperature to the ignition point of the containment system materials.

7.2 COMPATIBILITY EVALUATION AND REQUIREMENTS

All components of the oxidizer system must be compatible with fluorine, or with the FLOX concentration specified for use in the vehicle. Additionally, where the component may interface directly or indirectly with the oxidizer system (e.g., temperature or pressure transducers or pressure regulators), compatibility evaluation should include seals, O-rings, gaskets, conduit, or other hardware (or software) that isolates electrical circuits or noncompatible components from contact with the oxidizer.

Some of the compatibility considerations to take into account during design or modification of the vehicle system are given as follows:

(1) Surface coatings or insulating materials exposed to possible venting or leakage of fluorine or FLOX should be coated with the most resistant nonmetallic material appropriate for the function, such as polytetrafluoroethylene or polychlorotrifluoroethylene (refer to compatibility studies in chapter 3).

(2) Grease or coatings for lubricating purposes should not be used in a fluorine or FLOX environment. Components that cannot function without lubrication should be redesigned (in most instances). The use of Kel-F greases in some fluorine system applications is possible (section 4.3.3). Also, fluoride films have shown promise as possible lubricants for some components (section 4.5.2).

(3) Cables and harnesses between components in the launch vehicle should be covered with polytetrafluoroethylene or metal and tied or secured with metallic or fluoropolymer materials only. Common lacing cord should not be used where fluorine or FLOX oxidizer gases could be present.

(4) Wiring-cable entrances into instruments or components, and connections between cables, should be sealed against fluorine, FLOX, or hydrogen fluoride penetration in a suitable manner (e.g., with AN-type fittings) to ensure a vapor-proof passage for the wiring.

(5) All components of the launch vehicle system that are sensitive to exposure to a fluorine or hydrogen fluoride environment should be completely sealed from contact with fluorine or FLOX vapors. Where sealing is not practical, a continuous purge with inert gas should be used.

7.3 CLEANING AND PASSIVATION OF FLIGHT SYSTEMS

During fabrication and assembly of fluorine or FLOX flight systems, the cleaning procedures outlined in chapter 6 (sections 6.2.1, 6.2.2, and 6.2.3) should be used as applicable. Additional considerations are discussed in the following sections.

7.3.1 Assembly and Postassembly

(1) All components and subsystems for the oxidizer system should be assembled in a liquid-oxygen "clean" condition by using strict application of current liquid-oxygen cleaning specifications (refs. 1 and 2).

(2) Nonmetallic materials that may come in contact with fluorine or FLOX should be prepassivated with gaseous fluorine to assure complete fluorination of any organic contaminants.

(3) Metallic components that are exposed to fluorine or FLOX in operation that cannot be thoroughly passivated in the assembled system should not be prepassivated, but extra care should be taken to assure cleanliness.

(4) After vehicle-assembly and liquid-oxygen cleaning operations, a positive pressure of dry nitrogen or helium (nominally −100° F dew point) should be maintained in the oxidizer system to exclude moisture contamination. When unsealing of the oxidizer system is required, the system should be kept open to the atmosphere *only* for the time required to perform the particular assembly or maintenance operation. (If the system is being opened after containing fluorine or FLOX, it should first be thoroughly purged with dry helium or nitrogen; prolonged purge followed by ventilation with air must then be used to ensure a safe breathing atmosphere before entrance for maintenance is permitted.) Atmospheric moisture, whether by itself or combined with hydrogen fluoride, can cause unacceptable corrosion. After maintenance is completed, the vehicle should be purged with dry nitrogen or helium to remove all traces of moisture.

7.3.2 Operations

A system failure occurred during recent operations at a fluorine rocket-engine test facility during a NASA program. The initial reaction occurred at the oxidizer prevalve, which is located between the test engine and the isolating valve at the fluorine supply. Liquid-nitrogen jacketing was used on the fluorine transfer line from the isolating valve up to and including the prevalve; the transfer line downstream of the prevalve was uninsulated. A dry-nitrogen purge line was connected through the prevalve to purge the line downstream and through the test engine.

The operating procedure included first filling the liquid-nitrogen shield on the fluorine transfer line, starting a dry-nitrogen purge, admitting fluorine from the fluorine supply through the isolating valve to the prevalve, and finally operating the test system through an engine-firing cycle. Since the purge flow was not started until after the liquid nitrogen chilled the prevalve, moisture freezeout apparently occurred at the prevalve plug. The partial vacuum thus created drew in more moisture-laden air through the test engine to cause a buildup of cryogenic-temperature ice at the valve plug. Because of the low temperature and low vapor pressure of this ice, neither the purge cycle nor the following exposure to a near vacuum prior to engine start apparently caused the ice to sublime. When the prevalve was opened to fluorine flow, an initial reaction occurred with the ice, causing a pressure surge through the system that produced a high-pressure leak and reaction at the engine injector inlet. Both reaction zones were then acted on by the fluorine until the transfer line burned through at the prevalve, at which time an isolating valve closed to shut off the fluorine supply to the transfer line. The reaction continued until the available fluorine was exhausted.

This failure demonstrates the need even in a well-designed fluorine facility for stringent operating procedure. However, the use of liquid nitrogen jacketing and rapid shutdown techniques minimized damage in this incident. Particular attention must be given to developing operating procedures that will not permit a contaminant buildup in the system.

7.3.3 Shutdown and Reuse

If the launch vehicle system is cycled through operation and shutdown,

(1) The oxidizer system should be kept under a slight positive pressure with fluorine, FLOX, or inert gas to preclude contamination by the atmosphere.

(2) After prolonged shutdown or when removing the vehicle or systems from storage configuration, the following operations should be performed immediately prior to any cold-flow operations and/or test firing to assure a clean system:

(a) The liquid-oxygen-clean (and fluorine or FLOX clean) oxidizer system (refs. 1 and 2) should be thoroughly purged with dry purge gas (dew point, −100°F) to ensure a dry system.

(b) After the system is purged, fluorine gas should be introduced into the system, which is vented to a disposal system, and flow should be maintained until the fluorine concentration for passivation (operating FLOX concentration or greater) is reached. The vent should then be closed and the pressure increased to 50 pounds per square inch gage, or system operating pressure, and held for a minimum of 30 minutes at room temperature (longer for lower temperatures, or if desired).

(c) With completion of the purging and passivation, the oxidizer system is ready for cold-flow tests and/or other operations.

7.4 CORROSION CONSIDERATIONS

Launch vehicle systems should not normally present any problems of corrosion peculiar to fluorine or FLOX. If the system is kept clean and dry, fluorine is not corrosive; however, the presence of moisture can hydrolyze the fluoride film and attack the base materials of the system.

7.4.1 Internal Corrosion

By following the general procedures given in section 7.3, there would be little or no leakage of atmospheric contamination into the vehicle to create a corrosion problem. Large flight-weight vehicle systems were exposed to simulated operating conditions with FLOX during the FLOX test program with the Atlas booster. After tests and a year in a lock-up storage condition, no trace of corrosion was found. The same thing has been observed in Lewis systems with smaller ground-support-equipment tanks after prolonged exposure to pure fluorine. Stainless steel and Monel were the tank materials used for FLOX storage, and stainless steel, Monel, and aluminum were used for fluorine storage. The authors have observed similarly that copper and aluminum tubing were unaffected after prolonged exposure to fluorine. (Conversely, where contamination by atmosphere and moisture was involved, excessive corrosion occurred in a relatively short period of time.)

7.4.2 External Corrosion

The only time that external surfaces of the flight vehicle would be exposed excessively to corrosive atmospheres would be during captive firing tests. During these firing cycles, exhaust gases (mainly hydrogen fluoride) can envelop the base of the launch vehicle, and additional corrosion could occur from seepage, leakage, and venting from the oxidizer system. In the same tank (see section 7.4.1) in which FLOX storage produced no internal corrosion, a slight frosting was observed external to the tank where venting had impinged the metal. While resulting corrosion was slight, it could become significant with extended operations; in such cases the use of vent ducts, etc., might be required, for protection of the flight or test vehicle. Similarly, a single firing (e.g., flight test) would present no corrosion problems to the vehicle because of the short exposure times, but repeated captive firings might cause enough corrosion for concern.

7.4.3 Rocket Nozzles

Routine short-term firings of rockets will not corrode rocket nozzles unless, after firing, a moist atmosphere is permitted to hydrolyze the fluoride film, or a water deluge is used in the test-stand flame bucket. Where a water spray is used, hydrogen fluoride can be expected to form, with a resultant corrosion in areas where the aerosols settle. In Lewis firings of fluorine-oxidized rockets into "swimming-pool" or spray scrubbers, this corrosion phenomenon has been observed, although the rocket nozzle corrosion that resulted was mild and did not seriously affect the nozzle surface. Where repeated firing cycles of an engine will be required, however, consideration should be given to preventing accumulative hydrogen fluoride attack.

REFERENCES

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2. ANON.: Cleaning and Inspection Procedures for Ballistic Missile Systems. Tech. Manual No. T. O. 42C-1-11, USAF, Sept. 18, 1962. (Including Tech. Manual Suppl. No. 42C-1-11C, USAF, Mar. 1, 1963.)

Chapter 8. Production and Transportation

The information in this chapter is intended to give some safe methods for handling liquid fluorine or FLOX during transportation and transfer operations; specific procedures must be developed for the particular installation. The same safe handling practices apply for fluorine and for FLOX.

8.1 PRODUCTION OF FLUORINE

Fluorine is prepared by the electrolysis of a molten mixture of hydrogen fluoride and potassium fluoride; the by-product hydrogen is generally discarded. Two methods have been developed for large-scale production that differ chiefly in the temperature of the operation and in the relative proportions of hydrogen fluoride to potassium fluoride. The low-temperature process, which is most widely used in this country, employs an electrolyte of composition from 1 part potassium fluoride, 1.8 parts hydrogen fluoride to 1 part potassium fluoride, 2 parts hydrogen fluoride operated at 100° to 150° C. The high-temperature cell, at about 250° C was used with an electrolyte containing 1 part potassium, 1 part hydrogen fluoride. Both processes are continuous.

The modern cell has a steel body and a steel cathode. Carbon anodes are used with a standby nickel electrode for starting the cell or for application in case of polarization. About 1 to 2 percent of lithium fluoride is added to the electrolyte to produce smooth operation. The electrolyte must be free from water and other materials that are more easily oxidized than the fluoride ion for satisfactory operation; the anode material must oxidize much more slowly than the fluoride ion.

The fluorine gas is generally purified by a combination of cryogenic and chemical methods. It is first passed through a trap cooled by solid carbon dioxide, Freon, or some suitable refrigerant, and then passed over solid sodium fluoride, which reacts to form sodium acid fluoride. The hydrogen fluoride freezes out of the gas in the cold trap; this hydrogen fluoride is very pure and may be returned to the fluorine cell.

Lewis purchases fluorine shipments to the following specifications:

(1) 98.7 Percent liquid fluorine (minimum)
(2) 0.3 Percent (maximum by weight) hydrogen fluoride and carbon tetrafluoride
(3) 1.0 Percent (maximum by weight) oxygen, nitrogen, and other inert products

The process of purification previously detailed, which employs a sodium fluoride scrubber, can be coupled with appropriate condensation and filtering to produce laboratory or test quantities of fluorine that exceed the preceding specification requirements. Methods for analyzing fluoride for purity are discussed in chapter 6.

After the production of high-purity fluorine gas, it is normally piped into a cryogenic holding tank. In this tank, which is subcooled by liquid-nitrogen jacketing or similar means of refrigeration, the fluorine condenses out as liquid.

For packaging gaseous fluorine, liquid fluorine is vaporized into fluorine shipping cylinders. The standard shipping cylinder contains 6 pounds of fluorine gas at 400 pounds per square inch gage.

Liquid-fluorine shipping containers are normally filled directly from the cryogenic holding tank. Since the shipping containers are three-shell construction, with liquid-nitrogen jacketing surrounding the storage container, any liquid fluorine that vaporizes during the transfer procedure will recondense inside the mobile storage fluorine vessel.

8.2 TRANSPORTATION

8.2.1 Shipping Regulations

The Interstate Commerce Commission (ICC) Code of Federal Regulations (chapter 1, parts 71 to 78) covers the rules and regulations governing transportation of explosives and other dangerous materials by common carrier. The ICC classifies fluorine as a flammable gas, and states (ref. 1) that it must be shipped in metal cylinders complying with Specification 3A1000 (seamless steel described in section 78.36 of the ICC regulations), 3AA1000 (seamless steel described in section 78.31), or 3BN400 (seamless nickel, described in section 78.39). The cylinders must be equipped with valve protection caps. Safety-relief devices are prohibited on cylinders containing fluorine. Cylinders must not be charged to over 400 pounds per square inch gage at 70° F and must not contain more than 6 pounds of gas. For shipment, fluorine cylinders must bear the ICC red label for a flammable gas.

There are no general ICC regulations pertaining to tanks for liquid-fluorine transportation. Special permits are required from the ICC and Bureau of Explosives for shipment of tanks that contain liquid fluorine. Special permits have been obtained for cross-country transfer of liquid fluorine in quantities of 1200 and 5000 pounds. These containers utilize a multijacketed Dewar product container described in section 4.1.3.

8.2.2 Vessel Design

Mobile storage systems built to date have all used the three-shell storage-tank configuration and have employed liquid nitrogen as the coolant. A summary of liquid fluorine mobile storage design requirements is given in chapter 4.

8.2.3 Emergency Equipment

Every Lewis fluorine transport trailer is provided with personnel safety and emergency-use equipment to be employed in accordance with operating instructions for the mobile storage system. This equipment is periodically inspected against a checklist to ensure that all equipment is available for use.

A $2\frac{1}{2}$-gallon water fire extinguisher and a 10-pound dry chemical extinguisher are mounted on the trailer. These extinguishers can be used on tire fires, or on small grease or oil fires. Safety equipment, contained in a trailer storage box, consists of protective clothing and respiratory equipment that should be used when any exposure to fluorine or liquid nitrogen is anticipated, in accordance with instructions in a trailer operator's manual.

8.3 TRANSFER OPERATIONS

Because of the hazards involved in the improper handling of liquid fluorine, operating personnel must become thoroughly familiar with the fluorine equipment and then must be made aware of the prescribed safety precautions and emergency procedures. In addition, each driver should be provided with a driver's manual that instructs him in the operation of the trailer and use of all safety equipment furnished with the trailer.

8.3.1 Cleaning and Passivation

Operating personnel must be instructed not to expose any equipment to fluorine unless they are certain that the equipment has been cleaned and passivated. Cleaning and passivation procedures for fluorine systems are discussed in chapter 6.

8.3.2 Operating Procedures

In general, fluorine users are advised to prepare operating procedures and checklists instructing personnel on operation of fluorine equipment.

These procedures should indicate safety precautions, sequence of operations, and a detailed description of each operation. While transfer operations are specific to each facility, a typical trailer-to-trailer transfer operation (using the general equipment configuration shown in fig. 8–1) is described as follows as an example to illustrate the required details and meticulous procedures:

(1) Notify the proper authorities of the operation to be performed so that the transfer area can be isolated from traffic by unauthorized or unneeded personnel.

(2) Top off the coolant jacket of both the receiver and supplier fluorine trailers with liquid nitrogen. Weigh both trailers (either total trailer weight or Dewar only as appropriate).

(3) Locate both the supplier and receiver trailers for connection to each other, to the control connection umbilicals (for remote operation of valves), to the transfer pressurization source (helium storage trailer), and to the fluorine disposal system (carbon reactors).

(4) Ensure that each man involved in the transfer operations is equipped with a self-contained breathing apparatus and a headset. Ensure that two-way radios are available for emergency communications and that the communications circuit is being monitored.

(5) Connect the liquid-nitrogen supply to the receiver trailer coolant jacket. (Leave this connection mated since coolant loss during transfer requires replenishment of the liquid nitrogen either during or following the filling operations.)

(6) Use extreme care to prevent contamination of lines and fittings, connect all tubing, etc., for transfer pressurization, liquid-fluorine transfer, purging, and disposal.

(7) Connect all control umbilicals for remote operation of automatic valves.

(8) Connect the vacuum pump to the fill-and-drain line between trailers (through valve 5, fig. 8–1). Isolating valve 5 should be left closed.

(9) Adjust the purge pressure regulator on the supplier trailer to 60 pounds per square inch gage. Open the transfer purge valve and pressure-test liquid fluorine transfer line between trailer fill and drain valves (D and 18, fig. 8–1). Vent the test pressure through the disposal system by opening valves 6 and 7. Allow the purge to flow for 1 minute, then close the transfer purge valve on the supplier trailer and valve 6. (The transfer line must be liquid-oxygen clean in accordance with cleaning procedures described in section 6.2.)

(10) Open valve 5; pump down the fill-and-drain line with a vacuum pump to less than 1-millimeter of mercury and hold for at least 10 minutes. Close valve 5 and disconnect the vacuum pump. (If it is

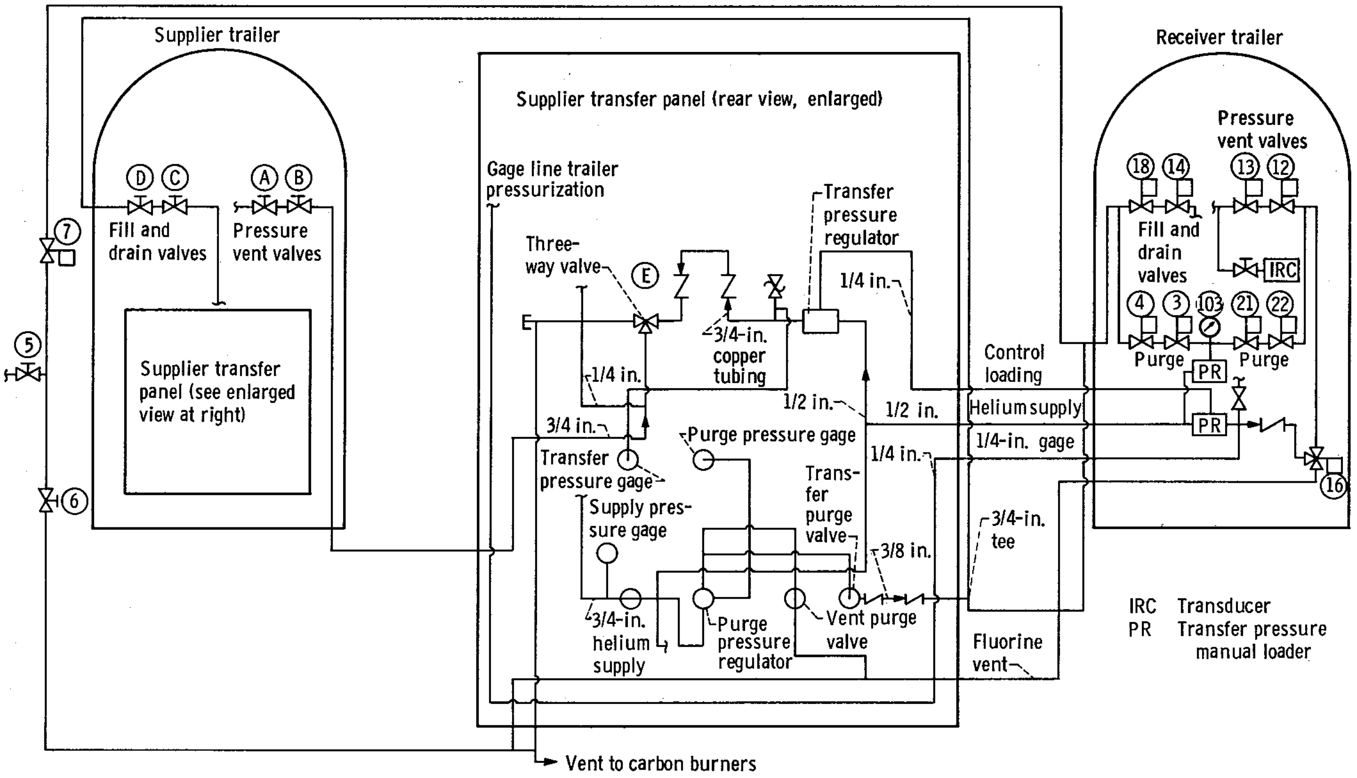


FIGURE 8–1.—Liquid-fluorine transfer valves and gages.

desired, a passivation step may be used at this point according to the general procedure described in section 6.2.4.)

(11) Open all manual lockup valves on transfer, pressurization, and vent systems for both trailers.

(12) Open the three-way valve (16, fig. 8–1) to pressure (vent closed) on the receiver trailer; this permits the fill-and-drain valves (18 and 14) to be operated.

(13) Open the fill-and-drain valves on the receiver trailer, first valve 18 and then valve 14. (With a vacuum in the transfer line, some residual liquid fluorine will be vaporized in the receiver tank with subsequent passivation of the transfer and vent lines.)

(14) Open the pressure-vent valves on the receiver trailer, first valve 12 and then valve 13.

(15) Open the pressure-vent valves on the supplier trailer, first A, then B, then open the three-way valve E to vent. Vent both the supplier and the receiver trailers to about 1 pound per square inch gage.

(16) Open the three-way valve on the supplier trailer, first D and then C. The trailers are now ready for transfer of liquid fluorine.

(17) Adjust the transfer pressurization manual loader to about 3 pounds per square inch gage (enough to provide a slight positive flow of fluorine from the trailer).

(18) After the transfer line has become thoroughly frosted, increase the setting of the transfer pressurization manual loader to about 30 to 50 pounds per square inch gage (30-psig setting will result in transfer of about 2500 lb/hr). Vent the receiver trailer as required to maintain a pressure of about 1 pound per square inch gage.

(19) Monitor the load cell readout (trailer weight) to determine when the transfer is complete; close fill-and-drain valve 14 on the receiver trailer to stop the transfer.

(20) Without delay, perform the following operations: open the three-way valve E to vent to depressurize the supplier trailer; when the pressure decays to about 1 pound per square inch gage, close the pressure-vent valve A, reduce the setting of transfer pressurization manual loader to 1 pound per square inch gage, and then open the pressure-vent valve A and the three-way valve E to the pressurize position.

(21) Open purge valves 3 and 4 to force liquid fluorine in the transfer line back into the supplier trailer until the pressure begins to rise, and then close valves 3 and 4. Close fill-and-drain valve C on the supplier trailer. (A slight positive pressure, 1 to 5 psig, should be kept on both the supplier and the receiver trailers at all times to prevent entrance of contaminants.)

(22) Open valves 6 and 7 in the disposal line to charcoal reactors to purge the transfer line. Operate valves 6 and 7, and 3 and 4 alternately to build up and release pressure in the transfer line for several cycles, then allow purge flow for about 10 minutes.

(23) Ensure that pressure-vent valve 13 is closed with 1 to 5 pounds per square inch gage trapped in the receiver trailer.

(24) With the three-way valve 16 in vent position, open purge valves 21 and 22 to purge the receiver trailer vent line through carbon burners; close pressure-vent valve 12 and purge valves 21 and 22.

(25) Top both the receiver and supplier trailers with liquid nitrogen. Return all manual loaders to zero pound per square inch gage and return all systems to standby condition (close lockup valves, disconnect umbilicals, etc.). Weigh both trailers after all systems have been shut down and all lines have been disconnected. (Extreme care should be taken to ensure cleanliness of mating connectors on transfer lines.)

8.4 MOBILE STORAGE EQUIPMENT MAINTENANCE

A program of maintenance procedures should be set up for all mobile storage systems to ensure that all systems and components are functioning properly and to ensure that over-the-road operation of the equipment is feasible. These maintenance procedures must cover both the fluorine containment and transfer systems, all secondary systems for the fluorine system, the trailer, and the truck running gear. These inspection schedules are set up for the same reason as aircraft check procedures, that is, to minimize the need for unscheduled maintenance and to detect potential troubles before they develop.

8.4.1 Routine Maintenance for Fluorine System

The following general procedures are used in performing routine maintenance on Lewis mobile fluorine storage systems:

(1) All valve bolts and nuts should be retightened to torque specification once a month or after every two transfers.

(2) The alarm system battery should be checked and the horn sounded at least once per week. The battery should be changed every 3 months.

(3) The nitrogen vent valve should be wired in the *open* position at all times. (Check after each nitrogen fill.)

(4) The valve packing nuts should be snugged down as necessary after each use.

(5) All lines and valves must be properly labeled and inspected every 3 months.

(6) The trailer undercarriage should be greased and inspected every 30 days.

(7) The tires should be inspected thoroughly every 30 days.

8.4.2 **Inspection Schedule for Mobile Storage Equipment**

Proper routine inspections should be conducted at all times on fluorine transport equipment by using checklist procedures. Particularly, it is important to ensure proper condition of all equipment in a transfer cycle, and when the equipment is being moved from one location to another. The following check procedures are some that are performed before Lewis storage equipment is moved from one area to another, or as routine checks (ref. 1). Figure 8.2 is a typical checklist for tractor-trailer inspection and trip log showing safeguards and precautions used to monitor in-transit fluorine shipments. Both the checklist and the following list are representative procedures used by drivers at Lewis.

Daily inspections.—On approaching the fluorine Dewar, note any detectable odor in the area. If an odor exists, leave the area and notify the supervisor. If no detectable odor exists, proceed as follows:

(1) Verify that the product pressure gage indicates slightly above zero ($\frac{1}{2}$ to 1 psig.)

(2) Check the nitrogen liquid level gage. It should read no less than three-fourths full. Refill the radiation shield with liquid nitrogen, if necessary.

(3) Check the vacuum on the Dewar annulus. It should read less than 150 microns.

(4) Check nitrogen shield pressure gage. It should read zero. The vent valve should be open.

(5) Check out the alarm system. Depress the fluorine vessel pressure alarm switch. Depress the nitrogen level (in coolant jacket) alarm switch and ensure that both function properly.

(6) Notify the supervisor of any malfunctions or conditions that are out of the ordinary.

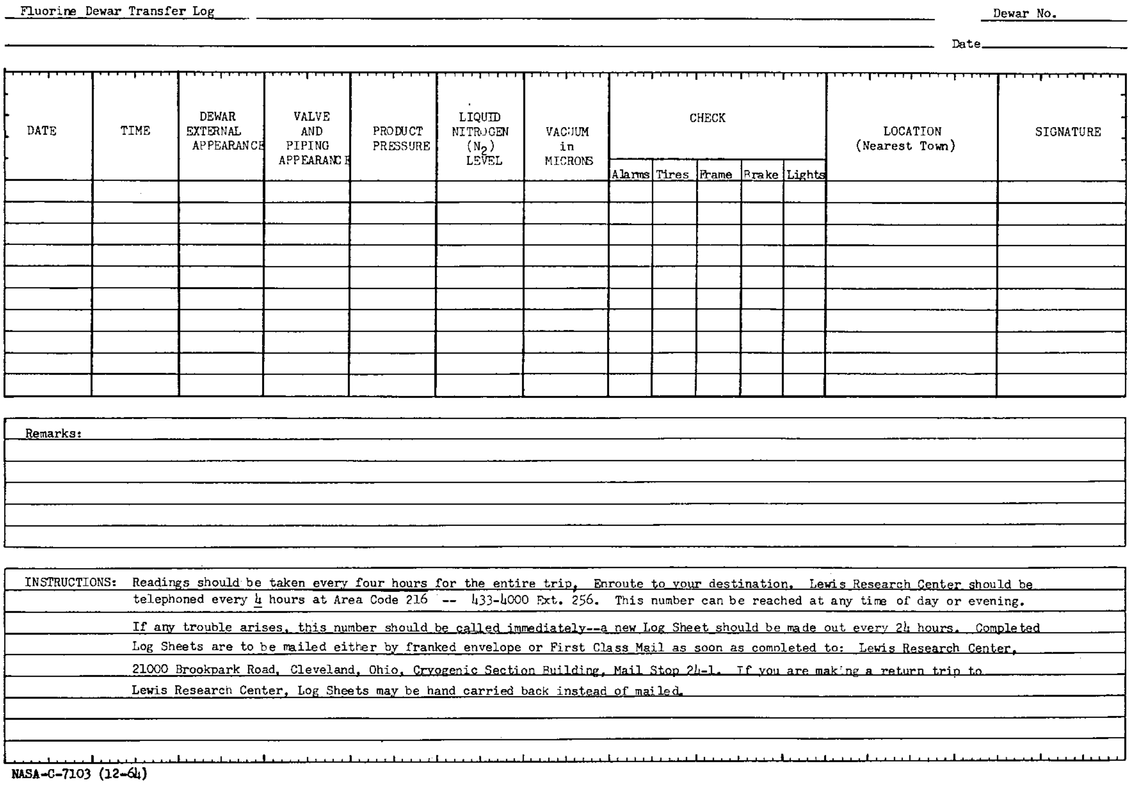
Preshipment check procedure.—Prior to moving the trailer for any pickup or delivery of fluorine, the following procedures are performed:

(1) Check the fluorine vessel pressure gage. It should read slightly above zero ($\frac{1}{2}$ to 1 psig).

(2) Fill the coolant shield to *full* with liquid nitrogen. Weigh the Dewar and record the weight on the check sheet.

(3) Ensure that the vacuum reading is below 150 microns.

(4) Check out the alarm system. Depress the product pressure alarm switch. Depress the liquid-nitrogen-level alarm switch.



Fluorine Dewar Transfer Log ____ Dewar No. ____

Date ____

DATE	TIME	DEWAR EXTERNAL APPEARANCE	VALVE AND PIPING APPEARANCE	PRODUCT PRESSURE	LIQUID NITROGEN (N_2) LEVEL	VACUUM in MICRONS	CHECK					LOCATION (Nearest Town)	SIGNATURE
							Alarms	Tires	Frame	Brake	Lights		

Remarks:

INSTRUCTIONS: Readings should be taken every four hours for the entire trip. Enroute to your destination, Lewis Research Center should be telephoned every 4 hours at Area Code 216 -- 433-4000 Ext. 256. This number can be reached at any time of day or evening.

If any trouble arises, this number should be called immediately--a new Log Sheet should be made out every 24 hours. Completed Log Sheets are to be mailed either by franked envelope or First Class Mail as soon as completed to: Lewis Research Center, 21000 Brookpark Road, Cleveland, Ohio, Cryogenic Section Building, Mail Stop 24-1. If you are making a return trip to Lewis Research Center, Log Sheets may be hand carried back instead of mailed.

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FIGURE 8-2.—Sample Lewis checklist and transfer log for mobile storage equipment.

(5) Ensure that the gaseous nitrogen vent valve is open. The nitrogen shield pressure gage should read zero.

(6) Place the fluorine tank vent and discharge valve knobs in the manual position. Ensure that they are closed and safety-wired in closed position.

(7) Ensure that the vacuum valves (2) are closed and safety-wired in the closed position (0.050 wire).

(8) After the tractor hookups, carry out the tractor and trailer checklist procedures (fig. 8–2).

Destination check.—The following procedures are performed after the trailer is moved from one location to another:

(1) Check the fluorine vessel pressure gage. It should read slightly above zero ($\frac{1}{2}$ to 1 psig).

(2) Check to ensure that the liquid-nitrogen coolant shield level is not less than three-fourths full. Refill with liquid nitrogen as required. Weigh the Dewar and record the weight.

(3) Check to ensure the vacuum on the Dewar outer annulus is less than 150 microns.

(4) Check that the nitrogen shield pressure gage indicates zero pound per square inch gage and that the vent valve is open.

(5) Check out the alarm system by depressing the fluorine vessel pressure alarm switch and nitrogen level alarm switch. Ensure that both function properly.

(6) Ensure that the fluorine tank discharge double valves are in the manual position and wired closed.

(7) Record inspection on check sheet provided on Dewar.

8.4.3 Leak Tests

Fluorine systems, lines, fittings, welded connections, and valves should be checked for leaks basically by using the procedures discussed in chapter 6. Any components that leak should be replaced or repaired. Prior to any disassembly or repair, it must be ensured that the fluorine systems have been emptied and purged.

Leakage between the fluorine tank and liquid-nitrogen annulus can be detected by applying a positive pressure to the fluorine containment vessel and monitoring the boiloff gases from the liquid-nitrogen shell with a halogen leak detector for any sign of fluorine. If the mobile storage tank has been emptied, this test may be performed by applying a positive gaseous fluorine pressure to the fluorine containment vessel. Since this involves working near a system under pressure (though moderate), the operation should only be performed under the direction of a technically competent supervisor, who has evaluated all the hazards and made provisions to prevent any injury to personnel, damage to equipment, or danger to surrounding areas.

Leakage in a vacuum system can be recognized if a good vacuum cannot be maintained. The vacuum system should maintain a good vacuum under normal conditions for an indefinite time.

8.5 IN-TRANSIT EMERGENCY PROCEDURES

If a tank truck transporting fluorine is involved in an accident, the following measures should be taken: The truck should be parked off the roadway if possible; in any event, flares and flags should be set out. Traffic should not be allowed to approach closer than 100 yards. Local police and fire authorities should be notified, but one man should stay with the truck.

If an emergency condition develops in which reaction of tank contents threatens (from rupture, tank leakage, loss of coolant, etc.) causing abandonment of the truck, operators should remove equipment to the most isolated area possible, then

(1) Warn all local emergency crews (fire, police, etc.) that fluorine is involved, and that the immediate area of the truck must be evacuated. Ensure that everyone is kept away from the transport equipment, particularly from downwind areas. In the event of a leak from the fluorine containment vessel into the liquid-nitrogen annulus, with resultant contamination of the nitrogen boiloff, the chief hazard would probably be the toxicity of vapors downwind.

(2) In the event of a system failure resulting in fluorine tank overpressure, such as loss of the liquid-nitrogen and/or vacuum in the heat shields, both explosion and major conflagration could result, and the area of evacuation should be as large as possible (particularly downwind, and at least a 1000-ft radius).

(3) If reaction of the tank contents occurs, ensure that local firefighting personnel are aware that fluorine is involved. While the probability is that no equipment could be brought to bear during the main reaction, fire companies should be warned to withhold attempts to control secondary fires until the fluorine reaction has had adequate time for completion. If water is to be used to fight secondary fires, it should be applied from a maximum distance upwind (to assure clearance from any reaction of water with residual fluorine). Carbon dioxide or chemicals are generally preferred to water.

A discussion of various factors involved in dispersion of spill products is given in section 5.2.4.1. Lewis spill-test results (section 3.4) describe the reactions of various common materials with fluorine in a spill situation.

REFERENCE

1. ANDERSON, ROGER E.: Design Handbook for Liquid Fluorine Ground Handling Equipment. Rept. No. AFRPL-TR-65-133, Second ed., Aerojet-General Corp., Aug. 9, 1965.

Chapter 9. Personnel Safety

The thousands of man hours of rocket testing experience at many fluorine-handling installations with no serious personnel injury has shown that fluorine can be handled safely in large quantities. In almost every case involving some loss of hardware resulting from system failure, the mishap occurred early in the program before the philosophy of scrupulous cleanliness was established and the extreme importance of proper operating procedures was recognized. Experience at these installations, including NASA Plum Brook and Lewis, shows that fluorine facilities can be designed for safe and practical operation. The use of strict safety procedures is, however, a prime requirement in safe facility operation.

While all general safety precautions associated with cryogenic facilities will apply to liquid fluorine or FLOX facilities, the toxic and reactive nature of fluorine requires additional precautions.

9.1 FAMILIARIZATION AND TRAINING

To ensure safe operation, it is necessary to have trained personnel operating the facility. For this reason, a thorough familiarization program must be initiated at each facility to train personnel in use of equipment, safety procedures, and other operations related to their work specialty.

Use of this report should be considered for training personnel for fluorine and FLOX operations. Generally, this training program can be divided into at least four sections:

(1) Training of fabricators
(2) Training of operators
(3) Training of service personnel (firemen, etc.)
(4) Training of medical staff

9.1.1 Training of Fabricators

The training program for fabricators should include a discussion of the basic properties of gaseous and liquid fluorine and recommended fabricating techniques. This program might also include a demonstration of the effect of liquid fluorine or FLOX on water, its effects on metallic materials and noncompatible cloth, paper, leather, greases, and oils.

The importance of cleanliness and freedom from contamination of equipment for fluorine service will then be vividly emphasized.

9.1.2 Training of Operators

The training program for operators should include a detailed coverage of materials, compatibilities, characteristics of liquid and gaseous fluorine and their toxicity, first aid, and safety practices. An examination should be given to be certain that the trainees have absorbed the essential information. The subject should be reviewed periodically to be certain that the information has been retained.

9.1.3 Training of Others

Other personnel who might be required in the facility area in emergencies, such as firemen, safety engineers, and supervisors, should be trained in the procedures for protecting personnel and equipment, giving first aid, and methods of coping with fluorine fires. They should be informed of possible occurrences so that they may prepare operating plans for all credible contingencies.

9.1.4 Training of Medical Staff

The facility medical staff should become thoroughly familiar with recommended procedures for treating FLOX, fluorine, and hydrofluoric acid injuries. The Lewis medical staff then recommends that training, informational material on treatment methodology, and specific medications be made available to nearby community hospital and medical personnel.

The specific treatment of fluorine exposure injuries varies with severity of exposure. The medical staff should categorize these exposures and specify treatments that may be performed by operating facilities personnel. Before any site becomes operational, a medical program should be formulated. (Methods, first-aid practices, and treatments are outlined in section 9.2.4.) More details on specific recommendations for treatment are available to medical personnel through the Lewis Medical Office.

9.2 MEDICAL PROGRAM

9.2.1 Physiological Indications of Fluorine Exposure

Areas where fluorine concentrations are present should always be avoided. If, however, an individual should be caught in such a concentration, he should hold his breath and move *cross-wind* until clear of the contaminated area. Experience of the author indicates that inadvertent inhalation of high concentrations of fluorine is unlikely, since a pulmonary spasm develops at the first intake of the gas, preventing any further intake. If the exposed individual gets clear of the contaminated area quickly, exposure effects could be expected to be slight.

To determine the effects of standardized fluorine concentrations on individuals, a limited series of tests were performed at Lewis. Some subjective results were obtained from these tests, which involved nine males, ranging in age from 25 to 50 years. The following significant results were obtained:

(1) In smell tests on low concentrations, all but one of the subjects were able to detect the odor of fluorine down to 0.11 part per million (ppm), and all could detect it at 0.14 ppm. This is a lower threshold than mentioned by most of the literature on fluorine.

(2) The subjects were about evenly divided in their description of fluorine odor. One group characterized it as "sour" and some thought it smelled much like vinegar; the other group detected no sour odor but variously referred to the odor as "musty," "swampy," or "onion-like".

(3) All subjects agreed that, within the range of 0.11 to 10.00 ppm the level of concentration could not be fixed from the smell.

(4) As concentration was increased, a level was reached at which each individual reported pungency. This level, which varied with each individual, resulted in discomfort in the nasal passages after only two or three breaths and ranged from 18 to 27 ppm.

(5) In skin exposure tests with concentrations from 90 to 240 ppm, exposure times were limited from 1 to 2 minutes. Only one person, who seemed more fluorine-sensitive than the others, noted a slight reddening and burning at the 90-ppm level. At 132 and 240 ppm about half the group felt the sensation of heat together with a feeling of stickiness of the hair in the exposed area. From the skin exposure tests, it is obvious that people will vary widely in their skin reaction to fluorine. For this reason, the sensation of heat cannot be relied on to warn *all* individuals when exposure levels exceed 100 ppm. The feeling of stickiness of body hair will *always* be present, however, in exposures to concentrations over 100 ppm.

9.2.2 Toxic Exposure Limits in Operations

In December 1963, Congress passed a law (ref. 1) designed to promote air-pollution control by various devices. It is the responsibility of facility management and operating personnel to provide clear-cut limits for all operations to conform to requirements of this Act. Some considerations involved in conforming to requirements of the Act are

(1) Notifying and working with local pollution-control authorities (state, county, or municipal control boards for air, soil, or water pollution)
(2) Providing pollution sampling and detection instrumentation and documenting peak and integrated pollution concentrations at the boundaries of the exclusion area and at the facility boundaries
(3) Selecting weather windows that will not permit pollutant drift (of hazardous quantities) downwind into populated areas; taking all precautions to prevent exposure of humans and animals outside the exclusion area
(4) Performing soil and water sampling before and after tests to record and document possible pollution

As part of their advisory function, the National Research Council of the National Academy of Sciences defined Emergency Tolerance Levels (ETL) for exposure to concentrations of fluoride and hydrogen fluoride. Preliminary information from studies being conducted by the University of Miami to arrive at final ETL values indicates that these values (table 9-I) are conservative. The value for ETL is nonoccupational; that is, it is an exposure level that would be rare in the working career of the individual.

Reference 2 states "It is recognized that both occupational and nonoccupational exposures can occur at predictable intervals when they can in no sense be considered to be accidents. An example is the static test

Table 9-I.—Emergency Tolerance Limits (ETL) for Fluorine or Hydrogen Fluoride Exposure

Exposure time, min	ETL, ppm [a]
Fluorine	
5	5.0
15	3.0
30	2.0
60	1.0
Hydrogen fluoride	
5	30
15	20
30	10
60	8

[a] By volume.

firing of samples of production batches of rocket propellants. There is no justification for submitting individuals to any appreciable risk in predictable exposure. Advance provisions should be made to control the exposure of employees by limits on quantities and distances, by physical security, and by personal protective equipment." Safety can be further enhanced by selection of proper weather windows (refer to section 5.2.4) to assure optimum diffusion of any toxic releases.

9.2.3 Preventive Medicine

A major part of the medical program for fluorine exposure at Lewis is devoted to preventive medicine. To this end, medical histories are maintained on individuals who will be handling or be exposed to fluorine, hydrogen fluoride, or FLOX. In the beginning of the fluorine program at Lewis, medical history bases were built up by frequent repetitions of physical examinations. Major tests and their frequency of repetition are shown in table 9-II. To establish confidence and to develop reliable early medical histories on personnel, it is recommended that a shorter interval between examinations be used in the early stages of the program. Table 9-II lists routine examinations; results are maintained on the individual medical history cards. If any irregularities are disclosed in the examinations, the individual should be reexamined at short intervals, as determined by the physician.

TABLE 9-II.—FREQUENCY OF MEDICAL EXAMINATIONS

Examination	Internal	
	Original	Present
CBC,[a] differential blood, urinalysis	4 Months	Yearly
Complete physical	6 Months	Yearly
Chest X-rays	Yearly	2 Years
Pelvic X-rays[b]	3 Years	3 Years

[a] Blood count.

[b] For chronically exposed employees only.

The following rules apply to personnel working in areas where fluorine or fluorine componds are handled:

(1) No worker with a doubtful chest X-ray, or one who is suffering from asthma or other pulmonary complaint, or from cardiovascular disease, should be employed in any operations where exposure to fluorine or its compounds is involved. Excess inhalation of gaseous fluorine results in pulmonary edema. Individuals having respiratory or respiratory-involved ailments would have greatly lessened chances

for survival if exposed to excessive fluorine concentrations.

(2) Any employee working in a fluorine area should be included in the list for periodic medical checkups.

(3) All employees working with fluorine or potentially hazardous fluorine compounds must be thoroughly grounded in first-aid procedures, emergency facilities available (location and use), and emergency procedures to be followed in the event of a fluorine exposure.

9.2.4 **Emergency Treatment (First Aid)**

Whenever any person is exposed to fluorine or hydrogen fluoride impingement, perform the following immediately (ref. 3) (*speed is essential in this part of the emergency treatment*):

(1) Remove the patient from the area of fluorine contamination to an area that includes water deluge (shower, eyewash, etc.) facilities.

(2) Drench the affected part of the body (including the eyes, if exposure is suspected) with water. While the patient is under the water flow, remove clothing that might have become contaminated. Continue flushing for at least 15 minutes.

(3) Perform the applicable first-aid procedure given subsequently. *Ensure that the medical department has been notified and that competent medical help is enroute, or transport the patient to the nearest medical center.*

9.2.4.1 *Major external surface (skin) exposure to fluorine. (ref. 3).*—When exposure of the skin has been to fluorine concentrations above 100 to 200 ppm (table 9-III), the following additional treatment should be carried out:

(1) *Provide for prompt medical attention by a physician.*

(2) Continue flushing affected skin, as stated in the emergency procedure, for a sufficient period to ensure removal of all hydrofluoric acid from the skin, a minimum of 15 minutes.

(3) Apply a cold saturated solution of magnesium sulfate (epsom salts) or cold 7-percent alcohol to the affected surface for at least 30 minutes. If the burn is in an area that cannot be immersed in the solution, apply the solution with compresses, changing compresses at least once every 2 minutes.

(4) Following the 30-minute (minimum) soaking in solution, apply magnesium hydroxide water paste liberally to the affected area using pressure bandages to ensure complete contact with the burned areas. Keep the bandages moistened. Usually this treatment will aid in relieving the condition, and will reduce the severity of the burn.

9.2.4.2 *Contact with eyes (ref. 3).*—If it is suspected that fluorine or hydrofluoric acid has entered the eyes, or if the eyes have been exposed to strong concentrations of the vapor, they should be irrigated immediately with clean water. (Arrange for medical care by a physician as soon as possible.) This irrigation should be continuous for a minimum of 15 minutes, with the eyelids held apart during the irrigation to ensure contact of water with all tissues of the surface of the eyes and lids. The eye irrigation may be continued for a second period of 15 minutes. Fluorine in the eyes requires additional irrigation with a 3-percent boric acid solution, but this and subsequent treatment should be directed by an ophthalmologist. Under no circumstances should ointments be applied either to the eyes or skin by unqualified personnel.

9.2.4.3 *Inhalation (ref. 3)*.—An individual who has been overcome by gaseous fluorine or hydrofluoric acid must be carried at once into an uncontaminated atmosphere. It is very urgent that a physician be called immediately, and *if a trained attendant is available, the administration of oxygen should be started at once.*

Oxygen inhalation must be continued as long as necessary in order to maintain the normal color of the skin and mucous membranes. In cases of severe exposure, the patient should breathe 100-percent oxygen under positive exhalation pressure for $\frac{1}{2}$-hour periods every hour for at least 3 hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color is good, oxygen inhalation may be discontinued. Throughout this time the patient should be kept comfortably warm, and at complete rest. The patient should be kept under observation until released by a physician.

9.3 PROTECTIVE CLOTHING AND EQUIPMENT

The Lewis policy on use of protective clothing and equipment (breathing gear, etc.), which has proved effective in its more than 15 years of safe operation with fluorine systems, can be summed up in one sentence: *use protective equipment only when it improves safety.*

Table 9-III gives various conditions and recommended clothing or apparatus to be worn or used in each condition. These practices are recommended for use at any fluorine or FLOX-using facility.

The main hazards involved in handling fluorine are

(1) Inhalation of fluorine or hydrogen fluoride contaminated air over a prolonged period
(2) Accidental exposure to high concentrations of the gas
(3) Accidental contact or impingement of liquid or gaseous fluorine on the body

If anyone detects a leak while working with fluorine, he should leave the area within a maximum of 15 minutes if a fluorine odor persists. In practice, the most effective and reliable fluorine detector has

TABLE 9-III.—RECOMMENDED SAFETY CLOTHING AND EQUIPMENT

When the condition is, or is expected to be, one in which—	Wear the following equipment: [a]
There is no odor of fluorine (less than 0.10 ppm fluorine in air)	Common work clothes
Fluorine can be smelled, but does not irritate the nose (0.10 to 15 ppm fluorine in air)	Easily removable plastic gloves, face shield, cloth head covering, work clothes; avoid staying in the area longer than ½ hour
Fluorine irritates the nose, but does not affect the skin or hair (15 to 100 ppm fluorine in air)	Filtered-air mask or portable air supply, easily removable plastic gloves, face shield, cloth or plastic head covering, and loose-fitting plastic jacket; minimize time in the area
Fluorine warms the skin and makes body hair sticky (above 100 ppm fluorine in air)	Full safety suit (preferably made of a fluoropolymer) and breathing-air supply
Rescue, standby, or accident surveillance as needed	Full safety suit and breathing air supply

[a] Comfortable footgear does not exist which would give protection against fluorine splash, impingement, or cryogenic puddles. Common work shoes are considered appropriate protection for the feet. Routine precautions should be followed to prevent spilling any cryogenic fluid into pockets, on shoe tops, sleeves, etc.

proved to be the human nose. Fluorine has such a sharp, penetrating odor that inhalation of toxic quantities is unlikely unless the individual is trapped in a location from which escape is impossible. If the fluorine odor is irritating to the nasal passages, this indicates a sizeable leak and the area should be evacuated immediately.

A fluorine burn on the skin should be treated as a combination chemical and thermal burn. If the exposure is slight, several hours may elapse before the patient is conscious of pain or injury. The fluorine-exposure area first becomes reddened, then swollen and pale with a macerated appearance that is accompanied by a severe throbbing pain. Adequate treatment will usually stop pathological changes at this stage. Without treatment, necrosis and ulceration may occur in severe cases (ref. 3).

It is important that treatment be given at once for any exposures or suspected exposures to spills or excess concentrations of gas. First aid procedures are included in section 9.2.4.

Buildup of fluorine facilities, or the maintenance and repair of such systems that have been inerted, requires no special clothing other than everyday work clothes. Remotely charged and operated facilities are manipulated by personnel in standard clothes, except for those personnel involved in the connection and manual valve operation of the fluorine supply. This function requires only a face shield[1] and gloves (TFE cloth impregnated with TFE, or other fluorinated polymer[2]) for protection from fluorine "puffs" when removing tubing caps, or other similar occurrences. High-pressure gaseous systems that are manually operated must be provided with barriers and shielding for protection, which, in most cases, eliminates the need for additional protective clothing. All protective clothing should be designed for rapid and easy removal, in case a fluorine or FLOX impingement should penetrate the body covering. When breaking into a system that has contained fluorine or FLOX, the mechanic should wear

(1) A transparent plastic full face shield[1] over a head covering of cloth or plastic
(2) Gloves made of TFE cloth impregnated with TFE, or one of the other fluorinated polymers,[2] designed for easy removal by vigorous arm movements
(3) A jacket, or similar covering, also made of TFE cloth impregnated with TFE or one of the other fluorinated polymers (also designed for ready removal[1])

If fumes cannot be avoided or if exposure is prolonged, filtered breathing air from a supply tank or a portable breathing apparatus, with self-contained supply tank and face mask, is required. With the philosophy of "controlled" fluorine exposure established, the requirements for protective clothing can be evaluated realistically. The use of protective clothing should be limited strictly to those conditions where it affords protection. *Extravagant use of protective clothing may provide a false sense of security, while in fact being only a physical hindrance.*

9.3.1 **Safe Work Practices**

Maintenance and repair functions provide the greatest risk potential for hazardous exposure to fluorine concentrations. This risk can be eliminated by use of remote deactivation, depressurization, purging, and general system inerting; by use of "system-wise" personnel only; and by *supplemental* use of appropriate protective clothing and equipment.

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[1] Face shields will not provide protection against a high-velocity impingement of fluorine. While amyl butyrate has been used for face shields, another material, Aclar, a film made from fluorohalocarbon, is preferred.

[2] While the TFE cloth is preferred, neoprene is also suitable for protection against inadvertent exposure to dilute puffs of fluorine or FLOX gas.

Normal fluorine exposures are limited to residual vapors in lines, tanks, or components that are being disconnected for maintenance, removal, or repair. In unusual circumstances, personnel may be exposed to a fluorine-contaminated area performing inspection *after* assurance of adequate safety has been determined. If fluorine gas is present and system inspection, adjustment, maintenance or repair is required, a recommended routine handling procedure might include

(1) Close isolation valves to isolate the system from fluorine, FLOX, and liquid oxygen storage areas.

(2) Open system exhaust lines to permit fluorine in lines to flow into charcoal reactor disposal system.

(3) Purge the system with dry helium or nitrogen gas.

(4) Verify that the fluorine and FLOX storage areas have been isolated. The facility is not to be approached until the fluorine and FLOX are isolated in no-loss containers (normally liquid-nitrogen-jacketed Dewars) pressurized at less than 10 pounds per square inch gage.

(5) Two or more persons (as required in the maintenance operation to be performed) should be equipped as follows:

> (a) The wearing of loose fitting plastic jacket, gloves, and plastic face shield (over standard cloth headgear) is preferred.
>
> (b) If high concentrations (table 9-III) are suspected, a self-contained breathing apparatus should be carried, to be worn under the plastic face shield. As noted in item (6), this breathing apparatus would not be worn initially, but would be applied to the face and used only when the breathing environment required it.

(6) Whenever any maintenance operation is carried out on a fluorine or FLOX system, at least one person should be completely equipped with full safety suit and air pack and stationed on rescue standby where he can observe the maintenance operation being performed. Personnel performing the maintenance may now approach the system. Detection of fluorine is as follows:

> (a) The sense of smell is used in determining the presence of fluorine during the approach to the facility system; detection devices may be used to *supplement* this method. If the odor of fluorine becomes annoying or irritating to the nose (about 18 to 27 ppm) the air-pack breathing apparatus should be donned before proceeding.
>
> (b) Since the body is not completely covered, the next concentration plateau for fluorine can be felt on the exposed skin of the body (up the sleeve, back of the neck, etc.), which will begin to feel warm at 90 to 240 ppm concentrations. At the same time, the exposed hair on the head and arms will feel sticky. If this concentration is ob-

served during the maintenance operation, or if monitoring instrumentation indicates fluorine or hydrogen fluoride in excess of 90 to 240 ppm, personnel should evacuate the area immediately, and remain clear until the concentration is reduced to a safe level (by dissipation or by operation of exhaust systems in enclosed areas). Personnel exposed to these concentrations (100 to 200 ppm) for over a few minutes will experience minor skin irritation, itching, and subsequent sunburn effect. To limit this aftereffect, exposed personnel should immediately flush exposed skin areas with water.

(c) Concentrations above the 90 to 240 ppm level are to be avoided under all circumstances, and exposure to excess concentrations should be handled as directed in section 9.2. Anyone caught in a toxic concentration (without self-contained breathing apparatus) should immediately hold his breath and move *crosswind* as rapidly as possible until clear of the contamination.

Good general safety practice is required at all times at fluorine or FLOX facilities. Eyewash facilities, showers, and appropriate first-aid equipment must be maintained accessible and operational. Personal cleanliness, cleanliness of tools, and cleanliness of work areas should be both rule and habit. This type of cleanliness is as vital to personnel safety as it is to the safe operation of the fluorine or FLOX facility.

In transporting, transfer, and storage of fluorine and FLOX, certain safety precautions must be observed to minimize risks. Personnel can prevent any major burnout by following established rules, regulations, and work practices, concentrating on their assignments, and by double checking each operation performed during facility operation.

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APPENDIX

TEMPERATURE INTERCONVERSIONS

	ΔT				
°K, °C ------	1	2	3	4	5
°R, °F ------	1.8	3.6	5.4	7.2	9.0
°K, °C ------	6	7	8	9	10
°R, °F ------	10.8	12.6	14.4	16.2	18.0

	ΔT								
°R, °F ------	1	2	3	4	5	6	7	8	9
°K, °C ------	0.56	1.11	1.67	2.22	2.78	3.33	3.89	4.44	5.00
°R, °F ------	10	11	12	13	14	15	16	17	18
°K, °C ------	5.56	6.11	6.67	7.22	7.78	8.33	8.89	9.44	10.00

°K	°C	°F	°R
0	—273.16	—459.69	0
3.16	—270	—454.00	5.69
5.38	—267.78	—450	9.69
5.55	—267.61	—449.69	10
10	—263.16	—441.69	18.00
10.94	—262.22	—440	19.69
11.11	—262.05	—439.69	20
13.16	—260	—436.00	23.69
16.40	—256.67	—430	29.69
16.67	—256.49	—429.69	30
20	—253.16	—423.69	36.00
22.05	—251.11	—420	39.69
22.22	—250.94	—419.69	40
23.16	—250	—418.00	41.69
27.60	—245.56	—410	49.69
27.73	—245.38	—409.69	50
30	—243.16	—405.69	54.00
33.16	—240	—400	59.69
33.33	—239.83	—399.69	60
33.72	—234.44	—390	69.69
38.89	—234.27	—389.69	70
40	—233.16	—387.69	72.00
43.16	—230	—382.00	77.69

Temperature Interconversions—Continued

	ΔT				
°K, °C ------	1	2	3	4	5
°R, °F ------	1.8	3.6	5.4	7.2	9.0
°K, °C ------	6	7	8	9	10
°R, °F ------	10.8	12.6	14.4	16.2	18.0

	ΔT								
°R, °F ------	1	2	3	4	5	6	7	8	9
°K, °C ------	0.56	1.11	1.67	2.22	2.78	3.33	3.89	4.44	5.00
°R, °F ------	10	11	12	13	14	15	16	17	18
°K, °C ------	5.56	6.11	6.67	7.22	7.78	8.33	8.89	9.44	10.00

°K	°C	°F	°R
44.27	—228.89	—380	79.69
44.44	—228.72	—379.69	80
49.83	—223.33	—370	89.69
50	—223.16	—369.69	90
53.16	—220	—364.00	95.69
55.33	—217.73	—360	99.69
55.56	—217.60	—359.69	100
60	—213.16	—351.69	108.00
60.94	—212.22	—350	109.69
61.11	—212.05	—349.69	110
63.16	—210	—346.00	113.69
66.49	—206.67	—340	119.69
66.67	—206.49	—339.69	120
70	—203.16	—333.69	126.00
72.05	—201.11	—330	129.69
72.22	—200.94	—329.69	130
73.16	—200	—328.00	131.69
77.60	—195.56	—320	139.69
77.78	—195.38	—319.69	140
80	—193.16	—315.69	144.00
83.16	—190	—310	149.69
83.33	—189.83	—309.69	150
88.72	—184.44	—300	159.69
88.89	—184.27	—299.69	160
90	—183.16	—297.69	162.00
93.16	—180	—292.00	167.69
94.27	—178.89	—290	169.69
94.44	—178.72	—289.69	170
99.83	—173.33	—280	179.69
100	—173.16	—279.69	180
103.16	—170	—274.00	185.69
105.38	—167.38	—270	189.69

Temperature Interconversions—Continued

°K	°C	°F	°R
105.56	—167.60	—269.69	190
110	—163.16	—261.69	198.00
110.96	—162.20	—260	199.69
111.11	—162.05	—259.69	200
113.16	—160	—256.00	203.69
116.49	—156.67	—250	209.69
116.67	—156.49	—249.69	210
120	—153.16	—243.69	216.00
122.05	—151.11	—240	219.69
122.22	—150.94	—239.69	220
123.16	—150	—238.00	221.69
127.60	—145.38	—230	229.69
127.78	—145.38	—229.69	230
130	—143.16	—225.69	234.00
133.16	—140	—220	239.69
133.33	—139.83	—219.69	240
138.72	—134.44	—210	249.69
138.89	—134.27	—209.69	250
140	—133.16	—207.59	252.00
143.16	—130	—202.00	257.69
144.27	—128.89	—200	259.69
144.44	—128.62	—199.69	260
149.83	—123.33	—190	269.69
150	—123.16	—189.69	270
153.16	—120	—184.00	275.69
155.33	—117.73	—180	279.69
155.56	—117.60	—179.69	280
160	—113.16	—171.69	288.00
160.94	—112.22	—170	289.69
161.11	—112.05	—169.69	290
163.16	—110	—166.00	293.69
166.49	—106.67	—160	299.69
166.67	—106.49	—159.69	300
170	—103.16	—153.69	306.00
172.05	—101.11	—150	309.69
172.22	—100.94	—149.69	310
173.16	—100	—148.00	311.69
177.60	—95.56	—140	319.69
177.78	—95.38	—139.69	320
180	—93.16	—135.69	324.00
183.16	—90	—130	329.69
183.33	—89.83	—129.69	330
188.72	—84.44	—120	339.69
188.89	—84.27	—119.69	340
190	—83.16	—117.69	342.00
193.16	—80	—112.00	347.69
194.27	—78.89	—110	349.69
194.44	—78.72	—109.69	350
199.83	—73.33	—100	359.69

Temperature Interconversions—Continued

	ΔT				
°K, °C ------	1	2	3	4	5
°R, °F ------	1.8	3.6	5.4	7.2	9.0
°K, °C ------	6	7	8	9	10
°R, °F ------	10.8	12.6	14.4	16.2	18.0

	ΔT								
°R, °F ------	1	2	3	4	5	6	7	8	9
°K, °C ------	0.56	1.11	1.67	2.22	2.78	3.33	3.89	4.44	5.00
°R, °F ------	10	11	12	13	14	15	16	17	18
°K, °C ------	5.56	6.11	6.67	7.22	7.78	8.33	8.89	9.44	10.00

°K	°C	°F	°R
200	—73.16	—99.69	360
203.16	—70	—94.00	365.69
205.33	—67.78	—90	369.69
205.56	—67.60	—89.99	370
210	—63.16	—81.69	378.00
210.94	—62.22	—80	379.69
211.11	—62.05	—79.69	380
213.16	—60	—76.00	383.69
216.41	—56.67	—70	389.69
216.67	—56.49	—69.69	390
220	—53.16	—63.69	396.00
222.05	—51.11	—60	399.69
222.22	—50.94	—59.69	400
223.16	—50	—58.00	401.69
227.60	—45.56	—50	409.69
227.78	—45.38	—49.69	410
230	—43.16	—45.69	414.00
233.16	—40	—40	419.69
233.33	—39.83	—39.69	420
238.72	—34.44	—30	429.69
238.89	—34.27	—29.69	430
240	—33.16	—27.69	432.00
243.16	—30	—22.00	437.69
244.27	—28.89	—20	439.69
244.44	—28.72	—19.69	440
249.83	—23.33	—10	449.69
250	—23.16	—9.69	450
253.16	—20	—4.00	455.69
255.38	—17.78	0	459.69
255.56	—17.60	.31	460
260	—13.16	8.31	468.00
260.94	—12.22	10	469.69
261.11	—12.05	10.31	470

Temperature Interconversions—Continued

°K	°C	°F	°R
263.16	—10	14.00	473.69
266.49	—6.67	20	479.69
266.67	—6.49	20.31	480
270	—3.16	26.31	486.00
272.05	—1.11	30	489.69
272.22	—.94	30.31	490
273.16	0	32.00	491.69
277.60	4.44	40	499.69
277.78	4.62	40.31	500
280	6.84	44.31	504.00
283.16	10	50	509.69
283.33	10.17	50.31	510
288.72	15.56	60	519.69
288.89	15.73	60.31	520
290	16.84	62.31	522.00
293.16	20	68.00	527.69
294.27	21.11	70	529.69
294.44	21.28	70.31	530
299.83	26.67	80	539.69
300	26.84	80.31	540
303.16	30	86.00	545.69
305.38	32.22	90	549.69
305.56	32.40	90.31	550
310	36.84	98.31	558.00
310.94	37.78	100	559.69
311.11	37.95	100.31	560
313.16	40	104.00	563.69
316.41	43.33	110	569.69
316.67	43.51	110.31	570
320	46.84	116.31	576.00
322.05	48.89	120	579.69
322.22	49.06	120.31	580
323.16	50	122.00	581.69
327.60	54.44	130	589.69
327.78	54.62	130.31	590
330	56.84	134.31	594.00
333.16	60	140	599.69
333.33	60.17	140.31	600
338.72	65.56	150	609.69
338.89	65.73	150.31	610
340	66.84	152.31	612.00
343.16	70	158.00	617.69
344.27	71.11	160	619.69
344.44	71.28	160.31	620
349.83	76.67	170	629.69
350	76.84	170.31	630
353.16	80	176.00	635.69
355.38	82.22	180	639.69
355.56	82.40	180.31	640

Temperature Interconversions—Concluded

	ΔT				
°K, °C ______	**1**	**2**	**3**	4	5
°R, °F ______	1.8	3.6	5.4	7.2	9.0
°K, °C ______	6	7	8	9	10
°R, °F ______	10.8	12.6	14.4	16.2	18.0

	ΔT								
°R, °F ______	1	2	3	4	5	6	7	8	9
°K, °C ______	0.56	1.11	1.67	2.22	2.78	3.33	3.89	4.44	5.00
°R, °F ______	10	11	12	13	14	15	16	17	18
°K, °C ______	5.56	6.11	6.67	7.22	7.78	8.33	8.89	9.44	10.00

°K	°C	°F	°R
360	86.84	188.31	648.00
360.94	87.78	190	649.69
361.11	87.95	190.31	650
363.16	90	194.00	653.69
366.49	93.33	200	659.69
366.67	93.51	200.31	660
370	96.84	206.31	666.00
372.05	98.89	210	669.69
372.22	99.06	210.31	670
373.16	100	212.00	671.69
377.60	104.44	220	679.69
377.78	104.62	220.31	680
380	106.84	224.31	684.00
383.16	110	230	689.69
383.33	110.17	230.31	690
388.72	115.56	240	699.69
388.89	115.73	240.31	700
390	116.84	242.31	702.00
393.16	120	248.00	707.69
394.27	121.11	250	709.69
394.44	121.28	250.31	710
399.83	126.67	260	719.69
400	126.84	260.31	720

Conversion Factors for Length

cm	mm	μ	mμ	Å
1	10	10^{4}	10^{7}	10^{8}
10^{-1}	1	10^{3}	10^{6}	10^{7}
10^{-4}	10^{-3}	1	10^{3}	10^{4}
10^{-7}	10^{-6}	10^{-3}	1	10
10^{-8}	10^{-7}	10^{-4}	10^{-1}	1

cm	m	in.	ft
1	0.01	0.3937	0.032808333
100	1	39.37	3.2808333
2.5400051	0.025400051	1	0.083333333
30.480061	0.30480061	12	1

Conversion Factors for Area

cm^2	m^2	sq in.	sq ft
1	10^{-4}	0.15499969	1.0763367×10^{-3}
10^{4}	1	1549.9969	10.763867
6.4516258	6.4516258×10^{-4}	1	6.9444444×10^{-3}
929.03412	0.092903412	144	1

Conversion Factors for Volume

cm^3	cu in.	cu ft	ml	liter	gal
1	0.061023378	3.5314455×10^{-5}	0.9999720	0.9999720×10^{-3}	2.6417047×10^{-4}
16.387162	1	5.7870370×10^{-4}	16.38670	1.638670×10^{-2}	4.3290043×10^{-3}
28317.017	1728	1	28316.22	28.31622	7.4805195
1.000028	0.06102509	3.531544×10^{-5}	1	0.001	2.641779×10^{-4}
1000.028	61.02509	0.03531544	1000	1	0.2641779
3785.4345	231	0.13368656	3785.329	3.785329	1

Conversion Factors for Pressure

dyne/cm^2	bar	atm	kg(wt)/cm^2	mm Hg[a]	in. Hg[a]	lb(wt)/sq in.
1	10^{-6}	0.9869233×10^{-6}	1.0197162×10^{-6}	7.500617×10^{-4}	2.952993×10^{-5}	1.4503830×10^{-5}
10^6	1	0.9869233	1.0197162	750.0617	29.52993	14.503830
1013250	1.013250	1	1.0332275	760	29.92120	14.696006
980665	0.980665	0.9678411	1	735.5592	28.95897	14.223398
1333.2237	1.3332237×10^{-3}	1.3157895×10^{-3}	1.3595098×10^{-3}	1	0.03937	0.019336850
33863.95	0.03386395	0.03342112	0.03453162	25.40005	1	0.4911570
68947.31	0.06894731	0.06804570	0.07030669	51.71478	2.036009	1

[a] At 0° C.

CONVERSION FACTORS FOR ENERGY

abs J	int. J	cal	t.[a] cal	Btu	int. kWhr	ft-lb(wt)	liter-atm	hp-hr
1	0.999835	0.239006	0.238849	0.947831×10^{-3}	2.77732×10^{-7}	0.737561	9.86896×10^{-3}	3.72505×10^{-7}
1.000165	1	0.239045	0.238889	0.947988×10^{-3}	2.777778×10^{-7}	0.737682	9.87058×10^{-3}	3.72567×10^{-7}
4.1840	4.1833	1	0.999346	3.96573×10^{-3}	1.162030×10^{-6}	3.08595	4.12917×10^{-2}	1.558562×10^{-6}
4.18674	4.18605	1.000654	1	3.96832×10^{-3}	1.162791×10^{-9}	3.08797	4.13187×10^{-2}	1.559582×10^{-6}
1055.040	1054.866	252.101	251.996	1	2.93018×10^{-4}	778.156	10.41215	3.93008×10^{-4}
3 600 594	3 600 000	860 563	860 000	3412.76	1	2 655 656	35534.1	1.341241
2 684 525	2 684 082	641 617	641 197	2544.48	0.745578	1 980 000	26493.5	1
1.355821	1.355597	0.324049	0.323837	1.285089×10^{-3}	3.76555×10^{-7}	1	1.338054×10^{-2}	5.05051×10^{-7}
101.3278	101.3111	24.2179	24.2021	0.0960417	2.81420×10^{-5}	74.7354	1	3.77452×10^{-5}

[a] Thermochemical.

CONVERSION FACTORS FOR MASS

g	kg	lb	metric ton	ton
1	10^{-3}	2.2046223×10^{-3}	10^{-6}	1.1023112×10^{-6}
10^{3}	1	2.2046223	10^{-3}	1.1023112×10^{-3}
453.59243	0.45359243	1	4.5359234×10^{-4}	5×10^{-4}
10^{6}	10^{3}	2204.6223	1	1.1023112
907184.86	907.18486	2000	0.90718486	1

CONVERSION FACTORS FOR SPECIFIC HEAT

cal/(g)(°K)	J/(g)(°K)	W-sec/(g)(°K)	Btu/(lb)(°R)
1	4.1840	4.1840	0.9995826
0.239006	1	1	0.238849
1.000654	4.18674	4.18674	1

CONVERSION FACTORS FOR ENTHALPY

cal/g	J/g	W-sec/g	Btu/lb
1	4.1840	4.1840	1.798823
0.239006	1	1	0.429929
0.555919	2.32597	2.32597	1

Conversion Factors for Density

g/cm^3	$g/in.^3$	kg/gal	kg/ft^3	lb/gal	lb/ft^3
1	16.3872	3.78543	28.3170	8.34545	62.4283
0.0610232	1	0.23100	1.72800	0.509268	3.80959
0.264171	4.32900	1	7.48052	2.20462	16.4917
0.0353145	0.578704	0.133681	1	0.294715	2.20462
0.119826	1.96360	0.453592	3.39311	1	7.48052
0.0160184	0.262496	0.0606365	0.453592	0.133681	1

Conversion Factors for Surface Tension

dyne/cm	erg/cm^2	mg/mm	mg/in.	lb/ft
1	1	0.10197	2.5901	6.853×10^{-5}
9.80665	9.80665	1	25.400051	6.72×10^{-4}
0.38609	0.38609	0.03937	1	2.6459×10^{-5}
14592.15	14592.15	1488	37794	1

Conversion Factors for Viscosity [a]

[b]poise	[c](lb force)(sec)/ft^2	lb mass/ft-sec
1	2.0886×10^{-3}	0.0672
4.788×10^2	1	32.174
14.9	3.108×10^{-2}	1

[a] Absolute viscosity; kinematic viscosity = absolute viscosity/density.

[b] Poise = 1 (dyne) (sec)/cm^2 = 1 g/(cm)(sec).

[c] 1 (lb force)(sec)/ft^2 = 1 slug/ft-sec.

CONVERSION FACTORS FOR THERMAL CONDUCTIVITY

$\frac{(\mathrm{W})(\mathrm{cm})}{(\mathrm{cm}^2)(^\circ\mathrm{K})}$	$\frac{(\mathrm{W})(\mathrm{in.})}{(\mathrm{in.}^2)(^\circ\mathrm{F})}$	$\frac{(\mathrm{cal})(\mathrm{cm})}{(\mathrm{sec})(\mathrm{cm}^2)(^\circ\mathrm{K})}$	$\frac{(\mathrm{Btu})(\mathrm{in.})}{(\mathrm{hr})(\mathrm{ft}^2)(^\circ\mathrm{F})}$	$\frac{(\mathrm{Btu})(\mathrm{ft})}{(\mathrm{hr})(\mathrm{ft}^2)(^\circ\mathrm{F})}$	$\frac{(\mathrm{Btu})(\mathrm{in.})}{(\mathrm{sec})(\mathrm{in.}^2)(^\circ\mathrm{F})}$	$\frac{(\mathrm{Btu})(\mathrm{in.})}{(\mathrm{hr})(\mathrm{in.}^2)(^\circ\mathrm{F})}$
1	1.411	0.2389	6.9340×10^{2}	57.79	1.338×10^{-3}	4.816
0.7087	1	0.1693	4.914×10^{2}	40.95	9.480×10^{-4}	3.413
4.1858	5.907	1	2.9027×10^{3}	2.419×10^{2}	5.602×10^{-3}	20.16
1.442×10^{-3}	2.035×10^{-3}	3.445×10^{-4}	1	8.33×10^{-2}	1.929×10^{-6}	6.944×10^{-3}
1.730×10^{-2}	2.442×10^{-2}	4.135×10^{-3}	12	1	2.315×10^{-5}	8.33×10^{-2}
7.4738×10^{2}	1.0548×10^{3}	1.785×10^{2}	5.184×10^{5}	4.3191×10^{4}	1	3.600×10^{3}
0.2076	0.2930	4.960×10^{-2}	1.44×10^{2}	12	2.778×10^{-4}	1

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[Numbers in parentheses refer to sections.]

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