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RFP-1739

September 13, 1971

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INVESTIGATION OF FLUORINE INTERACTIONS WITH COMMON
GLOVEBOX CONSTRUCTION MATERIALS

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Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

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Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

September 13, 1971
Publication Date

RFP-1739
UC-38 ENGINEERING
AND EQUIPMENT
TID-4500 - 56th Ed.

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INVESTIGATION OF FLUORINE INTERACTIONS WITH COMMON GLOVEBOX CONSTRUCTION MATERIALS

Louis J. Meile and Ralph O. Wing

Abstract. The interactions between common glovebox construction materials and fluorine gas (F_2) were investigated to ascertain the potential safety hazards of handling high pressure fluorine within a glovebox system. Construction materials from volatile-fluoride, plutonium recovery gloveboxes at Rocky Flats Plant were tested in various fluorine and air mixtures at concentrations of 1 to 100 percent. All of the materials tested remained stable in fluorine concentrations of 10 percent, which is the calculated maximum anticipated in the event of a major fluorine release within the prototype gloveboxes. Many test materials spontaneously ignited in fluorine concentrations exceeding 25 percent. Combustion spread rapidly between close-proximity test samples in a fluorine atmosphere. Data reported are for static gas conditions at specified temperatures. Conclusions are given with a list of recommendations for use of fluorine within a glovebox system.

INTRODUCTION

The volatile fluoride plutonium recovery work at Rocky Flats Plant has progressed from small-scale static bed experiments to a fluid-bed pilot plant and to a production-scale prototype now nearing completion. The production prototype system is housed within five separate gloveboxes. Proposed operating procedures call for the use of 50% fluorine (F_2) at a pressure of approximately 30 pounds per square inch gauge (psig)¹ within the system. The relatively high pressure and large volume of fluorine gas in the prototype operation suggested a need to investigate the potential fire hazards associated with a major fluorine release within a glovebox.

Calculations were made to determine the maximum fluorine concentration that could occur within a glovebox from a massive fluorine release. The calculations were based on the assumption that all the fluorine in the system would be released within the smallest glovebox. The dilution effect of air entering the glovebox was considered. The results indicate

a peak of approximately 10% fluorine concentration, for several seconds, before incoming air flow caused substantial dilution.

The materials, necessary to maintain the integrity of the glovebox, were considered to be the most critical construction materials. Disregarding the stainless steel glovebox framework, the integral components included polycarbonate window material, 30-mil leaded gloves, high efficiency particulate air (HEPA) intake and exhaust filters, and polyvinylchloride (PVC) O-ring bags. Other construction materials of interest were thermal insulation, Tygon® tubing, and various electrical wiring insulations used within the prototype gloveboxes. All of these materials were tested for resistance to fluorine gas during the course of the investigation.

Volatile fluoride pilot-plant operations have indicated certain conditions to be anticipated within the production prototype gloveboxes. Glovebox air temperatures of 40 to 45 °C, plutonium dioxide (PuO_2) dust accumulation, and air-to-fluorine ratio are factors which affect the interactions between fluorine and glovebox construction materials. To simulate such conditions in the study, each material was subjected to various fluorine concentrations as follows:

1. Room temperature (27 to 30 °C glovebox temperature)
2. Heated to 50 °C temperature
3. Room temperature, coated with PuO_2 dust
4. Heated to 50 °C temperature, coated with PuO_2 dust

One aspect of a fluorine release was not investigated. The possibility for example of a high pressure fluorine jet impingement upon a vulnerable glovebox material. In the event of rupture of a line or vessel, a relatively high pressure fluorine jet could become a distinct possibility. Thus, shielding for dispersion of pressurized fluorine should be incorporated in the design of equipment and lines in critical areas.

¹For metric conversion, use 1 psi = 7 kilonewtons per square meter.

CONCLUSIONS

All the glovebox construction materials tested resisted fluorine attack in concentrations up to 25%. Absolute HEPA intake or exhaust filters will ignite and destroy the integrity of the glovebox when exposed to fluorine concentrations greater than 30%. Other major construction materials will withstand much stronger fluorine concentrations without adverse effects. The presence of certain fluorine-sensitive coatings on the surface of construction materials may increase the probability of a reaction with fluorine. Various oils, plasticizers, adhesives, and plutonium dioxide appear to induce spontaneous ignition of some materials in a fluorine atmosphere. Normally fluorine-resistant materials may ignite when exposed to the combustion of nearby fluorine-vulnerable materials.

RECOMMENDATIONS

The following recommendations were formulated as guide lines for those engaged in fluorine chemical processing within a glovebox system and will be adopted by Rocky Flats Plant, where applicable.

1. Replace combustible glovebox construction materials with metal or nonburning materials, whenever possible.
2. Keep gloveboxes as cool as possible by providing substantial air flow through the system. Air will act as a diluent, if fluorine were accidentally released within the glovebox.
3. Keep gloveboxes as clean and free from combustible waste as possible. Do not allow plutonium dioxide (PuO_2) dust, oil, etc., to accumulate on interior glovebox surfaces.
4. Locate take-out bag ports in sections of the glovebox where fluorine is not used. If this is impractical, seal the bag port inside the glovebox with a metal cover during periods of nonuse.
5. Provide metal barriers to stop the spread of fire from one combustible material to another. Absolute air filters, in particular, should be provided with metal isolation barriers.
6. Provide metal shielding around pressurized fluorine vessels or lines to prevent fluorine jet impingement upon vulnerable construction materials.

EXPERIMENTAL

Equipment Description:

The construction material tests were conducted in the fluoride-volatility static bed system described by Moseley and Robinson.² Figure 1 is a schematic diagram of the equipment used in these experiments. The desiccant air-drying column was fabricated from a 0.5-inch by 3-foot³ long polyethylene tube, packed with silica gel granules. The mixing vessel is a Monel 835-cubic centimeter (cm^3) volume, flanged lid container. A Pyrex glass, 300-milliliter volume gas-washing bottle was modified for a reaction chamber. A glass thermocouple well, to which a nickel-screen sample holder was attached, projected through the cap into the vessel. The air-fluorine gas inlet tube also entered the vessel through the cap. A ground-glass joint, coated with Halocarbon oil, sealed the cap to the vessel. Two Monel charcoal-packed traps were utilized for fluorine gas disposal.⁴ Gas pressures within the system were measured on a Monel tube absolute millimeter mercury (mmHg) pressure gauge.

Testing Procedure:

The amounts of fluorine and air for a desired fluorine concentration were first calculated in terms of mmHg absolute pressure. The concentration was achieved by mixing fluorine gas and air in the Monel vessel, before transferring the mixture into the glass reaction vessel. Glovebox air was drawn into the mixing vessel through a silica gel column to remove moisture that might react with fluorine gas to form hydrogen fluoride (HF) gas. The amounts of fluorine and air were pre-calculated to yield the correct fluorine concentration at a pressure of 600 mmHg within the reaction vessel, at either ambient temperature or 50 °C temperature. The 600 mmHg pressure was approximately equal to the atmospheric pressure within the glovebox. Fluorine concentrations were increased in 5% increments until the sample material ignited or withstood a fluorine concentration of 100%. A fresh sample was used whenever the gas concentration increased. Plutonium

²J. D. Moseley and H. N. Robinson. *Static Bed Reactor for Studies of Plutonium Hexafluoride Volatility Process*. USAEC RFP-1048. Rocky Flats Division, The Dow Chemical Company, Golden, Colorado. December 5, 1967.

³For metric conversions use: 1 inch = 25.4 millimeters and 1 foot = 30.5 centimeters.

⁴J. D. Navratil. *Disposal of Fluorine*. USAEC RFP-1200. Rocky Flats Division, The Dow Chemical Company, Golden, Colorado. August 28, 1968.

FIGURE 1. Equipment Layout for Materials Testing in Fluorine Gas Atmosphere.

dioxide coatings were applied to test materials by shaking the sample in a vial containing PuO_2 . Before testing, excess of PuO_2 was shaken off the sample.

In each run, a fresh sample was first inserted into the sample holder. The cap was then fitted over the top of the vessel, thus positioning the thermocouple well and sample inside the reaction chamber. Using a roughing pump, the entire system, except the air-drying column, was then evacuated. When evacuation was complete, the valves to the reaction vessel and charcoal traps were closed. The valve to the air-drying column was opened to draw the desired amount of glovebox air into the mixing vessel. After closing the air valve, the fluorine supply valve was then opened to transfer the desired amount of fluorine into the mixing chamber. Then the air, fluorine supply, and mixing vessel valves were closed. The air and fluorine were held in the mixing vessel for a minimum of 5 minutes to achieve diffusion mixing of the gases. During this time interval, the valves through the charcoal traps to the vacuum pump were opened to evacuate the transfer line between the mixing and reaction vessels. When the pressure gauge dropped to <1 mmHg, the valve into the reaction chamber was again opened to insure the best possible evacuation of the vessel. If the test were to be conducted at 50°C , the reaction vessel was then heated with a hot air gun. Temperatures within the thermocouple well were recorded as the vessel was heated. The temperature was elevated between 52 to 54°C and then allowed to cool to 50°C for the test. This was done to insure that the walls of the reaction vessel

were no warmer than the sample inside at the time of the actual test. At this point, a transparent, polycarbonate safety shield was positioned in front of the reaction vessel for operator protection. As the temperature neared 50°C , the valves to the charcoal traps and pumping system were closed. When the temperature fell to exactly 50°C , the valve to the mixing chamber was opened, allowing the air-fluorine mixture to transfer into the reaction vessel and contact the sample. The same evacuation and gas-transfer procedures were used in the tests made at ambient temperature.

The sample was observed for detection of any visible reaction as the air-fluorine mixture was transferred into the reaction vessel. Temperature and pressure changes were recorded. Samples that did not ignite were left in the fluorine atmosphere for a 10-minute period. When spontaneous sample ignition did take place, the fire was permitted to burn out. In either instance, the valves to the charcoal traps and pumping system were opened at this point to evacuate the system in preparation for the next run.

Accuracy:

Fluorine concentration, pressure, and temperature were controlled as accurately as possible with the existing volatile fluoride-static bed system used. Fluorine concentrations were judged to be within a range of $\pm 5\%$. All tests were conducted at a pressure of 600 mmHg (± 5 mm) within the reaction vessel. Temperatures were recorded on a 1 to 200°C recorder;

consequently, temperature spikes in excess of 200 °C were not recorded. Accuracy of test temperatures within the 0 to 200 °C range was believed to be within ± 1 °C.

DISCUSSION

Materials:

During the investigation, 18 different materials were exposed to various fluorine concentrations in about 135 separate runs. A complete list of the materials follows:

1. Lexan® polycarbonate window material
2. Charco, Rad Bar dura-sol, 30-mil leaded gloves
3. Airpure® absolute high energy particulate air filter
4. Polyvinylchloride O-ring bag
5. Pittsburgh-Corning P-C® Foamglas insulation
6. Armaflex® sponge rubber insulation
7. Tygon® tubing
8. Scotch No. 27, glass electrical tape
9. Nylon® electrical cable straps
10. Dacron® electrical cable lacing twine
- ⁵11. International Telephone and Telegraph Company, Royal Type AF, asbestos-insulated cable
12. Vinyl Therm Type THW thermoplastic-insulated cable
13. Belden 8762 plastic-jacketed P.A. cable
14. General Type P-105 C cable
15. Plastic-jacketed, yellow, thermocouple cable

16. Cornish 14/4 STO plastic, oil-resistant cable

17. Neoprene®, black, 20 conductor cable

18. Liquatite Type UXTL flexible conduit

Table I lists the materials which withstood 100% fluorine exposure for a 10-minute period without visible reaction. The materials listed in Table II ignited in various fluorine concentrations under one or more of the test conditions.

Polycarbonate Window Material and Leaded Gloves:

Polycarbonate window material and leaded gloves appeared impervious to 100% fluorine under the conditions of the study. The window material was left with a slightly glazed appearance after fluorine exposure, but the transparency and visibility qualities were still excellent. After testing, the glove samples were undamaged and still resilient and pliable.

Absolute Air Filters and Polyvinylchloride Bag Material:

Absolute HEPA filters and PVC bags appeared to be the weak parts in the integral construction materials of gloveboxes for fluorine use. The absolute HEPA filter under test was fabricated from wood, a foam-type adhesive, and an asbestos filtration material. These three components were tested together. The adhesive and the wood ignited almost simultaneously in each run. The filtration material did not appear to burn, but was always left in a charred condition after exposure to the fire from the other components..

Ignition of the PVC bag material appeared to be directly dependent upon the condition of the sample—probably the amount of plasticizer on the surface. Some bag samples did not ignite under any of the test conditions, while others burned readily. None of the test bag samples ignited after being coated with PuO₂ dust.

Foamglas and Armaflex Insulations:

Foamglas insulation is used extensively throughout the volatile fluoride production-prototype gloveboxes. Since this insulation did not ignite in 100% fluorine under test conditions, it appears to be an excellent choice. Current plans call for the use of a substantial amount of Armaflex insulation in the prototype system.

⁵Items No. 11 through No. 18 are listed in Table I as *Miscellaneous Electrical Wire Insulation*.

TABLE I. Glovebox Construction Materials Resistant to Fluorine Gas.

Construction Materials	Clean Sample		Plutonium Dioxide Dusted Sample	
	Room Temperature	50 °C Temperature	Room Temperature	50 °C Temperature
	*(100% fluorine gas concentration)		*(100% fluorine gas concentration)	
Polycarbonate Window Material	Safe	Safe	Safe	Safe
30-Mil Leaded Glovebox Gloves	Safe	Safe	Safe	Safe
Foamglas Insulation	Safe	Safe	Safe	Safe
Nylon Electric Cable Strap	Safe	Safe	Safe	Safe
Miscellaneous Electric Wire Insulation	Not Tested	Not Tested	Not Tested	Safe

*Safe samples did not ignite in 100% fluorine gas (F₂) atmosphere.

TABLE II. Glovebox Construction Materials Reactive with Fluorine Gas.

Construction Materials	Clean Sample		Plutonium Dioxide Dusted Sample	
	Room Temperature	50 °C Temperature	Room Temperature	50 °C Temperature
	*(percent fluorine gas for sample ignition)		*(percent fluorine gas for sample ignition)	
Polyvinylchloride O-Ring Bag	60	100	**Safe	**Safe
Absolute Air Filter	45	45	35	30
Armaflex Rubber Insulation	80	65	70	65
Dacron Cable Lacing Twine	40	40	40	35
Scotch No. 27 Glass Tape	90	95	**Safe	90
Asbestos Wire Insulation	**Safe	60	65	45
Tygon Tube	100	100	**Safe	**Safe

*Samples did not ignite in a fluorine concentration 5% below that shown.

**Safe samples noted did not ignite in 100% fluorine gas atmosphere.

The Armaflex insulation burned as intensely as any material tested. The samples completely volatilized during the reaction. However, this material required at least 65% fluorine concentration to promote ignition. This characteristic may provide a sufficient safety factor to warrant the use of the material in any particular application requiring a resilient, flexible type of insulation.

Tygon Tubing:

Tygon tubing was used rather extensively as a flexible electrical wiring conduit in the production prototype gloveboxes. The tests indicated that the Tygon tubing was probably less resistant to fluorine

gas than the electrical insulation it covered. However, the 100% fluorine concentration, required to ignite the Tygon, should be impossible to achieve in the gloveboxes where this material is used. If a substantial amount of plasticizer were present on the surface of a particular piece of tubing, ignition of Tygon might be expected at lower fluorine concentrations.

Nylon Electrical Cable Straps, Glass Electrical Tape, and Dacron Electrical Cable Lacing Twine:

The three described materials were used to secure electrical cables in the production-prototype gloveboxes. The Nylon Straps did not ignite in 100%

fluorine atmosphere under any of the test conditions. Glass Tape was somewhat less resistant, and ignited at a fluorine concentration of 90%. The glass tape samples were folded to cover most of the adhesive backing, since the adhesive would not be exposed on the surface in most applications. The Cable Lacing Twine was one of the most reactive materials tested at fluorine concentrations above 35%. The ignition of the lacing twine promoted ignition of otherwise unreactive cable insulations, when they were tested together. Some cable lacing twine and glass tape samples completely volatilized in strong concentrations of fluorine gas. Dacron lacing twine and glass electrical tape should be replaced with the safer Nylon straps in most applications.

Miscellaneous Electrical Wire Insulations:

Asbestos-type insulation proved to be the only fluorine-reactive electrical insulation tested. A waxy coating on the surface on the insulation may have initiated the reaction with fluorine gas. Because of time limitations, all the other electrical insulations were tested under only one condition, 50 °C temperature with PuO₂ coating. All the insulations withstood exposure to 100% fluorine concentration under these conditions, which were considered to be the most dangerous circumstances likely in a glovebox. Some of these insulations did burn, however, when tested with a reactive sample of cable lacing twine.

Effects of Elevated Temperature and Plutonium Dioxide Coating:

Temperatures of 50 °C and PuO₂ coatings did affect the interaction between test samples and fluorine gas, but to a lesser degree than expected. Absolute HEPA filter material, Armaflex insulation, Dacron cable lacing twine, and asbestos electrical cable insulation generally followed a predictable pattern of ignition. Each was inclined to ignite at a lower fluorine concentration as temperature was increased or PuO₂ coating was added to the sample. The reverse was true of PVC bag material, glass electrical tape, and Tygon tubing samples. These materials generally ignited at higher fluorine concentrations, if at all, as temperature was increased or PuO₂ coating was added. The reasons were not investigated in depth, but two possible explanations were considered. It was theorized that the adhesive on the glass tape and the plasticizer in the PVC and Tygon may have triggered

the reactions with fluorine. Heating of the sample might well have volatilized some of this reactive material. The reaction vessel was being evacuated as it was heated; consequently, some of the more reactive components of the sample may have been removed as a gas. The addition of a PuO₂ coating might also have formed a protective barrier, which insulated the remaining adhesive or plasticizer from fluorine attack.

Miscellaneous Data:

Various data such as temperature and pressure increases, flame intensity, combustion residues, and ignition times were investigated also. In the large majority of tests, reactive samples ignited within 5 seconds after the air-fluorine mixture was transferred into the reaction chamber. In rare exceptions, several samples withstood fluorine exposure for a period of 2 to 4 minutes before ignition occurred. A 20- to 50-mmHg pressure increase occurred with each ignition, but quickly receded to the starting pressure when the flame went out. The flame produced by the burning samples varied in color from a dull orange to an intense white. Charred sample particles remained after most reactions, but several materials vaporized completely during combustion. Temperature spikes during ignitions varied because of differences in sample size or reactivity with fluorine. The majority of burning samples, however, produced temperatures in excess of 200 °C. When several samples were exposed to fluorine together, the first sample ignition almost invariably caused ignition of all the samples in the near vicinity. Temperature increases of 1 to 7 °C were recorded in tests of samples that did not ignite in fluorine. No visible damage, other than slight discoloration, was ever detected in unburned samples. The PuO₂ coatings on most unreacted samples appeared to convert to plutonium tetrafluoride (PuF₄) during exposure to strong fluorine concentrations.

The durability of the Pyrex Glass Reaction Vessel, used to contain the air-fluorine mixtures, produced an interesting result. The single vessel, used in all tests, was only slightly etched and still transparent at the finish of the study. Combustion residue was cleaned from the vessel with Freon solvent between runs. The Halocarbon oil used to lubricate the ground-joint cap seal appeared to be impervious to fluorine attack. The oil was never observed to interact with fluorine gas in the vessel, regardless of concentration.