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SOLID REACTANTS FOR FLUORINE GAS GENERATOR.

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BY MING G. LAI, HERMAN I. CORDOVA, RUSSEL BARDOS, DANIEL L. LOVE

RESEARCH & TECHNOLOGY DEPARTMENT

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Pyrolysis of CoF_3 results in the conversion of CoF_3 to CoF_2, releasing fluorine gas in the process. The kinetics of the pyrolysis is a function of temperature. The maximum fluorine yield was found to be about 67% of the theoretical value. Loss of fluorine is attributable to the reaction of fluorine with the surface of the reaction vessel at elevated temperature.

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SUMMARY

This report describes the reasons for the selection of CoF_3 as the candidate compound for a safe, inexpensive fluorine generator, and also the laboratory methods used to rapidly and efficiently extract the fluorine from CoF_3.

The results showed that the highest yield of fluorine from CoF_3 was about 67% of the theoretical value.

Data contained in this report should prove helpful in selection of fluorine-emitting compounds for future chemical laser applications, especially in a space environment where time and energy of fluorine generation are not critical.

The preparation of this report was sponsored by the High Energy Laser Program Office (PMS-405) of the Naval Sea Systems Command under Task No. S1082, Program Element 63754N.

Paul R. Wessel

PAUL R. WESSEL
By direction

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INTRODUCTION

For chemical laser systems a principal constraint is the storing, handling, and safety of the reactants. This constraint has established a need of solid reactant generators to produce gaseous reactants needed for HF/DF lasers. Solid reactant generators have potential logistical safety and handling advantages over storable gases or liquids such as F_2, ClF_5, and NF_3. Moreover, because of the inherent safety characteristics many design problems associated with the gas/liquid reactant systems may be solved with the employing of the solid reactants.

At present several solid oxidizers based on NF_4 salts have been developed. These salts, such as NF_4BF_4 and NF_4SbF_6 can be decomposed into NF_3 and F_2 to provide a system having comparable weight and volume to a gas/liquid system. Although the use of NF_4 salts in a system appears feasible, the safety aspect and benefits are not yet clear when compared to gas/liquid systems. Therefore, as an alternative, a continuous search for new solid reactants for the generation of gaseous F_2, F, or NF_3 is valuable.

OBJECTIVE

The objective of this program is to search for one or several solid reactants, that, upon combustion, would yield active fluorides or fluorine, to conduct laboratory experiments for characterization of the selected candidates, and to evaluate their potential applications in the high energy laser system.

BACKGROUND

Basically, two types of fluorine-containing compounds are suitable as solid reactants. These are inorganic fluorides and fluorocarbon compounds. Inorganics include the simple salts of higher-valence transition elements, coordination compounds, and double salts. These compounds are usually formulated with small amount of light-element fuels such as B or Mg to produce flame temperature in the range 1000-1500^{o}K, and combustion products comprised of the fuel metal fluoride, lower-valence fluorides of the transition elements, and a mixture of F and F_2.

Fluorocarbons include polymers of the general formula CF_n, where n has values ranging from 0.25 (tetracarbon fluoride) to 2 (Teflon). These compounds are formulated with a small amount of light-element fuel, preferably B, to produce very high values of flame temperature (3000°K), and combustion products of soot, F, and BF. These combustion products are then burned in a secondary combustion chamber with either air or oxygen to yield Co, F, BF_3, and N_2.

Among the fluorine-containing compounds, metal fluorides appear desirable for our initial investigation because of their inherent simplicity and high theoretical fluorine yields. Some of the metal fluorides have been used as fluorination agents, although this does not necessarily mean fluorine was a pyrolysis product. The possible problems in employing metal fluorides include (1) stability of the metal compounds, (2) self-sustaining combustion while maintaining adequate fluorine yields, (3) the production of metal fluoride vapor, which would degrade and possibly destroy laser action, (4) pressibility of the salts, and (5) the production and maintaining of the required heat flux into the salts if external heating is used.

Many of the metal fluorides have been found capable to decompose to lower fluorides and fluorine. Wartenburg[1] examined CoF_3 and MnF_3 at 600°C and detected gaseous fluorine above the solids at a partial pressure of 0.1 atmosphere. Additionally Nichols[2] found that CoF_3, when heated in an inert atmosphere above 350°C, yields CoF_2, and this implies F_2 is also produced. Thus, it would seem highly probable at higher temperatures a substantial partial pressure of F_2 may be produced.

Among other metal fluorides, MnF_4 slowly decomposes at room temperature to MnF_3 and fluorine gas.[3,4] This reaction could be speeded up at elevated temperature. CuF_2 also decomposes to yield CuF and F_2 upon heating, but requires a very high temperature (900-1200°C). Other metal fluorides, such as PbF_4 and TiF_4 also compose at relatively low temperature and thus offer some potential for generation of fluorine gas.

SCREENING AND SELECTION OF CANDIDATE REACTANTS

Laboratory studies were conducted for the screening and selection of candidate reactants. The studies are to survey potential fluorine source candidates, subject these candidates to a set of screening criteria, and select and recommend the most appropriate reactant systems for laboratory testing and characterization.

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1. H. Von Wartenberg, Zeitschrift fur anorg. u. allgen. Chem. 244, 337 (1940).
2. D. Nichols, Comprehensive Inorganic Chemistry, p 1093, Pergamon Press, Vol 3, N.Y. (1973).
3. R. Hopp, W. Dahne, and W. Klemm, Ann. Chem. (Paris) 658, 1 (1962).
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The selection criteria in order of importance are:

1. Fluorine yield
2. Combustion kinetics
3. Thermal stability
4. Availability
5. Decomposition temperature
6. Exhaust composition
7. Handling characteristics
8. Particulates

INITIAL SCREENING AND ANALYSIS

Forty inorganic metal fluorides were chosen as possible candidate compounds for the production of fluorine upon decomposition. A cursory examination of each compound as to its cost, similarity to other compounds, percent weight yield, availability, and temperature of decomposition condensed the list to fourteen.

Table 1 is a list of those inorganic metal fluorides chosen for further examination and pyrolysis testing.

PYROLYSIS TESTING APPARATUS

The pyrolysis testing apparatus, shown in Fig. 1, consisted of (1) external power supply, (2) external vacuum pump, (3) external helium gas supply, (4) temperature measuring and recording equipment, (5) tantalum heating strip, (6) platinum sample holding dish, and (7) Teflon column containing potassium iodide (KI) crystals.

(1) The power supply consisted of a variac feed from 115V AC line into a step-down transformer. The system was capable of delivering one kilowatt of electrical power into the heating strip.

(2) The vacuum source consisted of a large volume roughing pump capable of providing vacuums of less than one torr and a high sensitivity vacuum gauge.

(3) Bottled helium gas, with a purity of 99.995% minimum was fed into the system via a two-stage regulator, a stainless steel needle valve, and a flow-rate meter.

(4) Temperatures were measured by spot welding a chromel/alumel thermocouple to the bottom-center of the tantalum heating strip. The output was fed directly to a digital voltmeter which gave a visual readout and in addition drove a strip chart recorder.

(5) The tantalum heating strip measured 3.5" in length, 0.5" in width, and 0.010" thick. It contained a recessed area at its center which took the form of a 0.5" diameter by 0.1" deep dish.

TABLE 1

Inorganic Metal Fluorides

FORMULA		PURITY	COST/ LB	MW	THEOR %F
CoF_3	Cobalt Trifluoride	98.0	95	115.9	49.2
CuF_2	Cupric Fluoride	99.5	150	101.5	37.4
LiF	Lithium Fluoride	99.8	20	25.9	73.4
MnF_2	Manganese Difluoride	99.0	95	92.9	40.9
$NiBF_4$	Nickel Tetrafluoroborate	99.9	27	145.5	52.2
NbF_5	Niobium Pentafluoride	99.5	215	187.9	50.6
KPF_6	Potassium Hexafluoro-phosphate	NA	43	184.1	61.9
AgF_2	Silver Difluoride	99.8	488	145.9	26.0
$NaBF_4$	Sodium Fluoborate	Tech	5	109.8	69.2
Na_2SiF_6	Sodium Fluosilicate	99.0	22	185.1	61.6
TiF_4	Titanium Tetrafluoride	99.0	62	123.9	61.3
VF_4	Vanadium Tetrafluoride	98.0	759	127.0	59.8
ZrF_4	Zirconium Tetrafluoride	98.0	72	167.0	45.5
Li_2SiF_6	Lithium Fluosilicate	99.0	25	156.9	73.1

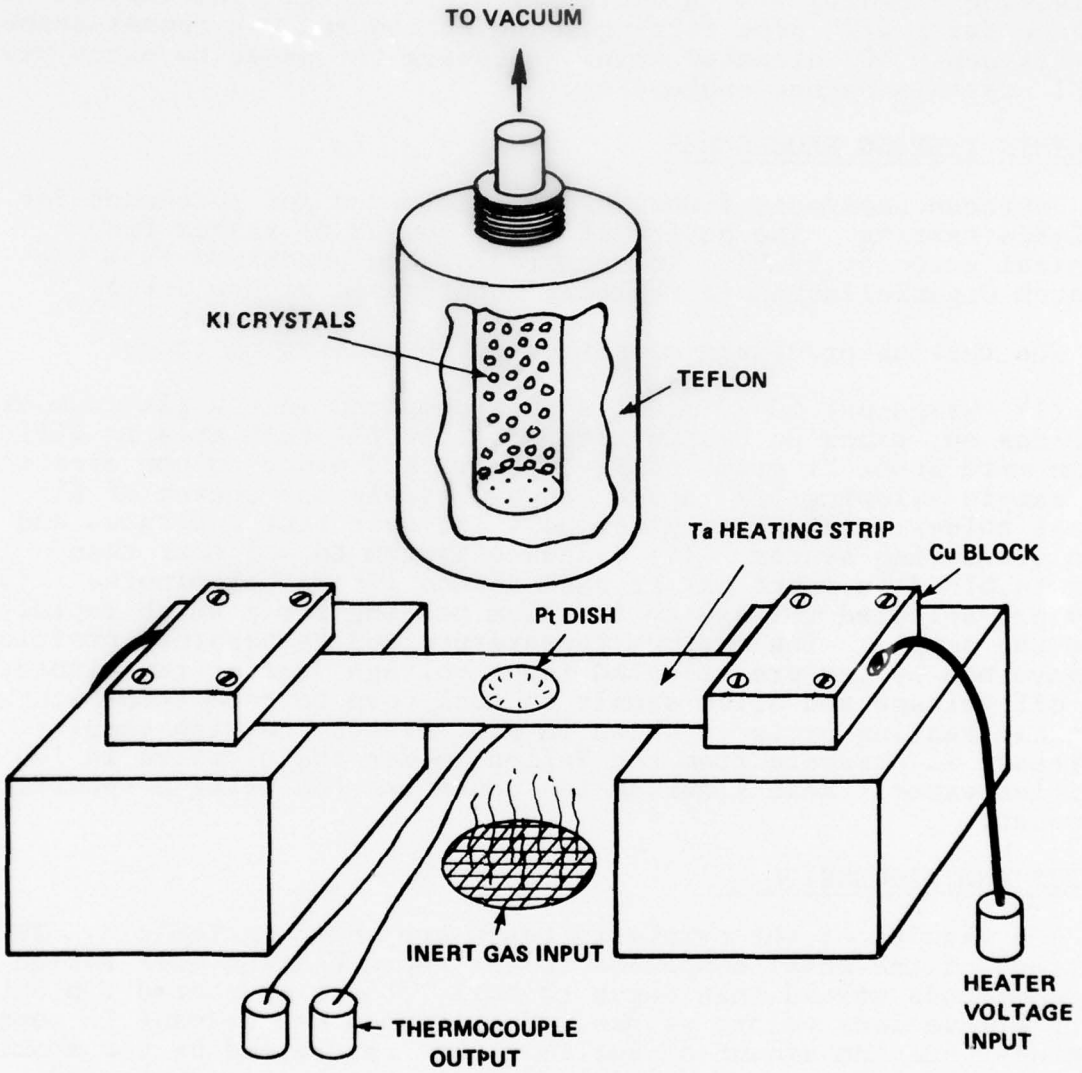

FIG. 1 PYROLYSIS TEST APPARATUS

(6) The platinum dish dimensions were 0.7" in diameter with a recessed area which conformed to the shape of the tantalum heating strip.

(7) The all-Teflon KI crystal holder was made from a solid Teflon piece 1-13/16" diameter by 4-1/4" long. The inside was bored out leaving a cavity 3/4" diameter by 3-1/2" long. The top end was threaded for a 1/2" pipe fitting. The bottom end was funnel-shaped with fifteen 0.40" diameter holes, allowing the gases to sweep past the KI crystals before exhausting.

PYROLYSIS TESTING PROCEDURES

Fourteen inorganic fluorides were selected and purchased for pyrolysis testing. The purity of these compounds ranged from technical grade to 99.9%. The chemicals were purchased from the Research Organic/Inorganic Chemical Corporation of New Jersey.

The testing procedure consisted of the following steps:

(1) Weigh out 10-70 mg of sample compound into a platinum dish and place on tantalum heating strip; (2) fill void area in Teflon column with about 21 grams of KI crystals and place column directly over sample allowing 1/2" space between sample and bottom of KI crystal holder; (3) place glass bell jar over test apparatus and begin evacuating system; (4) evacuate system to < 1 torr then begin to bleed in inert gas at rate of two liters per minute; (5) apply pre-selected voltage to tantalum heating strip which rapidly heats the sample. The maximum temperature and temperature profile are governed by the pre-selected input voltage. After two minutes turn off voltage and allow sample to cool down to room temperature. A typical heating cycle is shown in Fig. 2; (6) reweigh sample; (7) remove KI crystals from the Teflon holder and dissolve in 100 ml distilled water. Read fluoride ion concentration using a specific ion meter.

RESULTS AND DISCUSSION

The results of the pyrolysis tests are shown in Table 2. The reactions of the metal compounds to the rapid heating were varied - some compounds melted then began to boil, others sputtered violently, giving off various colors of gas. Sublimation was evident in some compounds, but the amount of sublimations, determined by the atomic absorption technique, was small in most of the compounds tested.

Among the reactants tested, CoF_3 was selected for further evaluation. The basis for the selection is that CoF_3 has the following characteristics:

(1) High fluorine content (49.2%)
(2) Well-known fluorinating agent

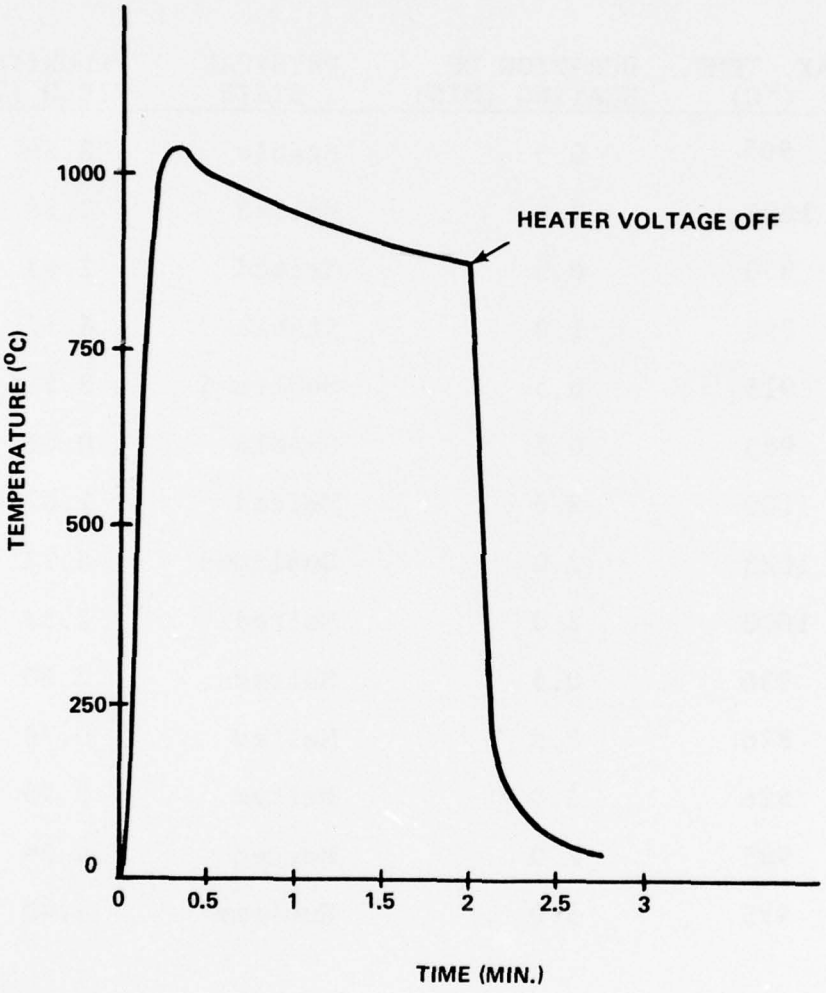

FIG. 2 TEMPERATURE–TIME PROFILE

TABLE 2

Results of Pyrolysis Testing

COMPOUND	MAX. TEMP. (°C)	DURATION OF HEATING (MIN)	PHYSICAL STATE	FLUORINE YIELD (%)
TiF_4	965	0.5	Stable	2.76
AgF_2	1000	2.0	Melted	3.28
CuF_2	950	0.5	Melted	2.63
CoF_3	895	1.0	Stable	6.77
VF_4	915	0.5	Sublimed	3.91
$NiBF_4$	965	0.5	Stable	0.66
LiF	1100	2.0	Melted	1.87
ZrF_4	1023	2.0	Sublimed	0.73
MnF_2	1000	2.0	Melted	2.53
$NaBF_4$	930	0.5	Melted	0.20
Na_2SiF_6	826	2.5	Melted	0.79
KPF_6	926	3.0	Melted	0.75
Li_2SiF_6	985	2.0	Melted	4.29
NbF_5	975	3.0	Sublimed	4.40

(3) Commercially available in quantity
(4) Low cost ($28/lb for > 1000 lb)
(5) Insensitive and safe to handle
(6) High fluorine yield on pyrolysis testing
(7) Rapid decomposition at relatively low temperature (> 200°C)
(8) Physically stable at high temperature

CHARACTERIZATION AND TESTING OF SELECTED REACTANT SYSTEMS

The selected solid reactant, CoF_3 was put through a series of laboratory studies, which included pyrolysis of the reactant under various conditions, determination of fluorine yield in the gas mixture, and the kinetic of pyrolysis. The purpose of the laboratory testing is to generate data, through varying test conditions, on the behavior of the reactant, thus providing information for the ultimate system design. In addition, the problems encountered during the studies can be utilized as a base for the determination of the overall feasibility of CoF_3 for the fluorine gas generator.

PYROLYSIS OF CoF_3

Cobalt trifluoride pellets (0.5 cm diameter x 0.3 cm height) were subjected to external heats under nitrogen atmosphere for a period of one hour. After the pyrolysis, the resulting solid (pink color) was dissolved in water, and chemical analysis of the solution was performed. The amount of Co was determined by atomic absorption spectrophotometry and fluoride by selective-ion electrode. The results (Table 3) indicate that the reaction product of CoF_3 pyrolysis, having a F to Co ratio of 2, is CoF_2. Furthermore, from the weight loss data, an essentially complete conversion of CoF_3 to CoF_2 at temperature greater than 300°C is indicated. These strongly suggest that the reaction representing the pyrolysis of CoF_3 in the absence of air would be

$$2\ CoF_3 \xrightarrow[N_2]{300^\circ C} 2\ CoF_2 + F_2 \qquad (1)$$

However, the production of fluorine gas in the reaction would have to be further confirmed.

When CoF_3 was heated at 400° - 500°C in the presence of air, at first a pink solid (believed to be CoF_2) rapidly appeared. Then the compound became black upon further heating. The black solid was analyzed by wet chemistry and by X-ray diffration technique. Both results indicate that the compound is cobalt oxide (Co_3O_4). Thus, the following reactions are suggested:

TABLE 3

Pyrolysis of CoF_3

$$CoF_3 \longrightarrow CoF_2 + 1/2\ F_2$$

TEMP (^{o}C)	MOLE RATIO (F/Co)	WEIGHT LOSS (%)	DECOMPOSITION (%)
100	2.19	13.5	82.3
200	2.08	14.1	86.0
300	2.01	15.8	96.3
400	1.98	16.0	97.6
500	2.00	16.2	98.8

$CoF_3 \longrightarrow CoF_2$ Theoretical Weight Loss = 16.4%

$$CoF_3 \xrightarrow{400\text{-}500^{\circ}C} CoF_2 + 1/2F_2 \qquad (2)$$

$$3CoF_2 + 2O_2 \longrightarrow Co_3O_4 + 3F_2 \qquad (3)$$

Finally, CoF_3 was heated to 400°C in vacuum for 16 hours, resulting in a gray/black solid. The material was analyzed to be greater than 90% metallic cobalt. The reaction can be assumed to be

$$2CoF_3 + 2O_2 \xrightarrow[\text{Vacuum}]{400^{\circ}C} 2Co + 3F_2 \qquad (4)$$

The reaction appears very slow.

From the results of CoF_3 pyrolysis several conclusions can be made:

(1) CoF_3 decomposes very rapidly upon heating.

(2) In the absence of air, CoF_3 is first converted to CoF_2 and eventually to Co metal.

(3) In the presence of oxygen, CoF_3 decomposes to CoF_2 which is, in turn, converted to Co_3O_4.

(4) During the pyrolysis, fluorine gas is believed to be the gaseous product (proven in the later experiments). The theoretical F_2 yield ranges from 16.4% to 49.1%.

(5) For potential high energy laser application, only reaction 1 warrants further pursuit. Although the F_2 yield is the lowest, the kinetics of the reaction appears sufficiently fast for the laser requirements. The complication of oxygen in the laser system from reaction 3 and the slow reaction rate of reaction 4 prohibit their potential application in the present laser technology.

KINETICS OF PYROLYSIS

Preliminary study has shown that decomposition of CoF_3 upon heating to product CoF_2 and F_2 is fairly rapid. A more detailed study was made to quantitatively determine the rate of reaction. In the study, weighed amount of CoF_3 crushed pellets was placed in a porcelain crucible and then heated in a muffle furnace. The desired temperature of the furnace was set and equilibrated prior to insertion of the sample. After a predetermined time, the sample was withdrawn from the furnace, cooled, and weighed. The weight loss, calculated from the difference of weights before

and after the pyrolysis, constitutes the amount of CoF_3 decomposed. The results are presented in Fig. 3 & Fig. 4. Fig. 3 represents the decomposition of CoF_3 which had been exposed to moisture intermittently for about two months, and Fig. 4 represents the decomposition of fresh CoF_3 relatively free of moisture. The results indicate that both types of CoF_3 appear to have similar kinetics behavior. The rate of decomposition is a function of temperature. At 400°C the conversion of CoF_3 to CoF_2 is completed in 5 - 7 minutes, while at 600°C it requires only 1 - 2 minutes. The product, CoF_2, was quite stable at 400°C. However, above 500°C CoF_2 undergoes further reaction as indicated by the further weight loss. The resulting product, bearing gray/black color, is believed to be Co_3O_4 as previously described.

The observed weight loss of the fresh CoF_3 matches well with the theoretical value for the complete conversion of CoF_3 to CoF_2. For the CoF_3 contaminated with moisture, the weight loss is about 25% lower. This was probably due to the partial hydrolysis of CoF_3, forming hydroxides. Assay of the CoF_3 content (fresh 99%, old 75%) confirms the observation.

In conclusion, the decomposition rate of CoF_3 at 600°C appears sufficiently rapid for the required fluorine gas generation. Since the decomposition rate is a function of temperature, it can be further increased with higher heating temperature. In addition, improvement of external heating devices may also enhance the decomposition kinetics.

FLUORINE GAS DETERMINATION

Analysis of the gases generated from the pyrolysis of the solid reactant is an important part of the experimental effort. Since fluorine yield is considered the most important factor in the solid reactant selection, the correct experimental determination of gaseous fluorine for the evaluation is imperative.

Fluorine analysis has been known to be one of the most difficult procedures in analytical chemistry because of the highly reactive nature of fluorine. The reactivity of fluorine is a function of temperature. At elevated temperature, fluorine reacts with all matter which is not in its highest valence state and is not completely fluorinated.

All metals react with fluorine. Some ignite spontaneously in fluorine at elevated temperature. Even gold and the platinum metals are attacked if the temperature is very high. Hydrocarbons burn spontaneously. Glass and asbestos burn in fluorine if they are strongly preheated.

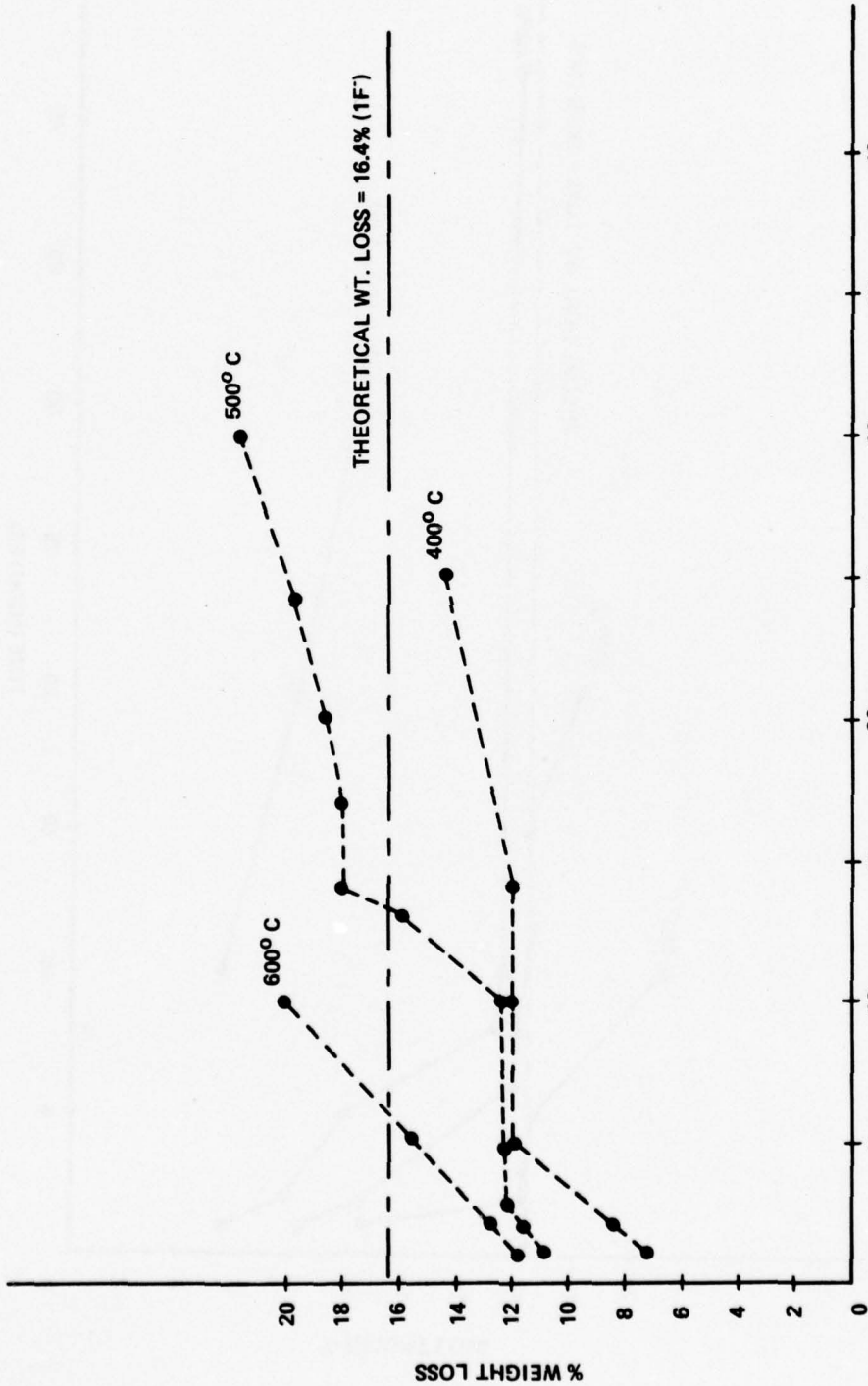

FIG. 3 WEIGHT LOSS VS. TIME
OLD CRUSHED PELLETS (75–80% ASSAY)

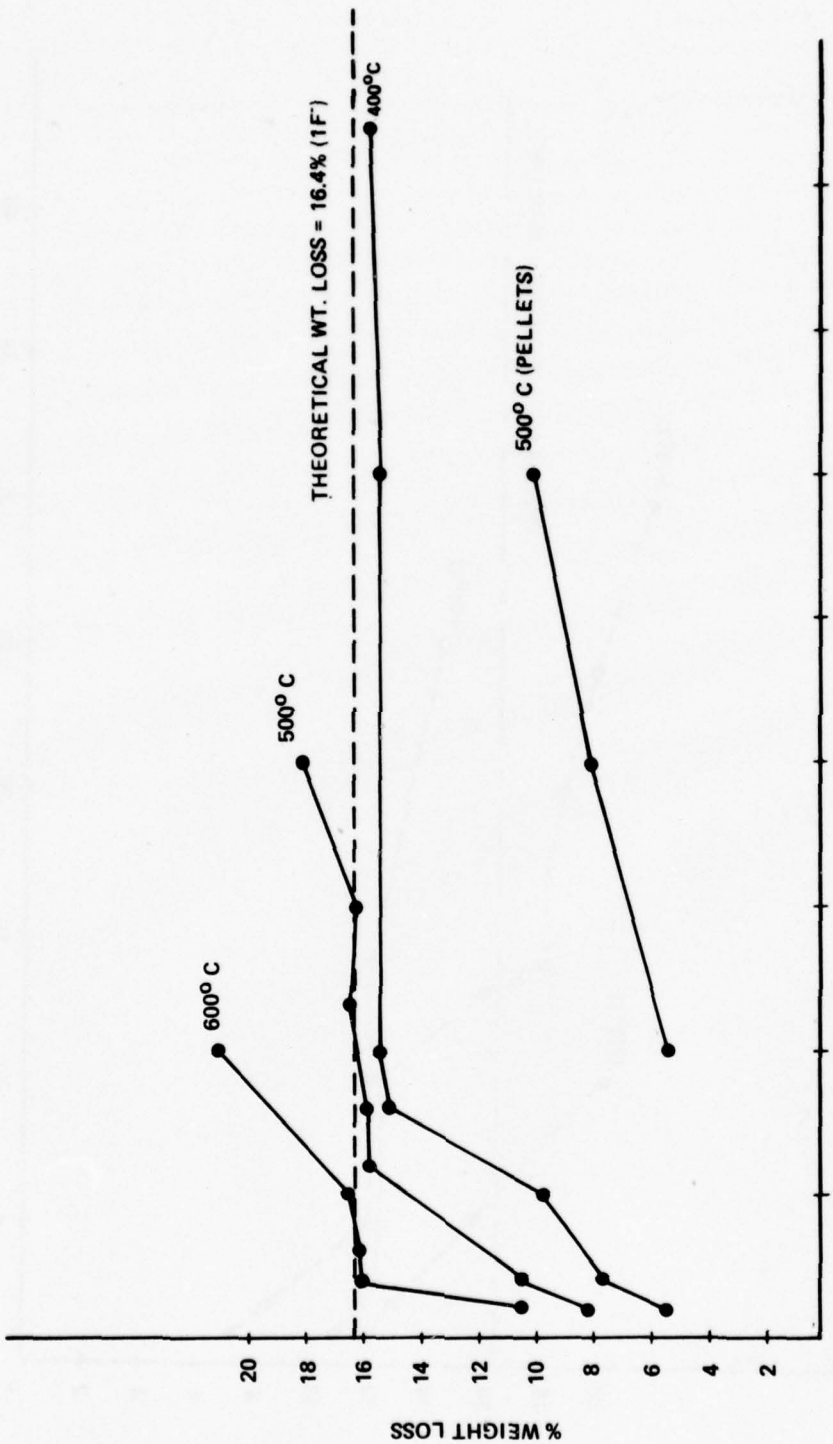

FIG. 4 WEIGHT LOSS VS. TIME
FRESH CRUSHED PELLETS (99% ASSAY)

The formation of a surface coat of a metal fluoride reduces the tendency for massive metals to react completely. This is called surface passivation. However, at temperature above 400°C, surface passivation often breaks down.

The inherent reactive property of fluorine presents several serious problems in its analysis.

(1) Valid sample collection during the pyrolysis is virtually impossible because fluorine reacts with the container walls of the reaction apparatus as well as the sample collection device. The loss of fluorine could be very serious if the walls were at an elevated temperature or the fluorine concentrations were very low. For the same reasons, the storage of samples also becomes a major problem. Unless samples are analyzed immediately after collection, loss of fluorine often occurs. Passivation of the containment surface may minimize the loss, but this is no assurance of complete passivation, particularly under elevated temperature.

(2) In the presence of moisture fluorine reacts with water to become HF, which affects the fluorine analysis. Keeping the entire system moisture free is by no means an easy task.

(3) Fluorine gas, after collection, must be accurately aliquoted for analysis. Again, during the aliquoting procedure, loss of sample can occur if extreme care is not taken.

In view of the above difficulties, we have concluded that the best method for the determination of fluorine generated from the pyrolysis of solid reactant is to react the gas as soon as generated, with a suitable medium, which quantitatively converts fluorine to a more stable compound. Then the compound is collected and analyzed. This procedure will circumvent the difficulties of sampling and analysis of fluorine.

Potasium Iodide Method

A simple, rapid method for the in situ determination of fluorine was developed. The method was based on the oxidation of potassium iodide solution in the reaction

$$F_2 + 2\ I^- \longrightarrow I_2 + 2\ F^-$$

where fluorine is converted to fluoride. The amount of fluoride can then be conveniently measured by a selective ion-electrode. In the procedure, instead of KI solution, filter paper (Whatman No. 1) impregnated with 20% KI solution was used. The impregnated filter paper was dried in an oven, shreaded to small pieces, and packed into a Teflon column (2 cm I.D. x 30 cm length). The column was connected to the fluorine gas generator. When fluorine

passed through the column, it was instantly converted to fluoride by the KI paper. After the reaction the KI paper was soaked in water and the released fluoride was determined by the selective ion-electrode.

The efficiency of the KI paper, shown in Table 4, is 100% with a flow rate of 0.1 ℓ/min. The efficiency decreases with an increase of flow rate. The efficiency is about 72% with a flow rate of 1 ℓ/min.

The KI paper method was subsequently used for most of the fluorine determination in the laboratory testing of CoF_3 reactant system. The only disadvantage of the method is that OF_2, if present, also reacts with the KI paper, contributing to errors in the fluorine analysis.

Gas Chromatography Method

In order to confirm the presence of fluorine in the generated gas mixture, it was desirable to collect some of the gas samples and analyze them by another method. The analysis was accomplished by the gas chromatographic technique, performed by the Naval Ordnance Station, Indian Head, Maryland.

In the method, fluorine quantitatively displaced an equivalent amount of chlorine by reaction with sodium chloride and, in turn, the quantity of liberated chlorine was determined by the gas chromatographic technique. A holocarbon oil column, coupled with a nickel filament thermal conductivity detector, was used for the separation and detection of chlorine. Again, OF_2 interferes with the analysis.

FLUORINE GAS GENERATOR

Through a series of changes and improvement, several types of fluorine gas generation were designed, fabricated, and tested. The objective of the test is to obtain a generator design which would give the best yield of fluorine and would be practical and adaptable for the ultimate high energy laser system.

Open System

A very simple system was designed and tested as fluorine gas generator. The system consisted of a large porcelain crucible and a Teflon chimney connected to a Teflon column containing KI paper (Fig. 5). First, the crucible was heated with a Bunsen burner to 500 - 600°C. The chimney-KI paper column assembly was placed above the crucible, and a vacuum was drawn, creating an air flow of about 1 liter/min through the column. A weighed quantity of CoF_3 was placed in the crucible, and the chimney-column assembly was immediately lowered to about 1 cm above the CoF_3.

TABLE 4

KI PAPER COLUMN EFFICIENCY

F_2(%)	FLOW RATE (LITERS/MIN)	EFFICIENCY (%)
5.5	1	71.3
1.1	1	72.9
2.1	0.25	92.2
1.5	0.10	100.0

DIMENSION = 2 cm I.D. x 30 cm length

KI SOLUTION = 20%

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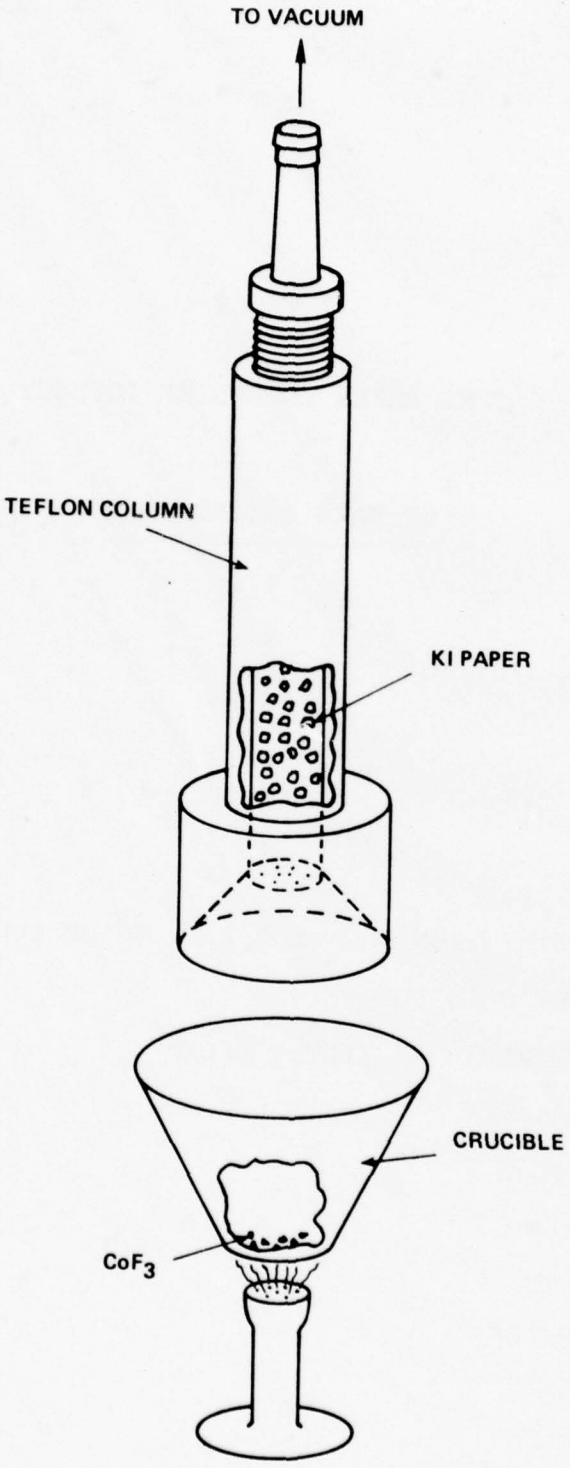

FIG. 5 OPEN SYSTEM

The heating was terminated after 1 to 3 minutes and the vacuum turned off. The KI paper in the column was analyzed for fluoride content.

The results of four runs are presented in Table 5. The fluorine yield, after correction for KI column efficiency, ranges from 10.8 to 17%. The longer the heating time and the larger the surface area seems to produce higher fluorine yield.

An experiment was performed to determine whether OF_2, which interfered with the fluorine determination, was present in the gas mixture. A cold trap containing liquid nitrogen was placed in front of the KI paper column. Liquid nitrogen has a boiling point of -195.8°C. At that temperature, OF_2 (B.P. -144.8°C) would be completely removed by the trap while most of the fluorine gas (B.P. -188°C) would pass through into the KI paper column. Preliminary test shows that a loss of fluorine in the cold trap is about 35%.

Pyrolysis of one CoF_3 pellet was conducted in the open system with the cold trap. The fluorine yield, corrected for cold trap loss and KI column efficiency was found to be 10.1%. This value, when compared with the one without cold trap indicates that no significant amount of OF_2 is present in the gas mixture.

In summary, the open system has clearly demonstrated that fluorine gas is generated upon the pyrolysis of CoF_3. The system, of course, is impractical for the actual use because it is not a controllable system. However, it has served as a guideline and base for the design of other systems.

TABLE 5

Open System

FLOW RATE = 1 LITER/MIN

TEMPERATURE = 500-600°C

CoF_3	TIME (Min)	WT LOSS (%)	F_2 YIELD (%)
1 Pellet	1	10.9	10.9
1 Pellet	3	13.5	14.2
4 Pellets	1	16.0	10.8
Small Pieces	1	16.1	17.0
Small Pieces	1	16.2	8.0

($L\text{-}N_2$ COLD TRAP)

Nickel System

The apparatus shown in Fig. 6 was designed for testing CoF_3 pellets to determine if upon heating fluorine gas would be released and if the F_2 gas could be contained and measured.

The apparatus was constructed such that any gases released would only see passivated nickel surfaces. The nickel surfaces were thoroughly cleaned, then the apparatus assembled and passivated according to procedures outlined in Fluorine Systems Handbook Appendix III-5.[5]

A CoF_3 pellet weighing approximately 6 grams was placed inside the Ni tube and a vacuum drawn on system to remove air and any moisture present in the system. Helium gas was then flushed into the system and allowed to sweep past CoF_3 pellet through KI paper column and into the vacuum system.

The Ni apparatus containing the CoF_3 pellet was then heated with a Bunsen burner to approximately 400-600°C for a period of 5 minutes. The helium gas flow rate was one liter per minute. The system was then allowed to cool down to room temperature and the pellet reweighed. The KI paper was removed from holder and analyzed for fluoride ion.

Three runs were conducted with the Ni system. The results, shown in Table 6, were rather poor. Fluorine yield of the pyrolysis of CoF_3 ranges from 1.4 to 4.4%. The low fluorine yield indicates that most of the fluorine gas, liberated during pyrolysis, reacted with the hot nickel walls and was not seen by the KI paper. Although the entire nickel system had been passivated prior to the experiment, the effectiveness of the passivation was unknown.

The poor recovery of fluorine initiated another test to determine if Ni metal could be passivated at elevated temperature. The test consisted of the same nickel apparatus heated to 400°C in an oven and known volumes of fluorine passed at various flow rates. The results of the test (Table 7) indicated that at the elevated temperatures required to decompose CoF_3, fluorine reacts with the passivated nickel walls. Thus, passivation at 400°C was not possible, and the nickel system appears undesirable to be used as a fluorine generation.

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5. Robinson,W.C., Fluorine Systems Handbook, Missile and Space Systems Division, Douglas Aircraft Co., DAC-59074 (1967).

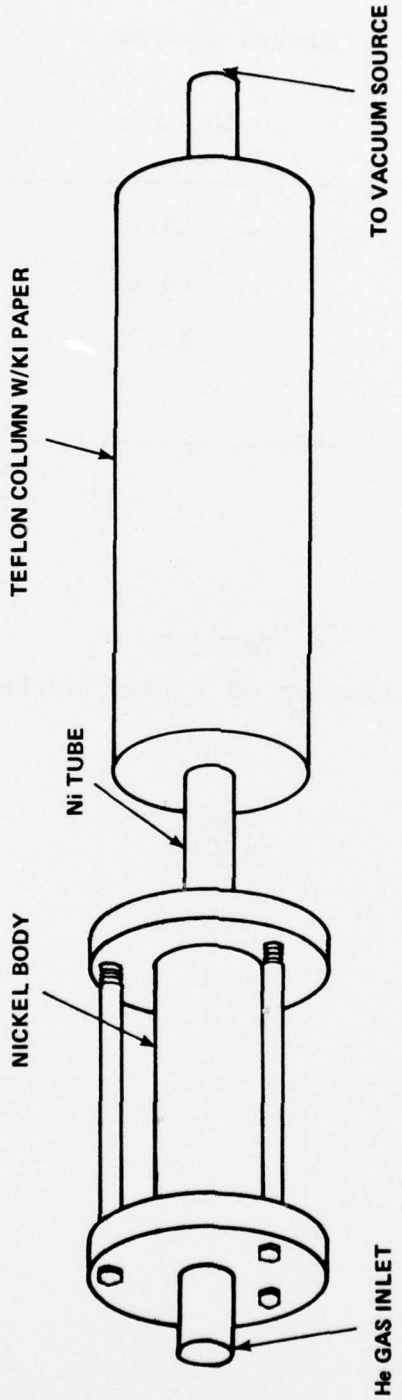

FIG. 6 ALL NICKEL SYSTEM

TABLE 6
Nickel System

CoF_3	Temp (°C)	Wt Loss (%)	F_2 Yield (%)
Pellet	600	13.1	1.4
Pellet	500	10.6	1.5
Powder	400	14.2	4.4

TABLE 7
Passivation of Nickel Surface

Flow Rate (l/min)	Temp (°C)	F_2 Recovery %
2.0	400	39.6
1.0	400	28.1

Hot Helium System

The objective of this test was to heat helium gas to several hundreds of degrees celsius, pass the hot gas around a CoF_3 pellet, then through a column containing KI saturated paper. The idea was to have only fluorine gas liberated, swept up by the helium flowing through the system and carried into the KI column which would react with the fluorine gas.

The apparatus used is shown in Fig. 7. A 0.25" diameter copper tubing was coiled and placed inside a tube furnace which could be temperature controlled. The copper tubing was then coupled to a heated 1.0" diameter nickel tube containing the CoF_3 pellet. A 0.25" diameter nickel tubing then carried the exhaust gases into the KI column. All the nickel material used was passivated prior to each run. The CoF_3 pellet was physically placed as near the exit as possible to reduce the exposure and possible reaction of the fluorine gas with the hot nickel walls. The results of the first run initiated another modification which was to insert a LN_2 trap just after the nickel reaction vessel and prior to the KI column. The purpose of the trap was to cool the exhausting gases to reduce their reaction with any container walls and to remove OF_2 or HF if present in the gas mixture.

Several runs were conducted with the system. The results are presented in Table 8. The fluorine gas yield is slightly improved from the hot nickel system. However, it is far from satisfactory. The loss, again, is probably due to the elevated temperatures (260° - $300^{\circ}C$) at the walls of the nickel reaction vessel, where the fluorine gas is generated and passes into the KI paper column.

TABLE 8

Hot Helium System

He $T^{\circ}C$	Tube $T^{\circ}C$	Flow Rate Liters/Min	L-N_2 Trap	Wt Loss (%)	F_2 Yield (%)
300	275	1	No	10.0	2.8
555	260	1	Yes	11.4	5.5
900	300	0.2	Yes	9.2	0.5

Nickel System - Cold Wall

Based on results of fluorine generators previously tested, it is obvious that elevated temperature applied to the reaction vessels

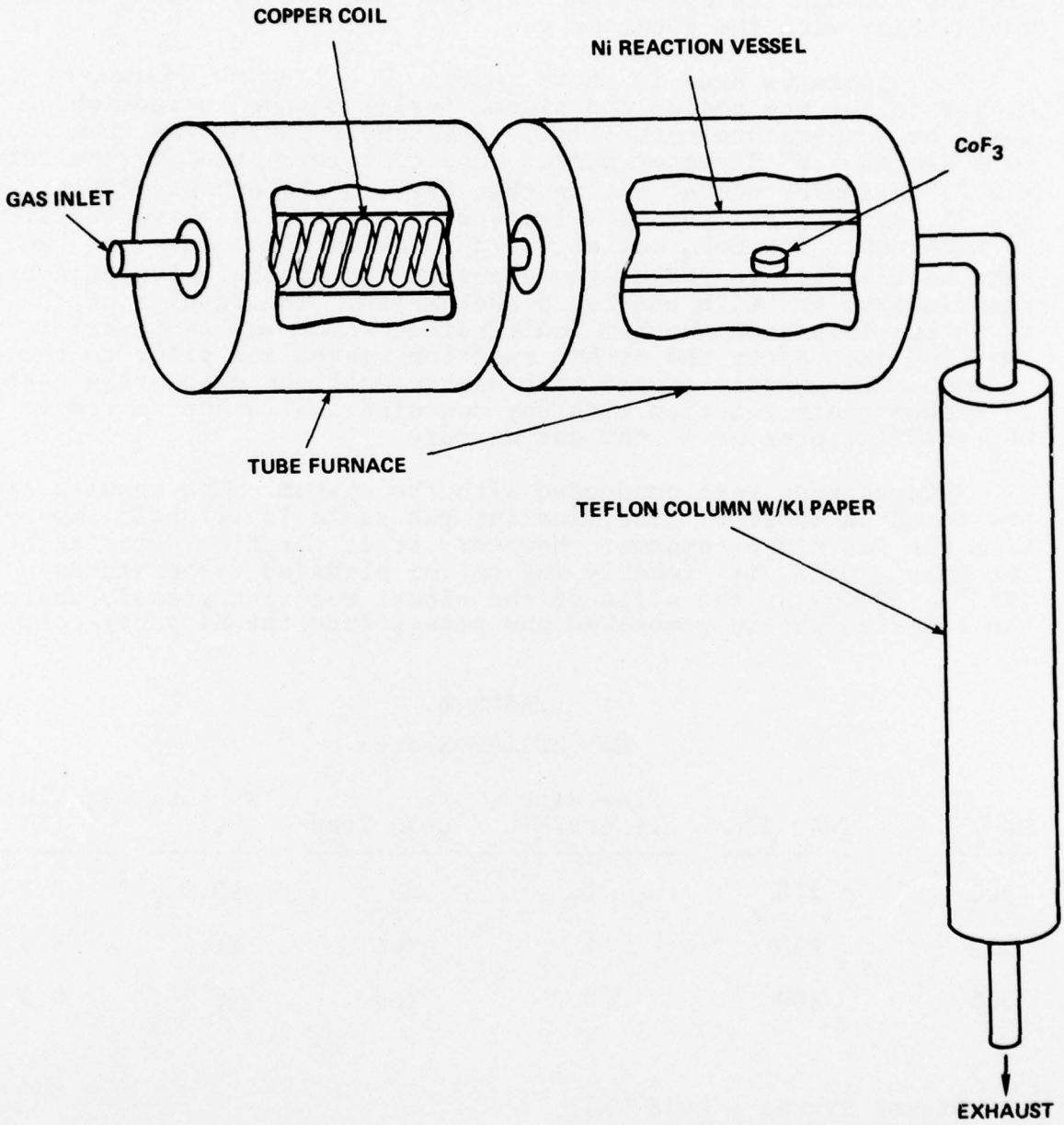

FIG. 7 HOT HELIUM SYSTEM

cannot be tolerated. Therefore, another system was designed to give a low containment wall temperature. The only spot in the system where the temperature would be high was the site of pyrolysis. Thus, once fluorine was generated, it would be swept out to the KI column without making contact of any hot surfaces.

The apparatus shown in Fig. 8 was constructed almost entirely from pure nickel rods and tubing. The main body was fabricated from 1-11/16 inch diameter tubing with wall thickness of 1/8 inch. End caps were made from solid nickel rod 2.0 inches in diameter. The heater and pellet holder was made from a solid 0.5 inch rod. This rod was machined such that its center section contained a rectangular cavity 5/16" x 3/4" x 7/32" (W.L.H.). The walls of the rectangular cavity were $\sim$ 0.050" thick. A chrome/alumel thermocouple was spot welded to the bottom center of the rectangular cavity and its leads were brought out via holes drilled through the center of the nickel rod. Gas integrity was obtained through the use of Teflon gaskets and seals. The 0.5" nickel rod was also insulated from the rest of the body because large electrical currents were used for heating the center section of the rod which decomposed the CoF_3 pellets contained in the rectangular cavity. Helium gas was brought near CoF_3 pellets via a 0.25" diameter nickel tube. The idea was to sweep away any fluorine gas liberated during the heating cycle. With the walls previously passivated and at room temperature the fluorine gas would have minimum reaction and thus give higher yields.

The test procedure was carried out as follows:

1. Nickel system was passivated
2. Four CoF_3 (1/2 - 3/4 gms) pellets were placed in rectangular cavity
3. Helium gas was flushed through the system to remove air and moisture for $\sim$ 10 minutes
4. Helium flow rate set at 0.2 liters/min
5. KI paper column connected to exhaust
6. Power applied - heat reached maximum within 10-15 seconds ($\sim$ 700°C)
7. Power turned off after two minutes
8. System allowed to cool and helium continues to flush out any gases generated (10 minutes)
9. Apparatus disassembled and CoF_3 pellets removed and reweighed
10. KI paper removed and checked for fluoride ion

Two runs were conducted with the system. Results are shown in Table 9. The results indicate that the fluorine yield is improved; however, the yield is still only about 55% of the maximum theoretical value. The loss of fluorine could be again contributed to the reaction of fluorine with the Ni rod, where pyrolysis of CoF_3 took place.

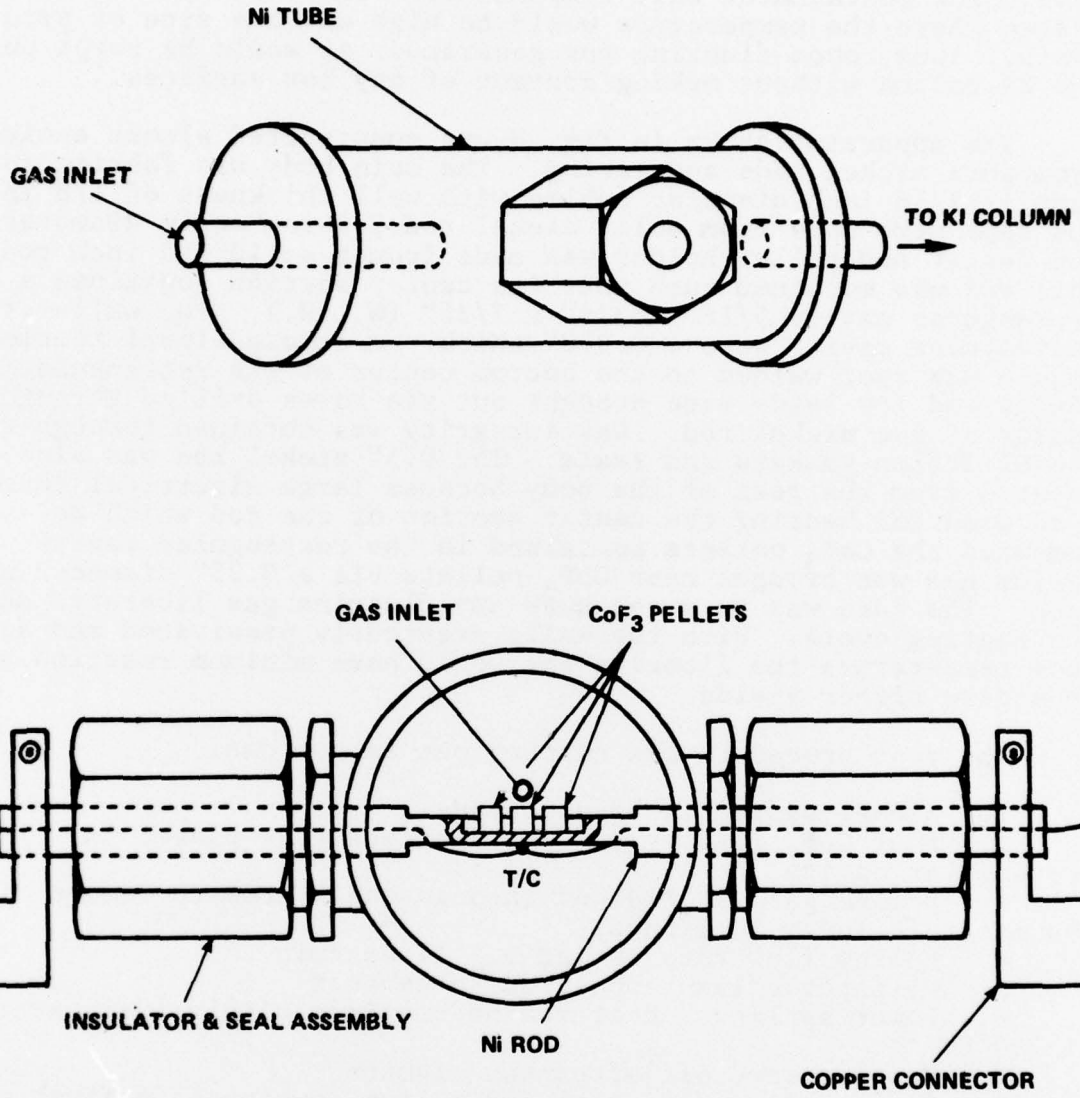

FIG. 8 NICKEL SYSTEM–COLD WALL

TABLE 9

Nickel System - Cold Wall

TEMPERATURE (^{o}C)	WT LOSS (%)	F_2 YIELD (%)
600	14.0	7.6
700	14.4	8.5

Teflon System

The all-Teflon system shown in Fig. 9 was developed to alleviate any contact of the fluorine generated by pyrolysis with other material causing a loss of the fluorine gas. The IR source consisted of a 1000 watt projection lamp being powered by a variac fed from a 115 vac line. The 3-1/2" diameter converging lens gathered and focused the IR rays onto the CoF_3 pellets. The sapphire window was 1-1/4" in diameter and 3/32" thick, transparent to the IR rays, fairly inert to fluorine gas, and provided observation of the reaction by the investigator. The sample holder consisted of a right circular cylinder 2" in diameter and 2" in height and sandwiched between two 2-1/2" discs. The Teflon sample holder had a 3/4" port on its side which coupled the sample holder to the fluorine collection system (KI paper column).

The experimental procedure was simply to place preweighed pellets of CoF_3 inside the chamber, evacuate the system, select a temperature range by adjusting variac to desired voltage, and turn the power on for a predetermined length of time. The gases liberated by pyrolysis of CoF_3 were drawn into the KI saturated filter paper column. The KI saturated paper is then removed from the Teflon holder and analyzed for fluoride ion.

Another system based on the all-Teflon system but made specifically for the collection of fluorine gas samples was developed, but due to the termination of the project only two gas samples were ever collected. The principle of this experiment was to provide the fluorine gas produced only on Teflon, passivated nickel or stainless steel walls. The temperature of the stainless steel collection bottle was that of LN_2 (-196^{o}C) which again would provide a lesser chance of reaction with fluorine gas.

The experimental procedure was similar to the all-Teflon system with the exception that the gases produced by pyrolysis would be equally dispersed throughout the system. Since the sample bottle contained 90% of the total volume and it is at LN_2 temperature, the fluorine gas would be liquified. Thus, the sample bottle would continue to act as a cryostatic pump. Upon

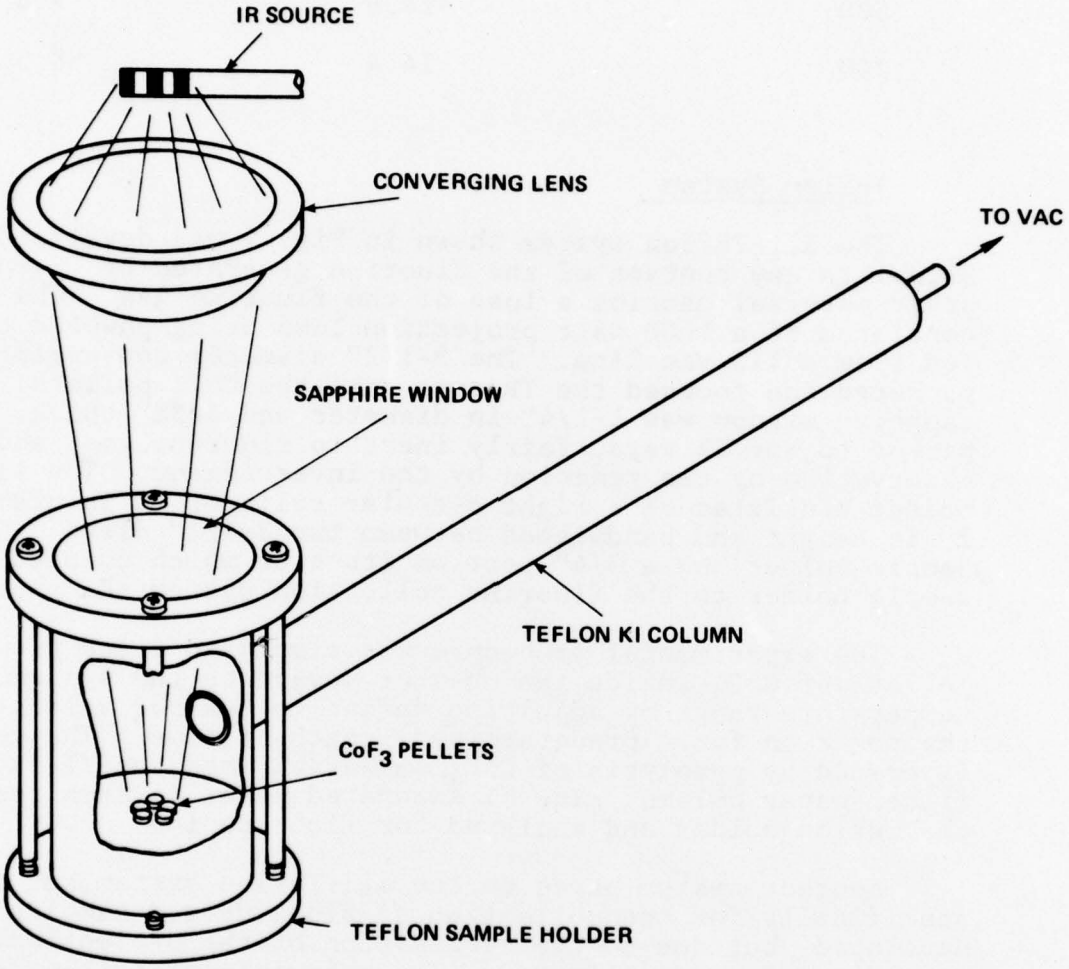

FIG. 9 TEFLON SYSTEM

completion of experiment a valve would close off the sample bottle now containing most of the fluorine gas produced and the sample bottle could be brought back to room temperature and analyzed.

Several runs were conducted with the Teflon system. The results are shown in Table 10. The fluorine yield increases to about 11%. This value represents about 67% of the theoretical yield.

The loss of fluorine is probably attributed to the fact that CoF_3 contains a small amount of moisture. When water is present, the following reaction becomes possible during the pyrolysis:

$$CoF_3 + 1/2 \ H_2O \rightarrow CoF_2 + HF + 1/4 \ O_2$$

Therefore, part of the fluorine becomes hydrogen fluoride as the product of pyrolysis of CoF_3.

As a confirmation, gas samples were collected and sent to the Naval Ordnance Station for fluorine analysis, using gas chromatographic technique. The results indicate that fluorine is present in the gas mixture, along with SiF_6, which is suspected to be a product of contaminant during the analysis.

TABLE 10

Teflon System

CoF_3	TIME (MIN)	WT LOSS (%)	F_2 YIELD (%)
Pellet (small)	6	10.8	9.9
Pellet (large)	10	8.9	8.9
Fragments	7	12.8	10.9
Fragments	10	13.9	11.0
Powder	10	14.4	10.6

CONCLUSION AND RECOMMENDATION

Results from the laboratory testing indicate that pyrolysis of CoF_3 results in the conversion of CoF_3 to CoF_2, releasing fluorine gas in the process. The kinetics of the pyrolysis is a function of temperature. The maximum fluorine yield was found to be about 67% of the theoretical value. Loss of fluorine is attributable to the reaction of fluorine with the surface of the reaction vessel at elevated temperature and the production of hydrogen fluoride in the presence of water.

Because of the sudden termination of the program, scale-up testing was not conducted to evaluate the practicality of CoF_3 as a solid reactant for the high energy laser system. However, the results in the laboratory testing strongly suggest that CoF_3, indeed, is an excellent candidate as a solid reactant for the generation of fluorine gas.

The potential of CoF_3 for high energy laser could not be known unless further work on this compound would be carried out. More studies on the basic chemical mechanisms and rates for the reactions involving CoF_3 to CoF_2 and CoF_2 to Co_3O_4 or Co metal should be conducted. In addition, investigations of high temperature corrosion of fluorine on various materials and means of applying external heat for the pyrolysis are also essential.

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