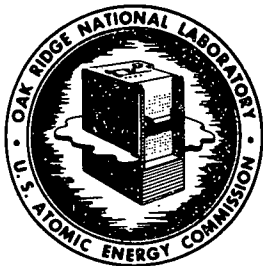


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 TO: F. L. Culler, Jr.
 FROM: J. B. Adams, L. M. Ferris, C. D. Scott

ABSTRACT

Progress in the Fluorox program for the period April 30, 1957 to January 14, 1958 is reported. The chemical reaction of primary interest in the Fluorox program is the oxidation of UF_4 with O_2 , $2UF_4 + O_2 = UO_2F_2 + UF_6$; however, to study this process at higher temperatures, the thermal decomposition of UO_2F_2 , $3UO_2F_2 = 2/3 U_3O_8 + UF_6 + 1/3 O_2$, is being investigated by thermogravimetric methods in the temperature range 750-900°C. A fluidized bed reactor and a flame reactor have been used successfully to perform the continuous oxidation of UF_4 with O_2 . The 3-in. fluidized bed reactor was operated up to 825°C on both a continuous and batch basis while the flame reactor was used to continuously react finely divided UF_4 with O_2 in a $CO-O_2$ flame at temperatures greater than 1200°C.

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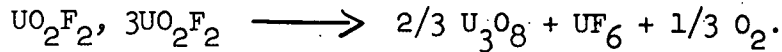
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INTRODUCTION

The Fluorox program is the study of processes which produce UF_6 without the use of elemental fluorine. This report presents the progress made in the Fluorox program from April 30, 1957 to January 14, 1958 as presented in a Seminar given before the Chemical Technology Division on January 14, 1958.

The chemical reaction of primary interest is the oxidation of UF_4 with O_2 or dry air, $2UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6$. The possible use of high temperature processes such as a flame reactor make it necessary to also investigate the high-temperature chemistry of UO_2F_2 , specifically the decomposition of



The study of the decomposition of UO_2F_2 is being done by a thermogravimetric technique in the temperature range of 750 - 900°C. This study when completed is intended to yield stoichiometry of the main decomposition reaction, the relative effects of any pertinent side reactions, and the rate of decomposition at different operating conditions.

Current engineering development work is aimed at design and testing of oxidation reactors. Two types of reactors have been built and tested, a fluidized bed reactor and a flame reactor.

In the fluidized bed reactor, sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized with dry O_2 or air at 800 - 825°C. Optimum operating conditions and equipment design are being determined by a series of tests.

The flame reactor is used to react continuously finely divided UF_4 with O_2 in a $CO-O_2$ flame at temperatures greater than 1200°C.

1.0 CHEMICAL DEVELOPMENT STUDIES² (L. M. Ferris)

The basic reaction of the Fluorox Process¹ is $2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UO}_2\text{F}_2 + \text{UF}_6$. According to preliminary studies² UO_2F_2 may decompose at temperatures above 800°C according to the reaction $3\text{UO}_2\text{F}_2 \longrightarrow \text{UF}_6 + 2/3\text{U}_3\text{O}_8 + 1/3\text{O}_2$. Thus the overall stoichiometry of a UF_4 - O_2 reaction at high temperatures might be $3\text{UF}_4 + 4/3\text{O}_2 \longrightarrow 2\text{UF}_6 + 1/3\text{U}_3\text{O}_8$. Since UO_2F_2 may be the prime constituent of a fluidized-bed Fluorox reactor³, more complete knowledge of the decomposition reaction is desirable. The decomposition reaction might also provide a basis for an alternative method for the production of UF_6 . The purpose of the chemical development studies was, therefore, to determine the stoichiometry of the decomposition reaction, and to obtain some information regarding the rate of decomposition. A more complete report⁴ of the chemical development work is also available.

The author is happy to acknowledge the assistance of Miss E. F. Gabbard and Mr. J. F. Land, who obtained the experimental data reported here.

1.1 Experimental Procedure

The stoichiometry and rate of the decomposition reaction were determined from weight loss data obtained with a recording thermobalance⁵, and chemical and x-ray analyses of the reaction residues. The thermobalance provided at each temperature a continuous record of the weight of a decomposing sample.

1.2 Results

Thermodynamics - Before performing the experiments, estimates were made⁶ of the standard free energy changes for several postulated decomposition reactions. These are shown in Figure 1.1. All the reactions are thermodynamically unfavorable (the F° is positive), but in the most favorable case (Curve D) the decomposition products are U_3O_8 and UF_6 . The calculated equilibrium constant for the reaction $3\text{UO}_2\text{F}_2 \longrightarrow \text{UF}_6 + 2/3\text{U}_3\text{O}_8 + 1/3\text{O}_2$ is sufficiently high to suggest that the reaction would proceed through the removal of the gaseous products with an inert sweep-gas.

X-ray Analysis of Reaction Residues - All the experiments were performed at temperatures between 700 and 1000°C using dry helium (flow rate, 300 ml/min at 25°C) as the inert sweep-gas to drive the reaction. Only U_3O_8 was found by x-ray

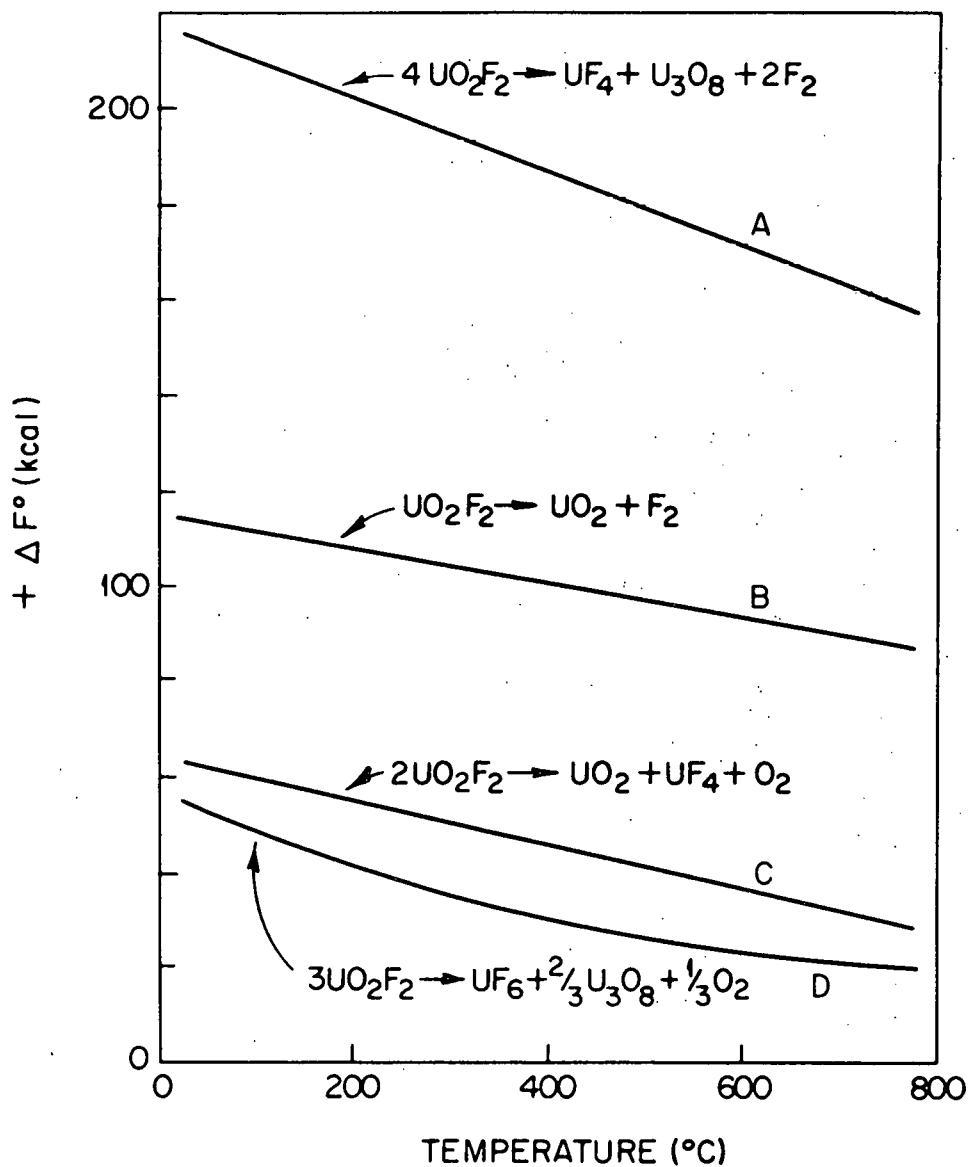


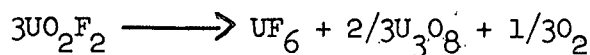
Fig. 1.1. Estimates of the Temperature Dependence of Standard Free Energy Changes for the Decomposition of UO_2F_2 .

analyses as a solid decomposition product at temperatures below 900°C in agreement with the thermodynamics. Above 900°C the presence of UO₂ was detected in addition to U₃O₈.

Stoichiometry From Weight Losses and Chemical Analyses - The weight losses and chemical composition of the reaction residue expected from complete decomposition according to the various postulated reactions (Figure 1.1) were calculated and compared to those obtained experimentally. In this manner the stoichiometry was unequivocally shown⁴ to be $3\text{UO}_2\text{F}_2 \longrightarrow \text{UF}_6 + 2/3\text{U}_3\text{O}_8 + 1/3\text{O}_2$. The agreement obtained between data from weight losses and chemical analyses is illustrated in Table 1. The effect of time on the per cent conversion is not included with these data, and is not relevant to the argument at hand. A case in point is that of the two runs at 840°C; one run was obviously shorter than the other. The significant result is the good agreement between the % conversion calculated from weight losses and that calculated from chemical analyses of the decomposition residue. This agreement, supplemented by the good material balances, confirms the stoichiometry given above.

TABLE 1

DECOMPOSITION OF UO₂F₂ ACCORDING TO THE REACTION



Temperature, °C	Average Conversion, %		Average Material Balance, %
	By Weight	By Chemical Analysis	
750	3.08	3.63	98.1
775	10.4	9.05	105
825	38.0	32.4	99.4
825	26.1	29.2	101
840	27.8	30.4	99.7
840	71.0	72.5	97.6
850	95.7	92.7	95.6
860	82.0	78.6	97.7
> 900	106	104	114

Reaction Rate Constants - The following mathematical treatment was used to analyze the weight-time plots obtained from the thermobalance. It was assumed that UO_2F_2 sublimed simultaneously with its decomposition. The rate at which a sample, $UO_2F_2 + U_3O_8$, will lose weight is given by

$$-\frac{dw_s}{dt} = fk_w + k_v w \quad (1)$$

where, t = time

w_s = sample weight, i.e. the sum of the weights of UO_2F_2 and U_3O_8 , at time t

w = weight of UO_2F_2 at time t

k = rate constant for the decomposition reaction

k_v = rate constant for the sublimation process

f = stoichiometry factor

The stoichiometry factor, f , is calculated from the following equation:

$$f = 1 - \frac{2/3M_{U_3O_8}}{3M_{UO_2F_2}} \quad (2)$$

where M is the molecular weight of the respective compound. If decomposition and sublimation are parallel, first order processes

$$-\frac{dw_s}{dt} = (fk + k_v)w^0 \exp -(k + k_v)t \quad (3)$$

where the superscript zero refers to zero time. For convenience, the following terms are defined:

$$X = fk + k_v \quad (4)$$

$$Y = k + k_v \quad (5)$$

After integration and rearrangement, the following equation is obtained

$$\log \frac{Y (w_s - w_s^0)}{X w^0} + 1 = -Yt/2.303 \quad (6)$$

which relates the measurable variables w_s and t . Equation (6) cannot be used directly to evaluate X and Y . However, inspection of Equation (3) reveals that the quantity X may be evaluated from the initial slope of a plot of sample weight versus time; i.e. at $t = 0$, Equation (3) reduces to

$$-\frac{dw_s}{dt} = Xw^0 \quad (7)$$

Once X is known it is possible to evaluate Y from Equation (6) by successive approximations. Arbitrary values of Y are used in the calculation of the logarithmic portion of Equation (6). This logarithmic quantity is then plotted versus time. If the value chosen for Y is not the correct one a curved plot will result. Successive approximations are continued until the plot becomes linear. Then, as required by Equation (6), the value of Y used in the calculation of the logarithmic term will be equal to that calculated from the slope of the line. The rate constants k and k_v can then be obtained by solving Equations (4) and (5) simultaneously.

For the special case where no sublimation occurs, Equation (6) reduces to

$$\log \frac{(w_s - w_s^0)}{f w^0} + 1 = -kt/2.303 \quad (8)$$

A plot of the logarithmic term versus time should be linear with k evaluable from the slope.

Figure 1.2 contains plots of typical first order behavior as described by Equation (8). As shown from this figure, sublimation of UO_2F_2 is negligible below $825^\circ C$. Curve D illustrates the type of plot which results if sublimation is ignored at the higher temperatures. Figure 1.3 illustrates the type of plot obtained through use of Equation (6). It should be noted that the upper curve in Fig. 1.3 was plotted with the same data used in plotting Curve D, Figure 1.2. An Arrhenius plot of $\log k$ versus $1/T$ is shown in Figure 1.4. The temperature dependence of k corresponds to an apparent activation energy of 72 kcal./mole.

A few runs were made using air and pure oxygen as the sweep-gas. As expected from the stoichiometry the rate decreased markedly (approximately a factor of 5) when oxygen was present in the sweep-gas. The data obtained were insufficient to permit evaluation of the quantitative relationship between rate and oxygen partial pressure.

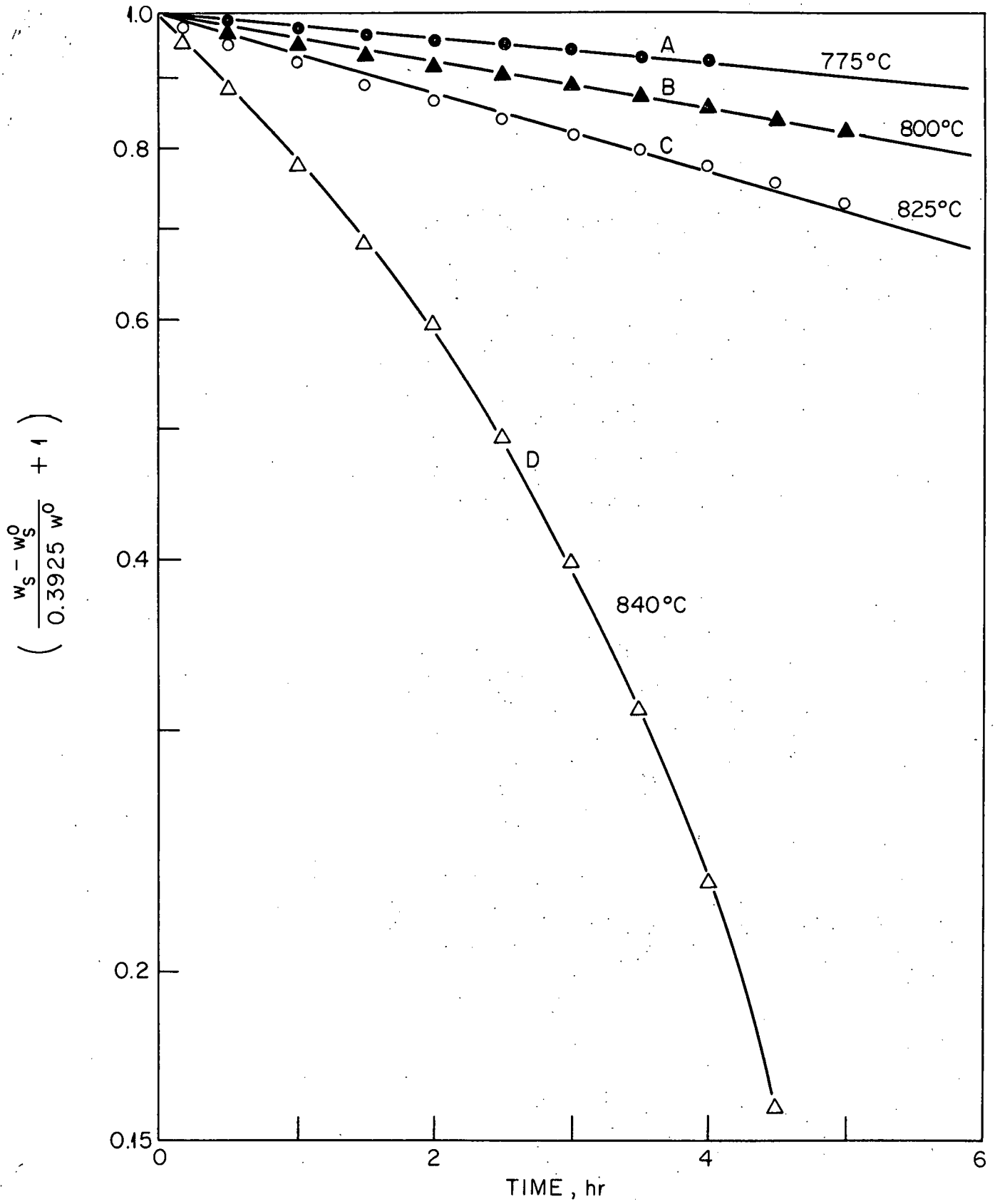


Fig. 1.2. Decomposition of UO_2F_2 , Showing a Single First-order Process Below 825°C.

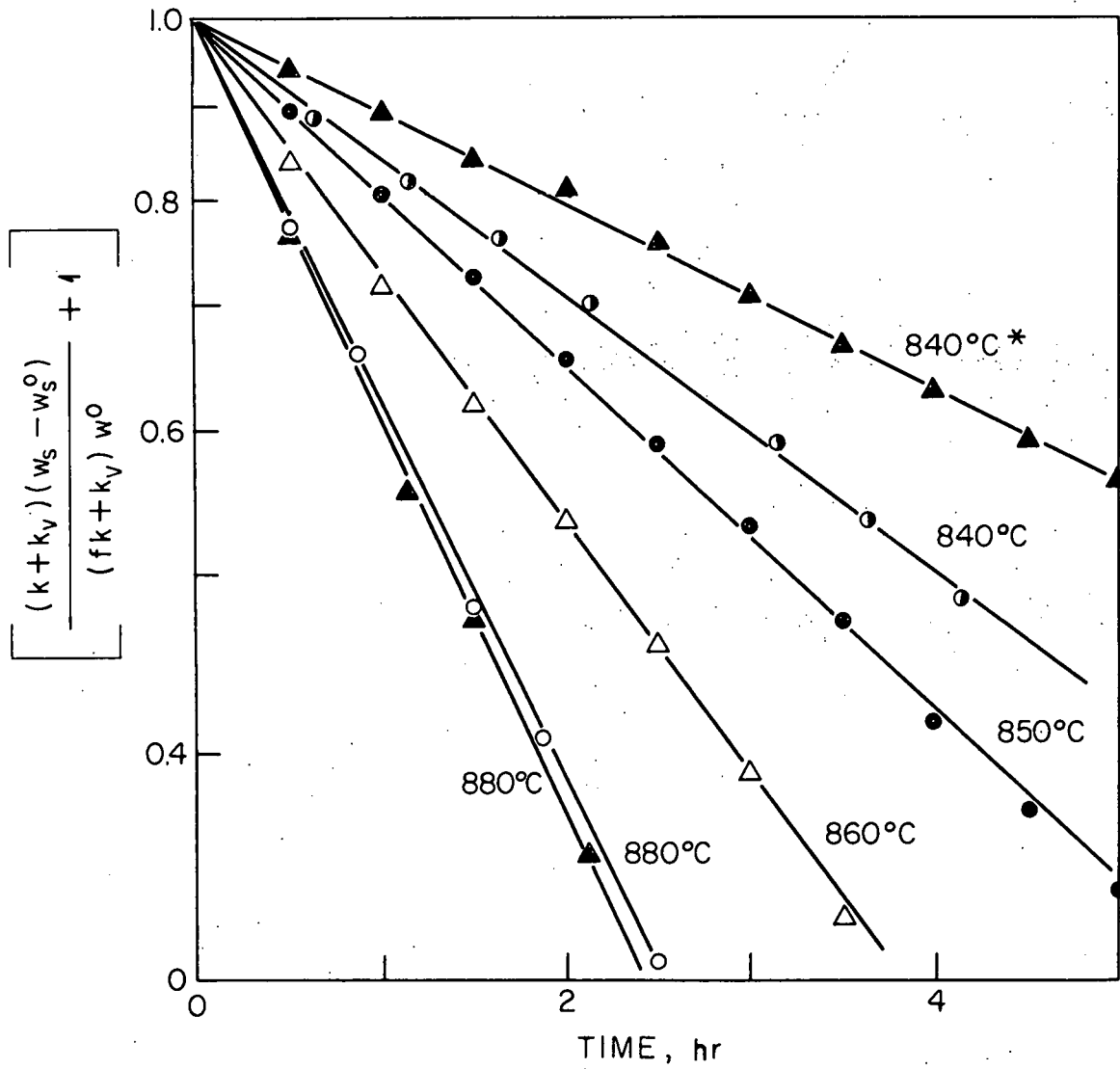


Fig. 1.3. Photo obtained when Decomposition and Sublimation of UO_2F_2 are Considered Parallel. First-order Processes at Temperatures above $825^\circ C$. Curve plotted from same weight-loss data as $840^\circ C$ curve in Figure 1.2.

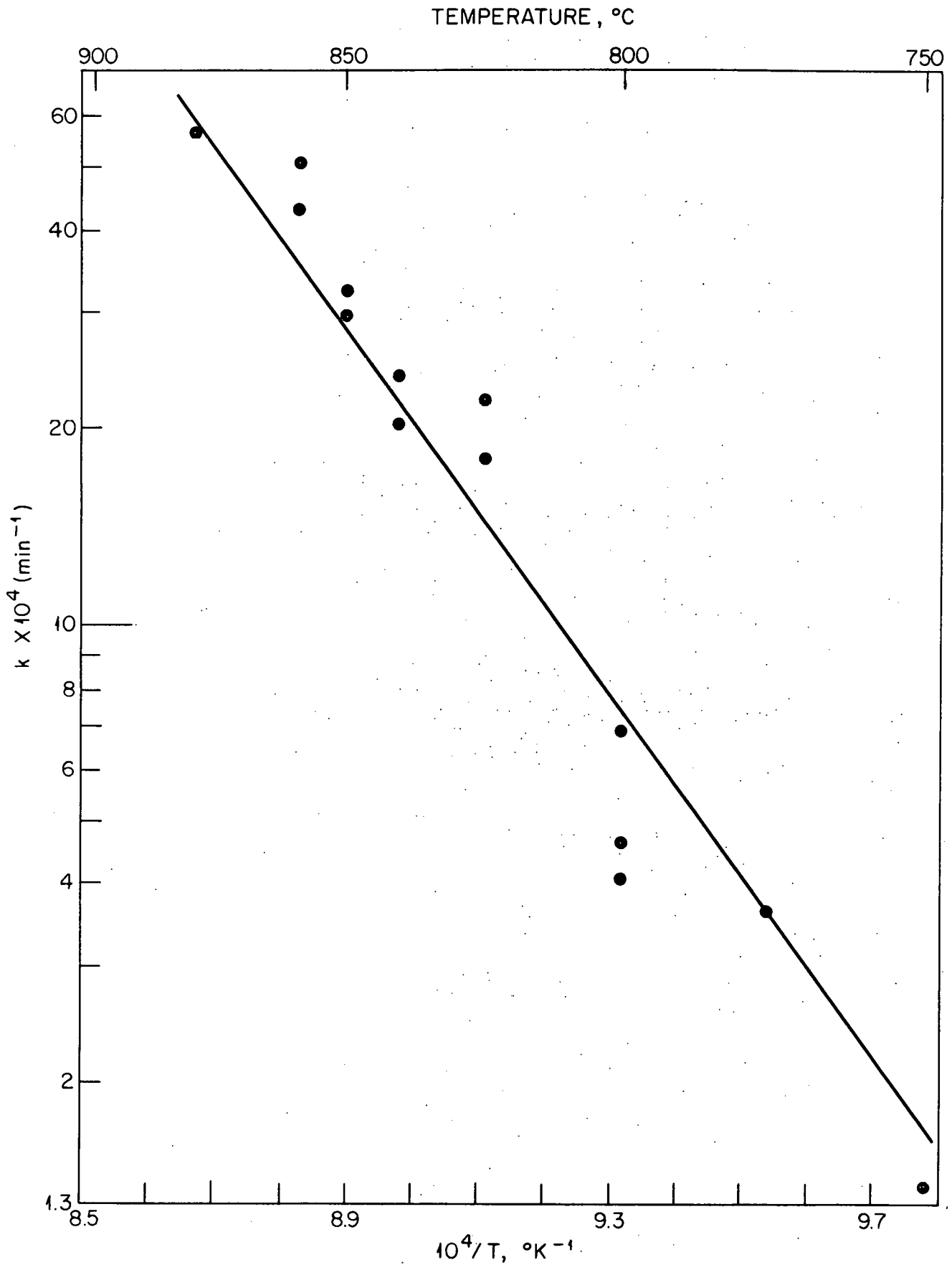


Fig. 1.4. Rate Constants for the Reaction $3\text{UO}_2\text{F}_2 \longrightarrow 2/3 \text{U}_3\text{O}_8 + \text{UF}_6 + 1/3 \text{O}_2$.

1.3 Conclusions

It was concluded from the data obtained that UO_2F_2 is relatively stable in an inert atmosphere at temperatures below $800^\circ C$ (the half-time for decomposition at $800^\circ C$ is 25 hr; at $880^\circ C$, 2 hr; at $1000^\circ C$, about 10-15 minutes). The use of UO_2F_2 as the prime constituent of a fluidized-bed reactor should pose no chemical problems, particularly in the presence of oxygen.

At temperatures above $900^\circ C$, UO_2 can be expected as a decomposition product. Since no UF_4 was identified in the decomposition residues, it was tentatively concluded that the UO_2 was formed by slow decomposition of U_3O_8 . Whether or not UO_2 is found after reacting UF_4 and oxygen at temperatures above $900^\circ C$ would therefore be dependent on the relative rates of the reactions concerned.

The decomposition reaction is potentially the basis for a primary method for producing UF_6 . However, even in a low molecular weight inert gas such as helium, the rate of decomposition appears to be prohibitively low at reasonable temperatures ($< 800^\circ C$). Any increase in reaction temperature would pose severe engineering problems.

Future work by the Chemical Development Section could include the determination of the effect of oxygen partial pressure on the rate of decomposition of UO_2F_2 , a study of the UO_2F_2 decomposition reaction under vacuum, and measurement of the rate of decomposition of U_3O_8 .

1.4 References

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2.0 FLUIDIZED-BED REACTOR DEVELOPMENT - (J. B. Adams)

Since the last Fluorox Seminar, considerable progress has been made in fluidized-bed reactor development for the oxidation of UF_4 . Presently, a continuous reactor is being operated at $800^\circ - 820^\circ C$. UF_6 product has been collected in cold traps for direct measurement of recoveries and overall material balances have been made. Prior work was done in a batch charged reactor at 650° to $730^\circ C$. UF_6 produced was not measured directly and results were inferred from the change in composition of the reactor contents with time.

There were several reasons for going to a continuously fed reactor. The major reason, however, was that a batch reactor can not be operated at $800^\circ C$. Operation of a batch reactor requires a high concentration of UF_4 in the reactor during most of a run, since all the feed is charged at once. It was found that high temperatures at the wall caused fusion and sintering of the UF_4 . Even in a run with less than 20% UF_4 diluted with UO_2F_2 this sintering occurred.

A continuous reactor is operable since the bed is almost entirely UO_2F_2 with a small concentration of UF_4 at steady state. During the current runs, the steady state concentration of UF_4 was less than 1% at a feed rate of 1 lb UF_4 /hr since the reaction rate is quite rapid at $800^\circ C$.

A continuously fed reactor posed additional problems. There appeared to be considerably more dusting with continuous feeding, resulting in more trouble with off-gas lines plugging. The obstructions, such as the thermowell or even small horizontal sections in the off-gas line, resulted eventually in plugged lines. The plugging problem has been corrected by installing completely straight off-gas lines. Feeding caused some trouble. Metering powdered UF_4 against 5 - 15 psi back pressure was somewhat difficult.

Figure 2.1 shows schematic flow sheet of the reactor system. At the left is the gas and electrical supply system. Variacs are used for electrical heating control. Gases are metered through rotameters from a cylinder supply and dried to a $-100^\circ F$ dewpoint with adsorbents. The reactor was fabricated from 3-in. Inconel pipe with a two foot section heated by clamshell heaters. Fluidizing gas enters at the base and the off-gas is taken overhead. The off-gas from the reactor containing UF_6 oxygen and dust is lead to the filter where the dust is removed by porous metal filters. The gas is then passed through the cold traps

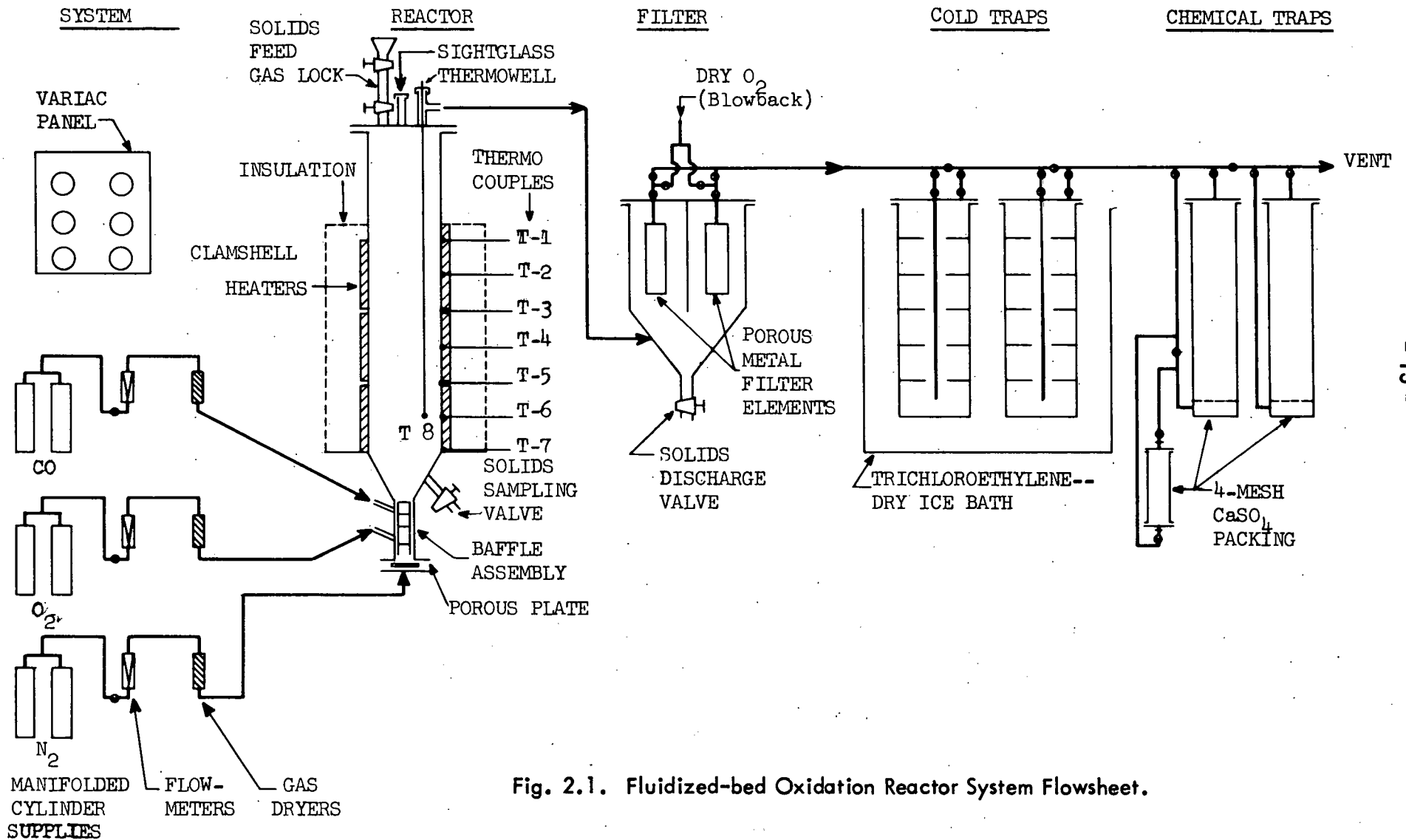
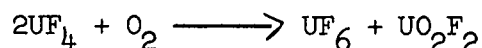


Fig. 2.1. Fluidized-bed Oxidation Reactor System Flowsheet.

to condense UF_6 . The traps are maintained at $-75^{\circ}F$ by a trichloroethylene-dry ice bath. Residual UF_6 is absorbed in chemical traps packed with calcium sulfate and the gas passed to the hot off-gas vent.

In four recent runs, recoveries varied from 25 to 70% in the cold trap based on the yield for the theoretical reaction:



In three of the runs shutdown occurred early in the run due to plugged lines and a leaky solids feeder. Material balances and recovery calculations on these runs are not accurate. With the small amount of feed, one to three lb of UF_4 charged to the relatively large amount of UO_2F_2 (15 lb) in the bed, losses due to side reactions of UF_6 with impurities in the UO_2F_2 exaggerated errors. One run resulted in a fairly good though incomplete material balance. Eleven lb of UF_4 were fed over a 13 hr period. Actual recovery in the cold trap was about 40% of theoretical.

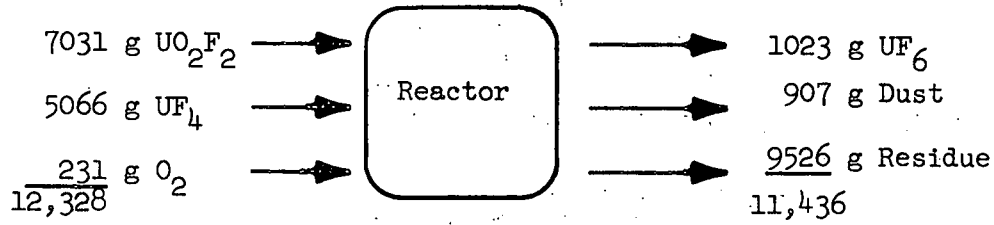
Figure 2.2 is a weight balance for this run. All numbers in the figure are weights in grams. 7031 g of UO_2F_2 were charged to the reactor. 5066 g of UF_4 were fed during the run. It was calculated that 231 g of oxygen were consumed. 1023 g of UF_6 were recovered in the cold trap while 907 g of dust in the filter and 9526 g of solids were removed from the reactor, leaving 872 g total weight unaccounted for. By comparison, the component balances for uranium and fluorine showed that 615 g of uranium and 171 g of fluorine were unaccounted for.

Figure 2.3 gives a material balance by compounds for the system indicating the major losses involved. Again all of the numbers are weights in grams. Of 5108 g of UF_4 available for reaction, 111 g were unreacted and 478 g were involved in U_4F_{17} formation. Of the UF_6 losses, 76 g were involved in U_4F_{17} formation. U_4F_{17} is the UF_4 - UF_6 intermediate found in the dust filter.

Additional losses of UF_6 included 115 g lost by reaction with small amounts of water in the reactor system and 438 g consumed by reaction with U_3O_8 . Unaccounted for were 883 g of UF_6 . The side reactions involved are listed at the bottom of the figure. The actual weight of UF_4 available for reaction is larger than the number listed in the weight balance in Figure 2.2 due to two factors. In the weight balance, the item marked UF_4 actually contains UO_2F_2 and U_3O_8

Figure 2.2

Weight Balance (FRB #13)

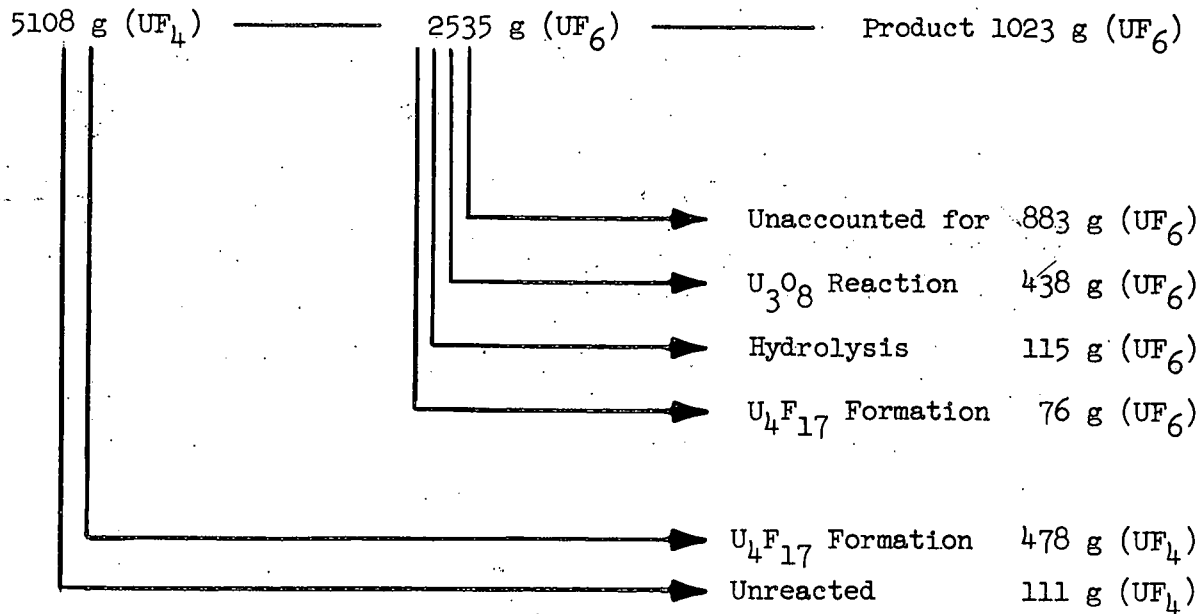


Unaccounted For:

Total	872 g
Uranium	615 g
Fluorine	171 g

Figure 2.3

Material Balance (FRB #13)



impurities. Note also that in the reaction of UF_6 with U_3O_8 some UF_4 is produced in the reactor. The net effect of these two factors is that there was slightly more UF_4 available for reaction than was charged to the reactor.

The UF_6 unaccounted for was lost in at least two ways. In this particular run the calcium sulfate chemical traps were not operative so losses from the cold traps could not be measured. The remainder was probably consumed in corrosion reactions.

Difficulties with corrosion have become much more evident since operations began at $800^\circ C$. Small amounts of a bright orange material appeared regularly in the off-gas system. This occurrence was never noted in work at lower temperatures. Tentatively, the orange material has been identified as chromyl fluoride. There is a possibility that chromium tetrafluoride and pentafluoride are also present in part of the system.

Since the corrosion became evident a number of samples have been analyzed from the system to determine the distribution of corrosion products.

Figure 2.4 gives the spectrographic analysis of several products of corrosion. The metallic impurities are components of the material of construction used in the hottest parts of the reactor system, Inconel. The UF_4 used as feed was essentially free of metallic impurities. The dust taken from the filter contained a considerable amount of impurities. The occurrence of titanium indicates that some part of the system may be made of Inconel-X, a titanium-bearing version of Inconel.

The last two columns represent material taken from the reactor. During operations a small amount of scale builds up in the reactor. A sample of the contents of the reactor was removed and the scale and UO_2F_2 were separated for analysis. The scale contains almost all of the impurities with relatively small amount in the UO_2F_2 . It is suspected that the nickel analysis was in error and that actually most of the impurities in the UO_2F_2 were due to small amounts of scale that could not be removed before analysis.

As far as actual contamination of UF_6 product, chromium is probably the major impurity. Figure 2.5 gives the analysis of a UF_6 hydrolysis liquor, resulting from adding water to the cold traps containing UF_6 product and washing the contents out for analysis. This particular solution analyzed 30 g/liter of uranium and 197 mg/liter of Cr. All the other metallic impurities were insignificant compared to the chromium.

Figure 2.4

Spectrographic Analysis (%/wt)

Constituent	UF ₄	Dust	UO ₂ F ₂	Scale
Cr	0.0003	1.25	0.005	2.5
Ni	0.0001	0.50	0.1	1.25
Fe	0.005	0.38	0.03	0.75
Ti	--	0.25	--	0.06
Cu	0.00001	0.04	0.005	0.003
Mn	0.00004	0.013	0.002	0.025
Si	--	--	0.01	--

Figure 2.5

Analysis of UF₆ Hydrolysis Liquor

Constituent	Concentration Mg/L
Cr	197
Ni	0.8
Ti	1.5
Mn	0.1
Si	2.1
Mo	1.0
U	30,000

In addition to chemical analysis of the impurities and corrosion products, a thermowell from the reactor was removed and examined by the Metallurgy Division (see Figure 2.6). The thermowell was a piece of 1/4-in. Inconel tubing that had been placed in the fluidized bed. It was sectioned in five places. The sections at 5, 15, and 24 inches from the tip of the thermowell had been in the fluidized solids. Those at 31 and 42 inches had been in the gas phase above the fluidized bed. At sections taken in the bed a general attack of 1 - 3 mils was found and on oxalic acid-etching an additional attack of 4 mils by chromium depletion at the grain boundaries was found. Little or no attack occurred at sections that were exposed to the gas phase only. The total operation on this thermowell was about 40 hr above 700°C, most of the time in an atmosphere containing UF₆.

At present, the major problems appear to be corrosion and the resulting impurities and the obtaining of a complete material balance. Corrosion resistance of some ceramic materials will be tested. The Norton Company will flame-spray-coat some samples with very refractory Al₂O₃ and ZrO₂ and with a MgO-bearing ceramic. The MgO material appears to have the most promise in this system but MgO is difficult to apply as a coating. More runs will be made in the present reactor in an effort to obtain a run in which 30 lb or more of UF₄ are fed within 24 hours. Such a rate would allow an accurate material balance with minimum interference by side reactions of UF₆, recovery of a large amount of product (Approximately 10 lb) for direct analysis, and would offer an opportunity to test ceramic coatings. If any ceramic proves to be a reasonable material of construction at temperatures above 850°C, the direct decomposition of UO₂F₂ to UF₆ would become of considerable interest.

Figure 2.6

Corrosion of Thermowell

Distance from Tip (in.)	Depth of Attack (mils)	
	Unetched	Etched
5	1-3	} 3 (plus mil Cr depletion)
15	1-2	
24	1-2	
31	0	--
42	0	--

3.0 FLAME REACTOR DEVELOPMENT - (C. D. Scott)

Another engineering approach in the Fluorox Process is the flame reactor study. The flame reactor reacts continuously finely divided UF_4 with oxygen in a carbon monoxide-oxygen flame. To date, successful tests have been made in which UF_4 was continuously fed into a flame. The results of these tests indicate that UF_6 was being produced.

There are several reasons for investigating the flame reactor for the Fluorox Process. The flame reaction zone is very hot with an estimated flame temperature of $2000^\circ C$. (The theoretical flame temperature for a 50% mixture of carbon monoxide and oxygen is $2800^\circ C$.) Finely divided UF_4 , minus 325 mesh, produces a feed of high specific surface area. Limited high-temperature thermodynamic data indicate that the combination of the high-temperature reaction zone and the high specific surface area of the feed would produce a reaction half time which would be on the order of a fraction of a second. Some of the results of the flame reactor runs also indicate that the reaction half time is in this range.

There are several possible reactions which can occur in the high temperature region. Figure 3.1 shows possible reactions that can occur in the flame reaction zone. Reaction #1 is the classical Fluorox reaction which can be expected in all of the low temperature work and which may be the first step in any high temperature reaction. At high temperatures, above $1000^\circ C$, the UO_2F_2 will decompose and form more UF_6 and uranium oxides, as shown by reactions #2 and #3. Reaction #4 shows the total reaction if it is assumed that all the UF_4 reacts to UO_2 and UF_6 . Since reaction #4 gives a higher yield of UF_6 per mole of UF_4 reacted than does reaction #1, it would be more desirable.

Reactions #5 and #6 show the effect of water vapor in the reaction zone. Reaction #5 is the pyrohydrolysis of UF_4 and reaction #6 is the hydrolysis of UF_6 . Both of these reactions decrease the UF_6 yield.

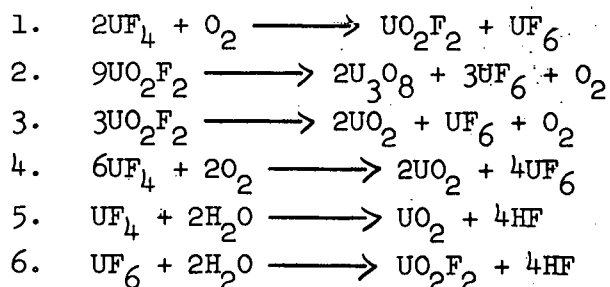


FIGURE 3.1 - POSSIBLE REACTIONS IN A FLUOROX FLAME REACTOR

Figure 3.2 shows a simple chemical flow sheet of the uranium compounds involved in the flame reactor process, assuming that all of the UF_4 is reacted entirely to UO_2 and UF_6 . The UF_4 reacts in the flame forming the UF_6 product and a solids residue of UO_2 which is recycled back to the UF_4 feed stream by simple hydrofluorination. If there is not complete reaction to UO_2 , the recycle stream would be more complicated.

Another advantage of the flame reactor is that the actual reaction zone is not in contact with the wall. By proper geometry control of the flame, the reaction zone can be kept away from the wall and high temperature corrosion problems will be decreased.

The flame reactor equipment, as shown in Figure 3.3, is composed of a solids feeder which meters UF_4 into the oxygen fluidizing stream. This fluidized UF_4 stream then is fed into the burner assembly where it enters the reaction zone enclosed in the reactor. The residue solids settle to the bottom of the reactor where they can be sent to recycle while the off-gases composed of CO_2 , O_2 , and UF_6 proceed to the off-gas system where the UF_6 product is collected.

3.1 Fuel Gas

The main reason for using CO as the fuel gas is that it is a non-hydrogen bearing gas which does not produce water as a product of reaction. It is essential to keep water away from the reaction zone because of the pyrohydrolysis of UF_4 and the hydrolysis of UF_6 . In initial tests, commercial grade CO was used. However, since this type of CO contains some impurities, later tests were made with pure grade CO. Figure 3.4 shows typical gas analysis of the two types of CO. It shows that the amount of hydrogen and saturated hydrocarbons combined with the higher dew point of the commercial grade CO would produce prohibitive amounts of water vapor in the flame reaction zone. Pure grade CO is very pure with respect to hydrogen contaminants and although it is more expensive, it should still be an economical fuel if used in large quantities.

There is one disadvantage to burning CO with oxygen in the absence of water vapor. Small amounts of water vapor have a catalyzing effect on the CO-oxygen reaction making the resulting flame easier to ignite and maintain. When pure grade CO is used, the flame is difficult to ignite and flame stability is lower than with the commercial grade CO.

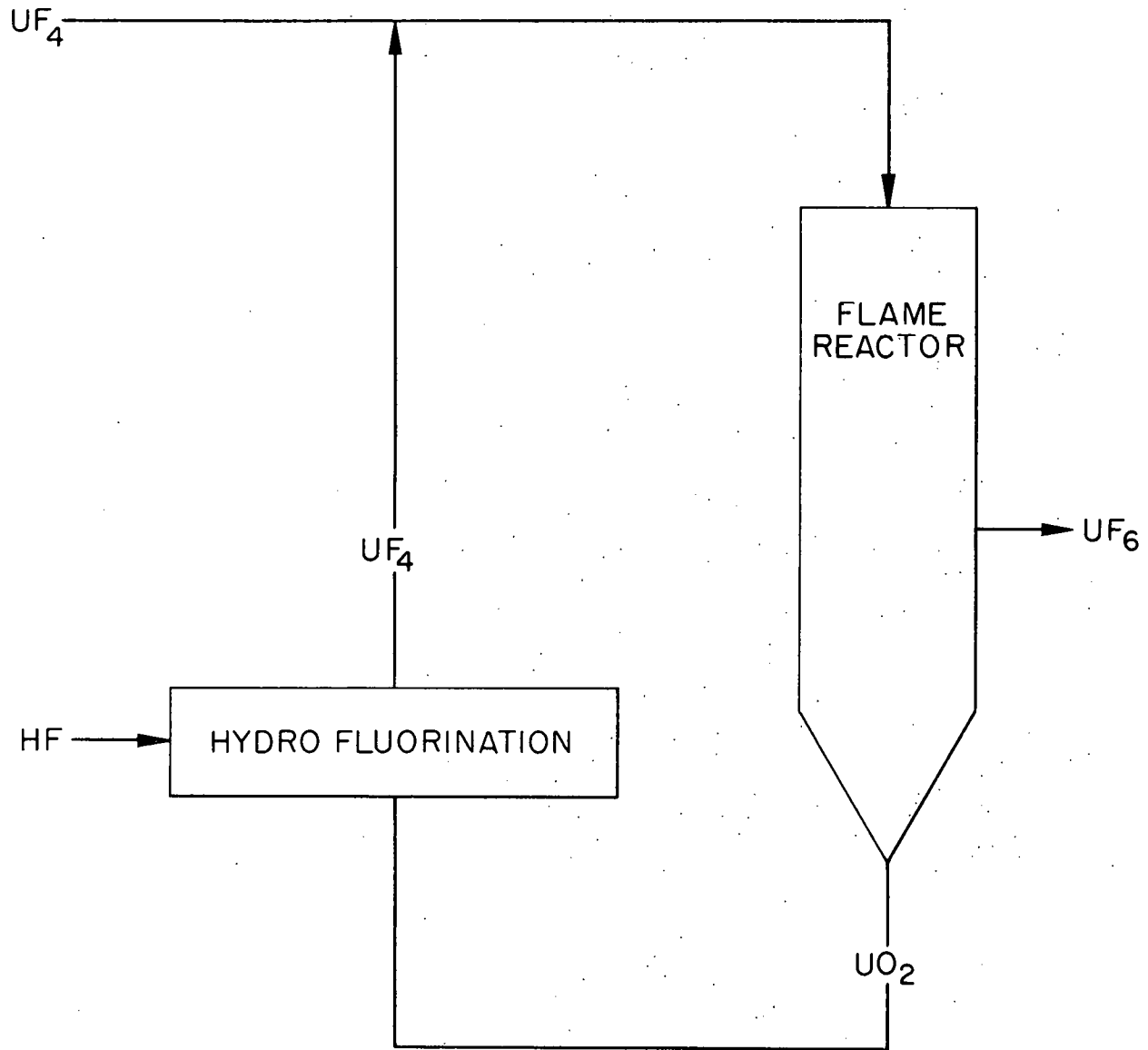


Fig. 3.2. Fluorox Flame Reactor Flow Sheet.

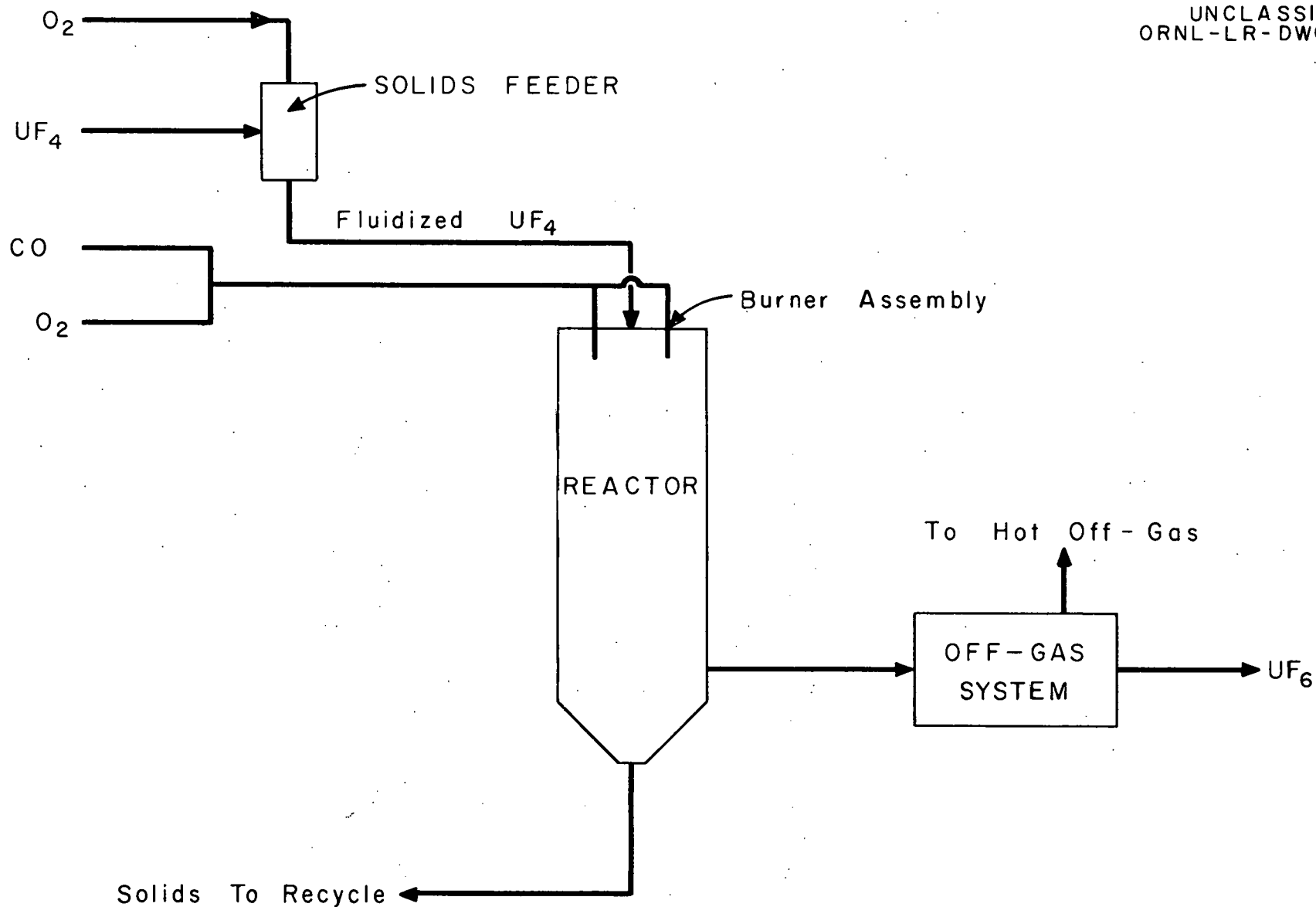


Fig. 3.3. Fluorox Flame Reactor Equipment Schematic.

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	COMMERCIAL GRADE	PURE GRADE
CO	96.8	99.87
CO ₂	0.36	—
H ₂	0.97	< 0.02
O ₂	—	0.02
N ₂	1.0	0.10
SATURATED HYDROCARBONS	0.8	—
DEW POINT	0°F	-60°F

Fig. 3.4. Typical Analyses of CO Gas.

3.2 Experimental Equipment

The design of the experimental equipment is essentially complete and much of it was reported in the last seminar. There have been a few changes in the equipment since then. Figure 3.5 shows a picture of the burner assembly as it was set up for flame tests. Notice the ceramic burner, the Inconel solids nozzle, and the pilot light. Several materials of construction have been investigated for the ceramic burner. It was found that Lavite and a ceramic clay insulation material were both suitable, at least for the limited tests that have been made. More work will be done to investigate nozzle design and materials of construction.

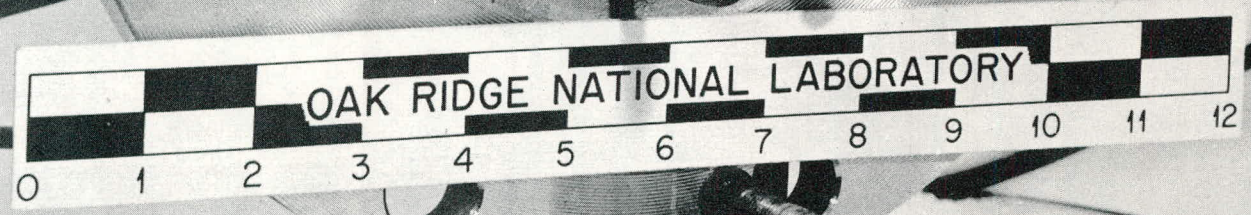
An all-metal burner, (see Figure 3.6), was fabricated and tested. This burner was made of three concentric Inconel tubes. Fluidized UF_4 was fed into the flame through the center tube while the outer two annuli were used for the CO and oxygen. The main advantage of this burner is that the reaction zone is entirely outside the burner, tending to give longer life with less corrosion. Unfortunately the all-metal burner also produced a more unstable flame which must operate in a narrower range than did the ceramic burner.

Further development was necessary for the solids feeding system. The first attempt was to use a screw feeder which emptied into the fluidizing stream. However, at very small feed rates and with fine UF_4 (minus 325 mesh) the feeder produced slugging and even plugging.

A much simpler device was suitable for the feeder, the fluidizing chamber as shown in Figure 3.7. It is a chamber into which a known level of UF_4 powder is charged. The oxygen stream is metered into the chamber by a rotometer through a fluidizing nozzle which fluidizes a certain amount of the UF_4 into the off-gas stream. This off-gas stream was fed into the flame. Although the fluidizing chamber has not been completely calibrated, it was found that the UF_4 feed rate was dependent upon the gas flow through the chamber and the UF_4 powder level. To date feed rates have been reproducible within 15 - 20% which is suitable for the work.

The off-gas system was composed of a solids collection chamber and a water scrubber which scrubs the off-gas prior to its discharge to the hot off-gas line.

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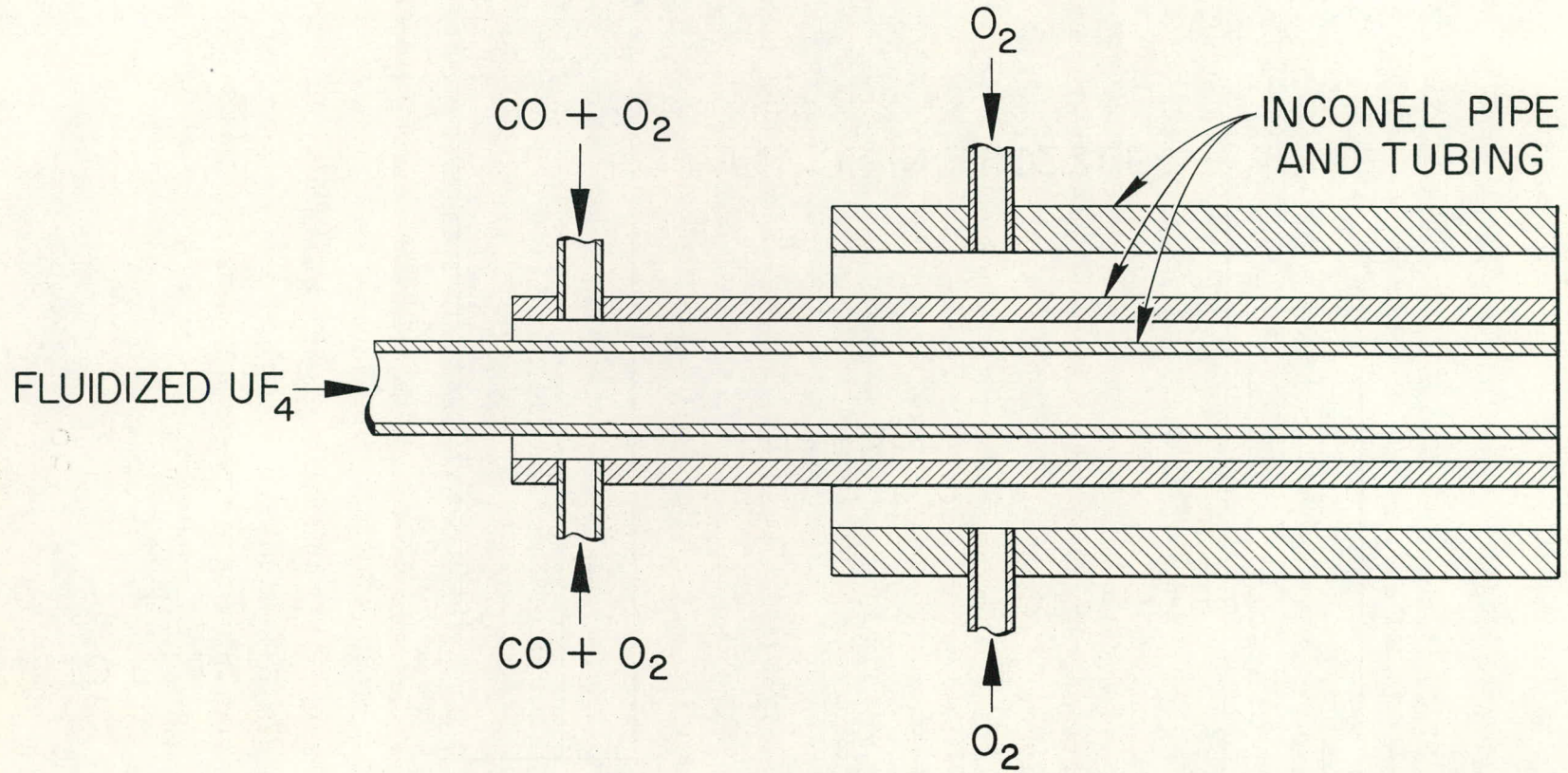


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Fig. 3.5.

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Fig. 3.6. Fluorox Flame Reactor all Metal Burner.

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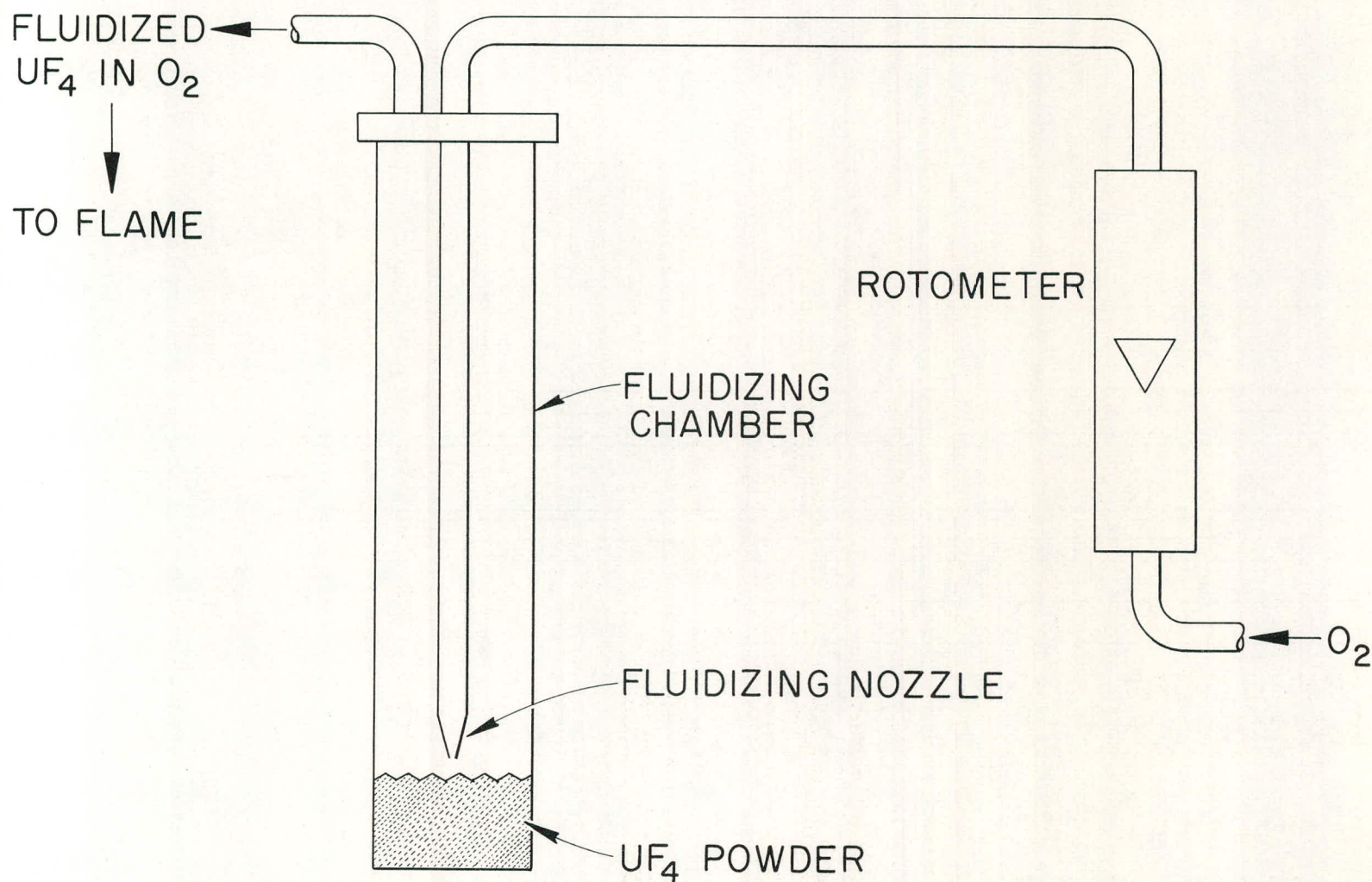


Fig. 3.7. Fluorox Flame Reactor Fluidizing Chamber.

3.3 Experimental Tests and Procedures

Before introducing UF_4 to the flame, tests were made on the individual components of the system. First the burner assembly was tested for proper flame lighting procedure, and for determination of the flame geometry, and for flame stability at different gas rates and CO concentrations. It was found that the flame was 2-1/2 in. to 3-1/2 in. wide and that it had a length of 6 - 14 in.

Figure 3.8 shows a picture of the flame as it was tested in the same test rig shown in Figure 3.5. The flame length was dependent upon the total gas flow and the CO concentration. As the gas flow or CO concentration was increased, the flame length was increased. The flame stability was also dependent upon these factors. If the total gas flow was increased beyond a certain point, the flame tended to blow off the burner and if the total gas rate was decreased beyond a certain point, the flame tended to flash back into the burner assembly and gas lines.

The CO concentration in the fuel gas also caused blow-off or flashback. High concentrations of CO caused the flame to flashback and lower concentrations of CO tended to cause the flame to blow off. Each burner design tested had an operating range for total gas flow and CO concentration in the fuel gas. For the ceramic burner, the operating range was 3 - 6 scfm total gas flow with a CO concentration range of 30 - 50%. The operating range of the all-metal burner was much more limited.

High speed movies, 500 frames per second, were made of the flame in which the flame geometry and flame stability were measured. These movies showed that there was much more turbulence in the flame than was seen by the eye or even in low speed movies.

Attempts were made to measure the flame temperature by use of an optical pyrometer. However, the instrument gave consistently low results, or at least much lower than had been anticipated. These low readings were attributed to the fact that the flame had a low emissivity in the range needed for the optical pyrometer, particularly in the absence of water vapor. At present the Instrument Division is investigating other means of measuring flame temperatures.

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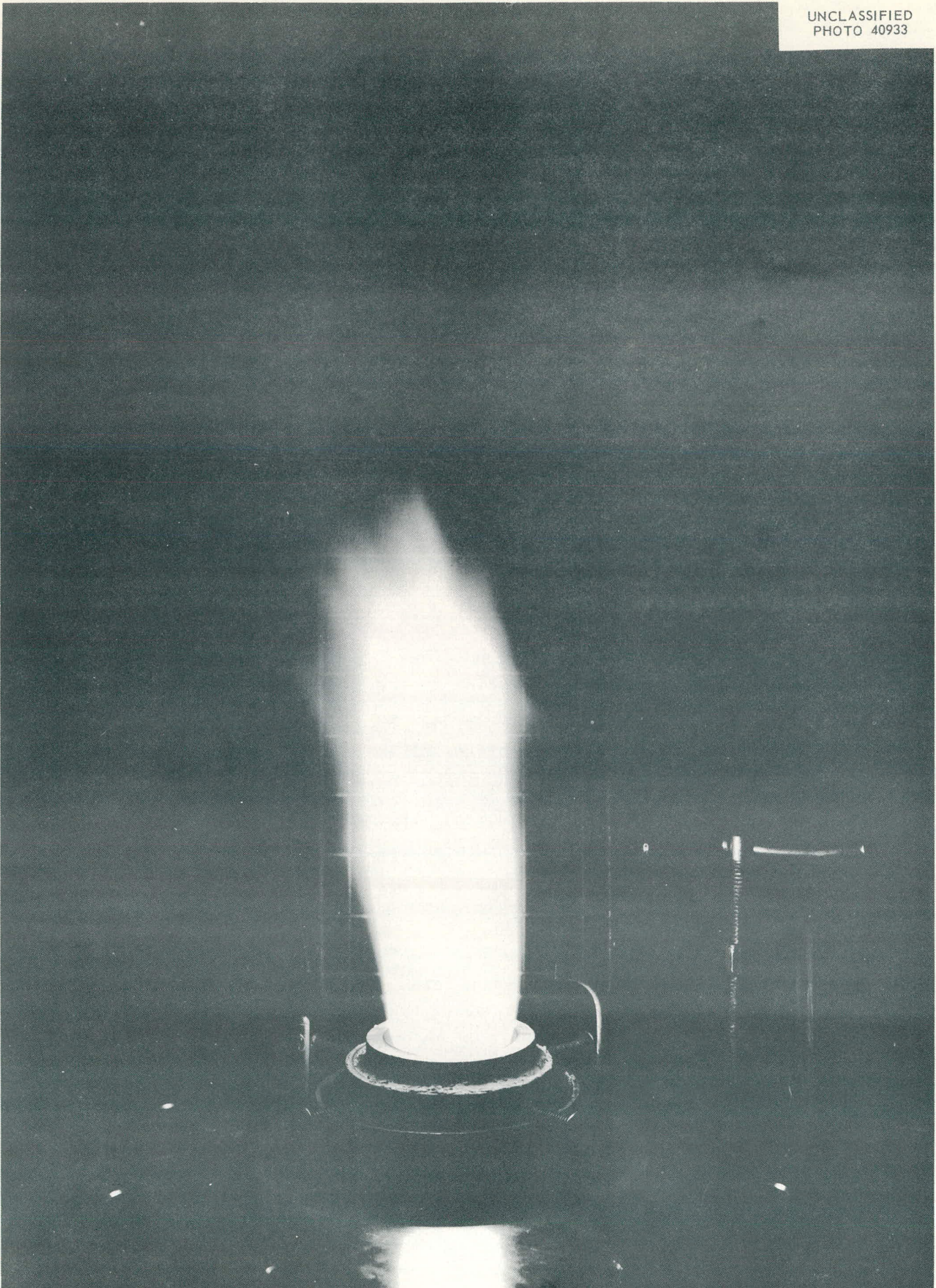


Fig. 3.8. Picture of a Typical CO-O₂ Flame from the Fluorox Flame Reactor Burner Assembly.

3.4 Experimental Results

Several tests were made in which UF_4 was introduced into commercial grade CO flames. The resulting residue solids indicated that there was some chemical change during the runs. Unfortunately it was impossible to determine whether this change was due to pyrohydrolysis and hydrolysis effect of the water vapor or whether the effect was due to the Fluorox reactions.

In tests made with pure grade CO and oxygen, it was found that in order to ignite the flame, a small amount of water vapor had to be added to the pilot light. After the main flame had been lighted, the water vapor was no longer needed. If the fuel gases were heated prior to their introduction to the flame, a more stable flame was produced and there was a reduction in the quenching effect that was experienced when UF_4 and cool fluidizing gas were sent through the flame.

Two successful runs were made in which UF_4 was sent through a pure CO-oxygen flame. UF_4 rates of 12 and 28 g/hr were used. The estimated flame temperatures were $2000^\circ C$, with a CO concentration of 50% in the fuel gas. The UF_4 retention time was also estimated by assuming that the UF_4 maintained a constant velocity throughout the flame and its velocity was that of the UF_4 in the fluidizing stream. These retention times were 0.4 and 0.5 seconds. Retention times calculated in this manner would be maximum values.

The solid residues which were isolated from the runs were found in three main places. A small amount was on the walls of the reactor. This material was UO_2 and U_3O_8 , as would be expected since it was in contact with oxygen at high temperature for several minutes. Trace amounts of material were collected in the off-gas collection chamber and the largest portion of the residue was obtained in the bottom of the reactor. Figure 3.9 shows the results of these runs based on the analysis of the feed and the residue found in the bottom of the reactor. They are also based on the total uranium balance, disregarding impurities, etc. In both cases the UF_4 content of the residue was decreased from the feed and the UO_2F_2 , U_3O_8 , and UO_2 content were increased, indicating that some of the Fluorox reactions were being carried out in the flame. The effect of retention time can also be seen. The longer hold-up time, 0.5 seconds, was experienced in run 9 and there was a greater loss of UF_4 and larger increase in UO_2F_2 and the oxides than in run 10 with a hold-up time of 0.4 seconds. In both runs, no UF_6 was collected. However, the amount of uranium that was recovered in the water scrubber would account for approximately 30% of the UF_6 that would have been formed if the residue solids gave the proper indication of chemical reaction.

Figure 3.9

Experimental Results of Runs 9 and 10

Based on the Uranium Balance

	%UF ₄	%UO ₂ F ₂	%U ₃ O ₈	%UO ₂
Feed	88.3	8.9	2.8	--
Residue from Run 9	60.6	23.4	6.3	9.7
Residue from Run 10	67.5	18.6	4.3	9.6

3.5 Production Feasibility and Future Plans

Although the flame reactor has promise for performing the Fluorox reaction, there are some engineering difficulties which could make it non-economical for a production-type reactor. First, essentially total reaction of the UF₄ would be necessary and it would be preferable for the reaction to go completely to UO₂ and UF₆. In order to accomplish this conversion, there would probably have to be an increase in the temperature and retention time. It would be difficult to increase the flame temperature much beyond that obtained in recent tests. Perhaps the UF₄ retention time could be increased by use of multiple flames in a single reactor. Another problem which might exist is an oxide coating being built up on the UF₄ particle which, by diffusion control, could decrease the reaction rate. Perhaps some of these difficulties could be alleviated by further size reduction of the UF₄ feed; however, there is an economical limit to the amount of size reduction which can be done on a production scale.

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