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SUBJECT: The Development of a Fluidized Bed Reactor for the Fluorox Process:
Unit Operations Monthly Status Reports for the Period November, 1958,
Through May, 1959

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ABSTRACT

Results of four experimental runs in the Fluorox fluidized bed reactor system are reported. The engineering feasibility of UF_6 production from UF_4 by use of dry air of O_2 , $2UF_4 + O_2 = UF_6 + UO_2F_2$, in an Inconel fluidized bed reactor at 800-850°C was demonstrated in two experimental tests in which greater than 90% of the theoretical amount of UF_6 was collected or measured. Two runs made with crude UF_4 (produced from unpurified mill concentrate) as the feed material, showed that UF_6 could be produced at 700-725°C but corrosion on Inconel was prohibitive.

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The Fluorox Program is the engineering development of processes which produce UF_6 from uranium compounds of lesser fluorine content without the use of elemental fluorine. The process under investigation at present is the green salt-oxygen reaction:

The UF_4 oxidation process is being carried out in a fluidized bed reactor constructed of Inconel. Sized UF_4 is continuously fed to a UO_2F_2 bed which is fluidized in dry oxygen at temperatures of $800^\circ C$ or greater and the UF_6 is removed from the off-gas by a cold trap.

The following sections contain the monthly status reports on the fluid bed Fluorox Process as reported in the Unit Operations Monthly Progress Report from November, 1958 through May, 1959.

1.0 NOVEMBER MONTHLY REPORT⁽¹⁾

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process of most interest at present is the oxidation of UF_4 with oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 .

The UF_4 oxidation process is being carried out in a 4-in. fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 at $800-850^\circ C$. The UF_6 which is produced is removed in the gas stream and subsequently recovered in cold traps. Preparation is now being made for an extended experimental run of approximately 100 hr duration.

In addition to the revisions mentioned in the UNOP September monthly report, ORNL CF No. 58-9-62, a continuous UF_6 analyzer for the off-gas and a batch UF_6 sampler are being installed in the off-gas system (Figure.1.1).

The continuous UF_6 analyzer is a Condensation Pressure Analyzer which was developed at K-25 by W. S. Pappas and C. W. Weber. The CPA sensing device is a constant temperature cold capillary through which part of the reactor off-gas is sent. This device condenses UF_6 from the off-gas and causes a pressure drop across the capillary. The pressure drop is maintained constant by control of the gas flow rate and a measure of the pressure at the downstream side of the capillary gives a measure of the UF_6 concentration in the off-gas. The volume per cent of the UF_6 in the off-gas, C_{UF_6} , is proportional to the partial pressure of UF_6 , P , at the capillary temperature and inversely proportional to the total pressure measured, π , at the downstream side of the capillary $[C_{UF_6} \propto P_{UF_6}/\pi]$.

Fig. 4.1. Condensation Pressure Analyzer, for Determining UF_6 Concentration in a Gas Stream.

2.0 DECEMBER MONTHLY REPORT⁽²⁾

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process of most interest at present is the oxidation of UF_4 with dry oxygen or air, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 . A continuous 4-in. fluidized bed reactor is being used to perform the reaction.

2.1 UF_4 Drying

It was necessary to dry the UF_4 feed which had been prepared for the 100-hr fluidized bed run since it had a water content of 1.5%. A total of 116 kg of the feed was dried on a continuous basis in the Fluorox fluidized bed reactor at 400°C with dry nitrogen. The average feed rate for this drying operation was 1 kg/hr and the bed inventory was ~ 9.5 kg. The fluidized bed reactor equipment operated satisfactorily with a maximum reactor pressure of 5 psig. The final water content of the dried UF_4 varied from 0.1% to 0.18%.

2.2 Air as the Oxidant

It was decided to make a short fluidized bed run in which dry air is used for the oxidizing and fluidizing media. This run will be made to determine the feasibility of air oxidation and as a "shakedown" run on the equipment after the extensive revisions made on the system. The air run will be made at a bed temperature of 800-825°C, a feed rate of 1 kg/hr and it will be of 10-12 hours duration.

3.0 JANUARY MONTHLY REPORT⁽²⁾

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study is the oxidation of UF_4 with oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 .

3.1 Fluidized Bed Development

The UF_4 oxidation process is being carried out in the 4-in. Fluorox fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 800-850°C. The UF_6 which is produced is removed in the gas stream and subsequently recovered in cold traps.

Two experimental runs were made in the 4-in. fluidized bed reactor. Run FBR-21 was a run of 9.25 hr duration in which dry air was the oxidizing and fluidizing gas and run FBR-22 was of 58.4 hr duration in which dry O_2 was used as the fluidizing and oxidizing gas.

Run FBR-21. Run FBR-21 was made to evaluate the use of dry air as the oxidizing and fluidizing gas in the Fluorox 4-in. fluidized bed reactor. The run was made at a bed temperature of $810^{\circ}\text{C} \pm 15^{\circ}\text{C}$ and an average feed rate of 1.37 kg/hr. Total operating time was 9.25 hr and the run was terminated when it was felt that enough information was available for evaluation of the run. Total amount of UF_4 introduced to the reactor was 12.7 kg and 5.12 kg of UF_6 was collected in the cold traps.

The experimental apparatus was similar to that used in run FBR-20 (Unit Operations Section monthly progress report for September 1958, ORNL-CF-58-9-62) except that a condensation pressure analyzer (Unit Operations Section monthly progress report for December 1958, ORNL-CF-58-12-35) was installed in the off-gas system to measure the UF_6 concentration in the reactor off-gas stream.

The operating procedure used was the same as that used in previous runs, and operation throughout the run was essentially smooth with no operational difficulties in the reactor systems. It was impossible to maintain the bed temperature above 825°C which probably reflected the excessive scale buildup on the reactor wall. As in previous runs, the fluidizing gas (air) was dried in molecular sieve beds to a dew point of -100°C .

There was difficulty in maintaining a constant cold bath temperature in the CPA. This variation (0°C - -10°C) resulted in erratic values for the UF_6 concentration in the reactor off-gas; however, there was enough constant temperature operation for determination of the off-gas UF_6 concentrations since the reactor system was operated at conditions which approached steady state.

Complete experimental and analytical results have made it possible to evaluate the run in a manner similar to that used in previous run evaluations.

The amount of UF_6 measured in the reactor off-gas by the CPA was 434 g more than the amount collected in the cold traps and chemical traps (Figure 3.1). The measured value of the UF_6 is probably the most accurate value because there was an observed loss of UF_6 through the CPA system. The measured value also gives a much closer check in the material balances, in particular the UF_6 balance, than does the amount of UF_6 collected in traps. The material balances are prepared with both of the UF_6 values for purposes of comparison.

The plot of measured UF_6 concentration in the reactor off-gas versus run time (Figure 3.1) shows that the system approached a steady state condition after about 1 hr of operation. The difference in reaction rate of UF_4 in air and O_2 can be easily seen since the UF_6 concentration increased from 1.8% to 3.4% when the oxidizing gas was changed from air to O_2 at the end of the run.

Fig. 3.1. UF_6 Concentration in Reactor Off-Gas as Measured by the Condensation Pressure Analyzer.

The over-all material balance of all reactor streams entering and leaving was 100.4% (Table 3.1 and Figure 3.2) based on the measured UF_6 value, while the over-all uranium balance was 100.5%. These balances resulted in weight differences between entering and leaving streams of 69 g and 72 g, respectively, which are within experimental error.

The UF_6 balance was 98.4% complete based on the measured UF_6 value (Figure 3.3) and the 5610 g of UF_6 measured in the reactor off-gas was 92.6% of the theoretical amount which should have been formed. UF_6 collected in cold traps and chemical traps was 85.4% of the theoretical amount.

Approximately 5.8% of the UF_6 formed was used up in side reactions with 0.2% reacting with the uranium oxides introduced with the feed, 1.4% reacting with reactor and thermowell walls to form corrosion products and 4.2% reacting with the water introduced with the feed. This amount of loss to side reactions probably represents a minimum figure in this apparatus.

The 92.6% of theoretical UF_6 measured in the gas stream was higher than any previous value of UF_6 recovery, and the 85.4% UF_6 collected in cold traps and chemical traps was 12% greater than UF_6 recovery in previous runs. These higher recovery figures are due mainly to reduced H_2O and uranium oxide content in the feed.

The apparent reaction rate constant determined for the operating temperature of 810°C with air as the oxidant was 1.29 hr^{-1} (Figure 3.4). This value compares favorably with the extrapolated value from laboratory data, 1.86 hr^{-1} (1).

As was expected the reaction rate in air was less than it was in pure O_2 . Since the UF_4 feed rate in this run was maintained at somewhat higher values than the runs in which pure O_2 was used, the combination of higher feed rate and decreased reaction rate resulted in a higher UF_4 content in the bed. This concentration was 21.9% by wt at steady state while in most of the earlier runs with oxygen, UF_4 concentrations of less than 10% were maintained.

As a result of high UF_4 concentration in the bed there was appreciable build-up of material on the reactor walls which resulted in a reduction of heat transfer from the walls to the bed and in a decrease in the fluid bed volume. It is probably desirable to maintain the UF_4 concentration in the bed at less than 5%.

A UF_6 sample which was cold trapped out of the CPA off-gas stream and liquid transferred to a plastic sampling container, was analyzed for uranium content and impurities. Although the laboratory techniques for these

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- (1) L. M. Ferris, "A Study of the Reaction $2\text{UF}_4 + \text{O}_2 \rightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$, II Kinetics Between 550 and 815°C , presented at the 133rd National ACS Meeting, San Francisco, California, April 13-18, 1958.

Table 3.1. Change in Amounts of Individual
Compounds in Run FBR-21

Compound	Entering Reactor, g		Leaving Reactor, g		Total	Uranium
	Total	Uranium	Total	Uranium		
UF ₄	12620	9580	1811	1373	-10809	-8207
UO ₂ F ₂	5917	4580	11746	9080	+5829	+4500
UO ₂	13	11	0	0	-13	-11
U ₃ O ₈	6	5	0	0	-5	-5
Metal F	18	0	64	0	+46	0
H ₂ O	26	0	0	0	-26	0
O ₂ *	562	0	0	0	-562	0
UF ₆ -Collected**	0	0	5176	3490	+5176	+3490
(Measured)	(0)	(0)	(5610)	(3795)	(+5610)	(+3795)
Totals	19162	14176	18797 (19231)	13943 (14248)	-365 (+69)	-233 (+72)

*The amount of O₂ entering the reactor was calculated to be the theoretical amount necessary for oxidation in the various reactions occurring.

**The amount of UF₆ reported as Collected is that amount collected in cold traps and chemical traps and the amount of UF₆ reported as Measured is that amount of UF₆ measured in the reactor off-gas by the Condensation Pressure Analyzer.

Material Balance (material leaving/material entering): 98.1% using UF₆ Collected
100.4% using UF₆ Measured

Fig. 3 2 Material Balance of the Constituents of Each Stream from Run FBR-21.

* UF_6 measured in reactor off-gas stream by CPA

Total UF_6 accounted for = 5529g or 91.2% of theoretical (based on UF_6 actually trapped from off-gas stream)
= 5963g or 98.4% of theoretical (based on UF_6 measured in reactor off-gas by CPA)

Fig. 3.3. Disposition of UF_6 Which was Formed in Run FBR-21.

ALL FLOW RATES ARE AVERAGES BASED ON STEADY STATE OPERATION. REACTION RATE CONSTANT, $k = (1171 \text{ g/hr} / 908 \text{ g}) = 1.29 \text{ hr}^{-1}$

Fig. 3.4. UF₄ Material Balance Across the Fluidized Bed Reactor and Apparent Reaction Rate Constant for Run FBR-21.

analyses do not give accurate uranium analysis, they do give indication of impurities.

The following impurities were found by both wet chemistry and spectrographic methods:

Aluminum	0.2 ppm
Calcium	0.5 ppm
Chromium	120 ppm
Copper	0.3 ppm
Iron	500 ppm
Magnesium	0.4 ppm

The oxygen utilization of the oxygen in the total amount of air used during run FBR-21 was 10.4%. This is a higher utilization than was obtained with any of the runs in which pure oxygen was used.

Run FBR-21 demonstrated the feasibility of using dry air as the fluidizing and oxidizing gas for the Fluorox reaction in a fluidized bed reactor. The close agreement between the fluidized bed reaction rate constant with the rate constant found in the laboratory by thermogravimetric methods indicate that these values could be used in a scale-up of the operation.

Run FBR-22. Run FBR-22 was made to test the reliability of the experimental equipment over a long period of time and to provide enough operating time to reduce the effect of short term operating variables.

The run was made at bed temperatures of 800-825°C with one temperature excursion to 775°C and with an average UF_4 feed rate of 1.6 kg/hr. The total run time was 58.4 hr with 6.75 hr downtime for maintenance; however, during the first 49.8 hr there was only 0.9 hr downtime for routine maintenance.

The experimental apparatus and procedure was the same as that used in run FBR-21. During the last 8.6 hr of the run there was a total of 6.75 hr of downtime due to three major mechanical failures, (1) a broken fluidizing gas line, (2) a cracked overflow line, and (3) loss of several fins on the feeder impeller which resulted in introduction of a large amount of UF_4 to the bed in a short time.

The combination of these three failures produced a high-temperature, static bed with a high UF_4 concentration. These conditions resulted in sintering of some of the UF_4 in the bed, a build-up of solid material on the walls, and formation of large amounts of the intermediate U_4F_{17} which solidified in the relatively cool section above the heated bed and caused severe restriction to gas flow. After the mechanical failures had been

corrected, it was impossible to refluidize the bed properly so the run was terminated.

A total of 83.8 kg of UF_4 was introduced to the reactor and 32.5 kg of UF_6 was collected in the cold traps.

The CPA was operated during part of the run; however, erratic operation of the analyzer due to inability to maintain a constant cold bath made it difficult to use the analyzer data effectively.

Complete analytical results from the run are not available.

3.2 Condensation Pressure Analyzer

The CPA (Unit Operations Section December monthly progress report, ORNL-CP-58-12-35) was calibrated by introducing a gas stream of known UF_6 concentrated into the analyzer system and recording the analyzer readings which indicate the UF_6 concentration. The actual UF_6 concentrations were then compared to the indicated concentrations.

Calibration data (Table 3.2) show some differences between the actual and indicated values. In using the analyzer data to obtain indicated UF_6 concentrations, the data which has the most uncertainty is the temperature of the cold bath which surrounds the capillary sensing element. In the calibration tests and in subsequent operation it was found that this temperature could not be maintained constant and the actual temperature at the cold capillary was not always known.

The UF_6 concentration in the gas stream to the analyzer was known to an accuracy of about 5%, and some of the differences between actual and indicated UF_6 concentrations were greater than 5%. However, it is felt that the CPA will be useful in determining UF_6 concentration in a gas stream if the analyzer cold bath can be maintained at a constant, known temperature.

4.0 FEBRUARY MONTHLY REPORT⁽⁴⁾

The Fluorpx program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study at present is the oxidation of UF_4 with oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 .

4.1 Fluidized Bed Development

The UF_4 oxidation process is being carried out in a 4-in. fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 800-850°C. The UF_6 which is produced is removed in the off-gas stream and is subsequently recovered in cold traps.

Table 3.2. Condensation Pressure Analyzer Calibration Data

Bath Temp., °C	Partial Pressure of UF ₆ , mm of Hg	Total Pressure, mm of Hg	UF ₆ Conc., Indicated	Volume %, Actual	% Error $\left(\frac{\text{Indicated}-\text{Actual}}{\text{Actual}} \right) \times 100$
-9.2	8.0	157	5.1	4.8	+6.3
-9.2	8.0	231	3.5	3.3	+6.1
-15*	4.5	136	3.3	3.3	0
-15*	4.5	330	1.4	1.7	-17.6
-15*	4.5	91	4.9	4.8	+2.1

*The cold bath at these temperatures was an ice slush in a saturated aqueous solution of NH₄Cl. The theoretical temperature of such a bath is -16.2°C and for partial pressure considerations, this was the temperature used.

Run FER-22. Run FER-22 which lasted for 58.4 hr was made to test the reliability of the experimental equipment over a long period of time and to give additional operating data which could be used in a possible scale-up of equipment. Complete analytical results are available, and the run was evaluated in the same manner which was used in previous runs.

The over-all material balance of all reactor streams entering and leaving was 99.4% (material leaving/material entering) with an over-all uranium material balance of 99.0% (see Table 4.1 and Figure 4.1). The apparent loss of 528 g of material and 659 g of uranium can be partially accounted for by UF_6 losses through the Condensation Pressure Analyzer off-gas system. (UF_6 vapor was observed in the vacuum pump off-gas.)

The UF_6 balance was 99.2% complete (see Figure 4.2) with 90.4% of the theoretical amount of UF_6 formed being collected in cold traps and chemical traps. 8.8% of the UF_6 formed was consumed in side reactions: 2.3% reacted with UF_4 to form U_4F_{17} ; 2.2% reacted with reactor and thermowell walls to form corrosion products; 0.5% reacted with the uranium oxides introduced with the feed; and 3.8% reacted with the water introduced with the feed. The 90.4% UF_6 collected in cold traps and chemical traps was the highest recovery of all runs to date.

Apparent reaction rate constants were determined for three periods of reactor operation in which average bed temperatures of 812°C, 813°C and 817°C were maintained (see Figure 4.3). The rate constants, 6.7 hr⁻¹, 8.5 hr⁻¹, and 11.3 hr⁻¹, respectively, check favorably with previous fluidized bed runs.

A significant amount of U_4F_{17} was formed and recovered in the lower part of the filter section in the reactor. The accumulation of solids in the upper part of the reactor caused a pressure buildup during the latter part of the run. The majority of the U_4F_{17} formation was during the last few hours of operation when there was a static bed of high UF_4 content at a high temperature. A failure of the powder feeding system occurred at the time of a forced shutdown due to a broken solids discharge line, resulting in abnormally high UF_4 feed rates with insufficient agitation. The run was terminated shortly after these occurrences.

Two UF_6 samples were submitted for chemical and spectrographic analysis. The following impurities were found:

Sample No.	Impurities, ppm							
	Al	Ca	Cr	Cu	Fe	Mg	Ni	Total
X-25	10	15	20	8	125	16	45	239
X-38	5	11	12	3	95	11	55	192

A UF_6 sample was also submitted to The Oak Ridge Gaseous Diffusion Plant for specification analysis.

Table 4.1. Change in Amounts of Individual Compounds in Run FBR-22

Compound	Entering reactor, g		Leaving reactor, g		Change, g	
	Total	Uranium	Total	Uranium	Total	Uranium
UF ₄	80802	61248	8627	6539	-72175	-54709
UO ₂ F ₂	8554	6610	43102	33305	+34548	+26695
UO ₂	264	233	0	0	-264	-233
U ₃ O ₈	6	5	0	0	-6	-5
U ₄ F ₁₇	0	0	6352	4739	+6352	+4739
UF ₆	0	0	33803	22858	+33803	+22854
Metal F	30	0	556	0	+526	0
H ₂ O	144	0	0	0	-144	0
O ₂ *	3488	0	0	0	-3488	0
HF**	0	0	320	0	+320	0
Totals	93288	68096	92760	67437	-528	-659

* The amount of O₂ entering the reactor was calculated to be the theoretical amount necessary for oxidation in the various reactions occurring.

** The amount of HF leaving the reactor was calculated to be the theoretical amount which resulted from the hydrolysis of UF₆.

Over-all material balance (material leaving/material entering) = 99.4%

Over-all uranium material balance (uranium leaving/uranium entering) = 99.0%

Fig. 4.1. Material Balance of the Constituents of Each Stream from Run FBR-22.

Fig.4.2. Disposition of UF_6 Which was Formed in Run FBR-22.

13.3 HOURS OF OPERATION AT AN
AVERAGE BED TEMPERATURE OF $812^\circ C$.

REACTION RATE CONSTANT,

$$k = \frac{1472g/hr}{221g} = 6.7\ hr^{-1}$$

13.5 HOURS OF OPERATION AT AN
AVERAGE BED TEMPERATURE OF $813^\circ C$.

REACTION RATE CONSTANT,

$$k = \frac{1484g/hr}{174g} = 8.5\ hr^{-1}$$

22.7 HOURS OF OPERATION AT AN
AVERAGE BED TEMPERATURE OF $817^\circ C$

REACTION RATE CONSTANT,

$$k = \frac{1490g/hr}{132g} = 11.3\ hr^{-1}$$

Fig. 4.3. Apparent Reaction Rate Constants for Three Periods of Run FBR-22.

Inconel corrosion coupons were attached to the thermowell during run FBR-22 in three positions: gas phase, interface, and in the fluid bed. The coupons will be checked for the type and amount of corrosion.'

Corrosion Rates in FBR-21 and FBR-22. Apparent corrosion rates of the Inconel reactor were determined at steady state operating conditions during runs FBR-21 and FBR-22. It was assumed that (1) corrosion occurred only in the fluid bed area of the reactor and (2) at steady state operation, the corrosion products in the overflow and cold traps represented the only corrosion taking place. On this basis, the apparent corrosion rates at $810^{\circ} \pm 15^{\circ}\text{C}$, based on a 360-day year, were: Run FBR-21 - 0.145 ipy and Run FBR-22 - 0.289 ipy.

4.2 Allied UF₄ Run

The fluidized bed reactor system is being prepared for a run in which crude UF₄ (produced from unpurified mill concentrate) will be used as the feed. Approximately 100 lb of such a material was received from Allied Chemical Corporation.

Initial tests indicate that this impure material has a melting point of $730-740^{\circ}\text{C}$ and appreciable sintering occurs at $690-700^{\circ}\text{C}$. The low melting point will necessitate a fluid bed temperature less than 730°C with the resulting decrease in reaction rate. Further tests will be made on the crude UF₄ mixed with UO₂F₂.

5.0 MARCH MONTHLY REPORT⁽⁵⁾

The Fluorox program is the engineering development of processes which produce UF₆ without the use of elemental fluorine. The process under study at present is the oxidation of UF₄ with oxygen ($2\text{UF}_4 + \text{O}_2 = \text{UO}_2\text{F}_2 + \text{UF}_6$) with subsequent recycle of the UO₂F₂ through reduction and hydrofluorination.

5.1 Fluidized Bed Development

The UF₄ oxidation process is being carried out in a 4-in. fluidized bed reactor. Sized UF₄ is continuously fed into a UO₂F₂ bed which is fluidized in dry O₂ or air at $700-850^{\circ}\text{C}$. The UF₆ which is produced is removed in the off-gas stream and recovered in cold traps.

Corrosion in Run FBR-22. Corrosion data on six Inconel corrosion coupons which were in the reactor attached to the center thermowell during run FBR-22 showed that corrosion on annealed Inconel was general with no noticeable pitting or intergranular attack. The corrosion rates which were based on 65.5 hours of reactor operation when the bed temperature was in the range of $775-830^{\circ}\text{C}$ varied from 0.058 ipy in the gas phase to 0.837 ipy in the fluid bed. There were some large temperature variations when the run was terminated, and there was approximately 20 hours of heating-up and cooling-down time when the bed temperature was less than 775°C .

The corrosion rates listed below are based on continuous operation for a 300-day year with the assumption that no corrosion occurred at temperatures less than 775°C.

Table 5.1

Annual Corrosion Rate on Annealed Inconel

at 775°C-830°C in Run FER-22

<u>Location of Corrosion Coupons</u>	<u>Average Corrosion Rate, ipy</u>
Gas Phase	0.048
Bed Interface	0.65
Middle of Fluid Bed	0.70

These rates are considerably higher than other measured rates calculated from thermowell corrosion or rates calculated from collection of corrosion products, probably due to the violent agitation in the center of the bed and to the apparent movement of the corrosion coupons in the fluid bed.

5.2 The Fluorox Reaction for Impure UF₄ from Ore Concentrate

Crude UF₄ (produced from unpurified mill concentrate) which was received from the Allied Chemical Corporation had a much wider particle size range than does the usual feed for the Fluorox fluidized bed (Fig. 5.1). Some of the +20 mesh material appeared to be mainly corrosion products. In order to facilitate the use of this material in the solids feeding system of the Fluorox fluidized bed reactor, a size fraction in the -20 mesh to +150 mesh range will be used.

Analytical results from the "as received" material, although somewhat inconsistent, make it possible to determine the composition of the crude UF₄ if it is assumed that all of the uranium is present as U⁴⁺ and that all fluoride impurities are present as their highest, non-volatile, fluoride. The use of these assumptions results in the following composition for the crude UF₄:

<u>Compound</u>	<u>wt, %</u>
UF ₄	88.52
UO ₂	2.72
AlF ₃	0.56
CaF ₂	0.12
CuF ₂	0.20
FeF ₃	4.89
MgF ₂	0.08
MnF ₂	0.10
NaF	1.72
NiF ₂	0.10
VF ₃	0.51
H ₂ O	0.15
Total	99.67

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Fig. 5.1. Sieve Analysis of Crude UF₄ Received from Allied Chemical Corp.

Further tube furnace tests on the reaction rate of the crude UF_4 in the Fluorox reaction ($2UF_4 + O_2 = UO_2F_2 + UF_6$) gave reaction rate constants comparable to other types of UF_4 in the temperature range of 700-720°C ($k = 0.20 \text{ hr}^{-1}$ at 700°C and $k = 0.42 \text{ hr}^{-1}$ at 720°C).

Although the crude UF_4 sinters at 690-710°C and melts at 730-740°C, severe sintering or agglomeration does not occur in a 90% UO_2F_2 -10% crude UF_4 mixture (weight %) until the approximate melting point of 730-740°C. Therefore, if the Fluorox fluidized bed is maintained at less than 10% crude UF_4 , the bed temperature can be maintained at 730°C where the reaction rate constant for the crude UF_4 is $k = 0.60 \text{ hr}^{-1}$ and the reaction half time is 1.15 hours.

Oxidation tests in a tube furnace also showed that essentially all the vanadium contained in the crude UF_4 is collected in the off-gas cold traps with the UF_6 .

Determination of Feed Rate for the Fluidized Bed Reactor. For any proposed run, the calculated feed rate to the Fluorox fluidized bed reactor is dependent on (1) the characteristics of the feed, (2) the UF_4 concentration to be maintained in the bed and (3) the reaction rate constant which is dependent on temperature and feed characteristics. The following equation yields the feed rate, F , as a function of the important variables:

$$F = \frac{k_t CW(1-0.51C)}{U-0.49UC-IC-NC}$$

where k_t is the reaction rate constant, W is the bed weight, C is the weight fraction of UF_4 in the bed, and U , I , and N are characteristic of the feed with U the weight fraction of UF_4 in the feed, I the weight fraction of inert impurities in the feed and N the equivalent weight fraction of the feed which results in solids from reaction of other impurities with UF_6 .

If a run is made with crude UF_4 at a bed temperature of 730°C with 10% UF_4 in the bed, then $U = 0.8881$, $I = 0.0831$, $N = 0.0595$, $C = 0.10$ and $k_{730} = 0.60 \text{ hr}^{-1}$. Since the bed weight is approximately 6000 g, the feed rate should be:

$$F = \frac{(0.60)(0.1)(6000)[1-(0.51)(0.1)]}{0.8881-(0.49)(0.8881)(0.1)-(0.0831)(0.1)-(0.0595)(0.10)} =$$

$$F = 368 \text{ g/hour}$$

Run FBR-23. Run FBR-23 was made to evaluate the use of crude UF_4 as the feed material in the Fluorox 4-in. fluidized bed reactor. The run was made with O_2 at a bed temperature of 690-725°C and an average feed rate of 341 g/hour. Total operating time was 13.60 hours with 0.13 hours down-time for routine maintenance. The run was terminated when a leak developed in the reactor and in the thermowell.

A total of 4600 g of crude UF_4 was introduced to the reactor and 454 g of material was collected in the cold traps. Experimental apparatus and operating procedure were similar to that in Run FBR-22 (Unit Operations Monthly Progress Report for January 1959 CF-59-1-74).

All recorded outside wall temperatures were maintained below 750°C except for one excursion to 800°C which occurred in the vicinity of the hole in the reactor.

A $1\frac{1}{2}$ " hole was corroded in the reactor wall midway up the 4 inch fluidized bed section (Fig. 5.2) in the same general area in which a hot spot developed during the latter part of run FBR-22. The leak in the $1\frac{1}{4}$ inch Inconel thermowell (0.035" wall) was due to severe corrosion in a 4 inch section roughly opposite the hole in the reactor wall. It is felt that severe corrosion on Inconel occurred when the bed or reactor walls were operated at a temperature above the melting point of the UF_4 feed and the hole in the reactor was due to a hot spot caused by uneven external heating.

Following is the over-all material balance for run FBR-23:

Material Introduced (does not include O_2):

Original Bed	5950 g
Feed	4600 g
	<hr/> 10550 g

Material Removed:

Final Bed	9044 g
Overflow	1173 g
Cold Traps	454 g
Total	<hr/> 10671 g

Analytical results are not available for this run.

Run FBR-24. The reactor has been repaired by replacing the damaged 4-in. section by new schedule 40 Inconel pipe. A second and final crude UF_4 run will be made (FBR-24) in which closer temperature control will be maintained. Following are the proposed operation conditions for this run:

Bed Temperature	$720-730^\circ\text{C}$
UF_4 Concentration in Bed	10%
Crude UF_4	350-375 g/hr

Inconel corrosion coupons will be placed in the reactor by attaching them to the thermowell at three positions; (1) in fluidized bed, (2) at interface, and (3) in the gas phase. The reactor has been "vidigaged" to determine the wall thickness, and it will be measured again after the run.

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Fig. 5.2.

6.0 APRIL MONTHLY REPORT⁽⁶⁾

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study is the oxidation of UF_4 with oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 .

Fluidized Bed Development

The UF_4 oxidation process is carried out in a 4-in. fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 700-850°C. The UF_6 which is produced is removed in the off-gas stream and is subsequently recovered in cold traps.

6.1 UF_6 Production from Crude UF_4 Produced by Allied Chemical Corporation

The crude UF_4 from the unpurified mill concentrate produced by the Allied Chemical Corporation was used as feed material for FBR-23 and FBR-24 after screening to remove +20 mesh and -150 mesh material. A chemical analysis of this screened material showed the following composition:

UF_4	85.00%
UO_2	2.62%
UO_2F_2	2.94%
H_2O	0.52%
Other fluorides	8.92%

An analysis of the "as received" material, before sizing, was reported in Unit Operations March Monthly Progress Report (ORNL CF 59-3-61).

The fluidized bed throughput is dependent on reaction rate which is in turn dependent on temperature. The lower melting point of the crude UF_4 (730°-740°C) as compared to purified UF_4 (> 850°C) restricted the bed operating temperature to a maximum of ~ 730°C. Test runs FBR-23 and FBR-24 were made to determine the feasibility of the production of UF_6 from impure UF_4 at "low" temperatures and to observe the operation of the fluid bed reactor with a relatively high concentration of impurities.

6.2 Details of Run FBR-23

The first run with crude UF_4 (Run FBR-23) lasted 13.5 hours. Complete analytical results are available and the run was evaluated in the same manner which was used in previous runs.

The overall material balance of all reactor streams was 97.2% (material leaving/material entering) with an over all uranium material balance of 96.4% (see Table 6.1 and Fig. 6.1). The apparent loss of 307 g of total material and 279 g of uranium may have been due to the loss of UF_6 which occurred when the thermowell and reactor developed leaks due to severe corrosion.

Table 6.1 Change in Amounts of Individual Compounds in Run FBR-23

Compound	Entering Reactor, g		Leaving Reactor, g		Change, g	
	Total	Uranium	Total	Uranium	Total	Uranium
UF ₄	4074	3088	239	181	-3835	-2907
UO ₂ F ₂	5862	4530	9062	7002	+3200	+2472
UO ₂	121	107	--	--	-121	-107
U ₃ O ₈	1	1	5	4	+ 4	+ 3
H ₂ O	24	--	--	--	- 24	--
Metal F	418	--	978	--	+560	--
UF ₆	--	--	384	260	+384	+260
HF	--	--	154	--	+154	--
O ₂ *	304	--	--	--	-304	--
Metal**	325	--	--	--	-325	--
Total	11,129	7,726	10,822	7,447	-307	-279

* Amount of O₂ theoretically necessary for the various reactions occurring.

** Amount determined from formation of new corrosion products.

Over all material balance (material leaving/material entering) = 97.2%.

Over all uranium balance (uranium leaving/uranium entering) = 96.4%.

Fig 61 Material Balance of the Constituents of Each Stream From run FBR-23.

The UF_6 balance was 85.3% complete (Fig. 6.2) with 17.9% on the theoretical amount of UF_6 formed being collected in cold traps and chemical traps. 67.4% of the UF_6 formed was consumed in side reactions: 10.9% reacted with water introduced with the feed, 3.7% reacted with oxide introduced with the feed, and 52.8% reacted with Inconel reactor and thermowell walls to form corrosion products. The apparent loss of 316 g of UF_6 from the system roughly checks with the total material and uranium unaccounted for in the over all material balance.

The UF_6 product collected in the cold traps was contaminated with vanadium, 0.9%, which was present in the feed and chromium, 2.1%, which was a corrosion product. The analytical results also indicated that an appreciable amount of HF , 10.2%, was collected in the cold trap. The following is the probable composition of the product UF_6 :

UF_6	83.8%
HF	10.2%
Other fluorides, mainly $CrOF_2$ and VOF_2	6.0%

The apparent reaction rate constant (see Fig. 6.3) as determined by:

$$k = \frac{UF_4 \text{ conversion rate}}{UF_4 \text{ inventory in the bed}}$$

was 1.3 hr^{-1} for the last 6.5 hours of operation when the average bed temperature was 723°C . This value for k is higher by a factor of 2.4 compared with laboratory data. This apparent high reaction rate may have been the result of the system not being at steady state with the actual UF_4 concentration in the bed at the time of sampling being less than the steady state amount.

Corrosion in Run FBR-23: There appeared to be very high localized corrosion on both the lower reactor wall and on the lower portion of the thermowell in Run FBR-23. A half inch hole was formed in the reactor wall and a 4-in. section of Inconel thermowell was badly corroded. Based on the leak which appeared in the 35 mil thermowell after 9.5 hours of operation, the corrosion rate was about 4 mils/hour. From the amount of corrosion products recovered from the system, the average corrosion rate for the Inconel fluid bed reactor at $710^\circ \pm 25^\circ\text{C}$ was about 0.7 mils per hour or 5.6 ipy. Thus, the corrosion rate of Inconel was higher for crude UF_4 at 710°C by greater than a factor of 10 compared to the corrosion by pure UF_4 feed at 800°C .

6.3 Details of Run FBR-24

Run FBR-24 was made to complete the evaluation of the use of crude UF_4 as the feed material to the Fluorox 4-in. fluidized bed reactor. The run was made with dry O_2 at a bed temperature of $710^\circ \pm 25^\circ\text{C}$ and an average feed rate of 309 g/hr. The total operating time was 29.5 hr with the feed being introduced during 24 hours of this time. The experimental apparatus and the operating procedure was similar to those used in Runs FBR-22 and FBR-23

Fig. 6.2. Disposition of UF_6 Which was Formed in Run FBR-23

ALL FLOW RATES ARE AVERAGES BASED ON
THE LAST 6.5 HOURS OF OPERATION

$$\text{REACTION RATE CONSTANT, } k = \frac{288 \text{ g/hr}}{222 \text{ g}} = 1.3 \text{ hr}^{-1}$$

Fig. 6.3. UF₄ Material Balance Across the Fluidized Bed Reactor and Apparent Reaction Rate Constant for Run FBR-23.

(UNOP) Monthly January 1959). There was no down time during the run and operation was smooth with the exception of a period of about 4 hours when there was a small pressure build-up due to accumulation of agglomerates in the bottom of the reactor. The run was terminated according to schedule after 24 hours of feed time.

A total of 7100 g of crude UF_4 was introduced to the reactor and 1180 g of volatile material was collected in the cold traps. The following material balance is available from initial experimental results:

Material introduced to reactor:

Initial bed	5940 g
Crude UF_4	<u>7100 g</u>
Total	13040 g

Material removed from reactor:

Final bed	7647 g
Overflow	2317 g
Samples from bottom reactor	1764 g
Material from cold traps	<u>1180 g</u>
	12908 g

The above material balance does not include the O_2 used in reactions, the HF recovered in chemical traps, or the Inconel metal which was corroded from the reactor and thermowell. Complete analytical results are not yet available from this run.

Corrosion in Run FBR-24: It was intended that outside reactor wall temperatures would be held below $750^\circ C$ to reduce the effect of corrosion; however, two hot spots developed on the wall due to scale accumulation at which temperatures as high as $805^\circ C$ were recorded.

A 1/2" dia. hole and 3 small holes were corroded in the lower reactor wall at about the same place as the hot spots. These holes were not detected until the reactor was cooled (about four hours after the crude UF_4 feed has been stopped). The 65 mil wall thermowell was corroded through after 7 hours of operation and there were no bed temperature measurements after that time.

When the reactor was opened evidence of severe corrosion was found. The lower 6" of the thermowell and the two Inconel corrosion sample attached to the thermowell had totally disintegrated. From the above data, Inconel corrosion was at a rate of 6-7 mils per hour.

After the hole in the reactor occurred, the part of the fluid bed above the hole was no longer fluidized and it loosely sintered into an easily broken-up cake while the bottom part of the bed remained fluidized. A large amount of scale and sintered bed material up to 1/4" thick accumulated on the reactor wall and partially plugged the solids overflow.

7.0 MAY MONTHLY REPORT⁽¹⁾

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study is the oxidation of UF_4 with anhydrous oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 .

Fluidized Bed Development

The UF_4 oxidation process is carried out in a 4-in. fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 700-850°C. The UF_6 which is produced is removed in the off-gas stream and is subsequently recovered in cold traps.

7.1 Evaluation of Run FBR-24

The second run with crude UF_4 (run FBR-24) lasted for 29 hours at a bed temperature of $710 \pm 25^\circ C$ (Unit Operations Section Monthly Progress Report for April 1959). Complete analytical results are available, and the run was evaluated in the same manner as previous runs.

The over all material balance of all reactor streams was 94.8% (material leaving/material entering) while the over all uranium material balance was only 81.7% (Table 7.1). This reflects a loss of 709 g of material which was probably a result of the hole which was corroded in the reactor. The apparent greater loss of uranium from the system probably reflects non-homogeneous sampling of solids.

The UF_6 balance was only 54.6% complete (Fig. 7.1) with 17.9% of the theoretical amount of UF_6 formed being collected in cold traps and chemical traps and 36.7% being consumed in parasitic side reactions. The apparent loss of 45.4% of the theoretical amount of UF_6 formed may have been partially due to the hole corroded in the reactor.

The UF_6 product collected in the cold trap was contaminated with vanadium, 2.5%, chromium, 1.3%, and HF, 37.0%. Following is the probable composition of the produce UF_6 :

UF_6	55.2%
HF	37.0%
Other fluorides, mainly CrO_2F_2 and VOF_2	7.8%

Table 7.1 Change in Amounts of Individual Compounds in Run FBR-24

Compound	Entering Reactor, g		Leaving Reactor, g		Change, g	
	Total	Uranium	Total	Uranium	Total	Uranium
UF ₄	6001	4549	663	503	-5338	-4046
UO ₂ F ₂	5975	4617	8773	6779	+2798	+2162
UO ₂	255	255	--	--	- 255	- 255
U ₃ O ₈	--	--	28	24	+ 28	+ 24
H ₂ O	24	--	--	--	- 24	--
UF ₆	--	--	536	362	+ 536	+ 362
HF	--	--	760	--	+ 760	--
O ₂ *	351	--	--	--	- 351	--
Inconel	337	--	--	--	- 337	--
Other**	766	--	2240	--	+1474	--
Totals	13709	9391	13000	7668	- 709	-1723

* Amount of O₂ theoretically necessary for the various reactions occurring.

** Other metal fluoride, oxides and oxyfluorides.

Over all material balance (material leaving/material entering) = 94.8%.

Over all uranium balance (uranium leaving/uranium entering) = 81.7%.

Fig. 7.1. Disposition of UF_6 Which was Formed in Run FBR-24.

The apparent reaction rate constant (Fig. 7.2) during a 4 hour period of approximately steady state operation at an average bed temperature of 717°C was 0.386 hr^{-1} . This value was about 20% lower than previous values obtained at these temperatures; however, it is within experimental error.

Corrosion in FBR-24

The apparent high corrosion rate in run FBR-24, 6-7 mils/hr, resulted in a $1/2$ " diameter hole in the reactor (Unit Operations Section Monthly Progress Report April 1959). The fluid bed section of the reactor was sectioned and cleaned for visual observation. It shows that the corrosion was uneven with some severe pitting (Fig. 7.3).

7.2 Discussion of Reaction Rate Data in Fluidized Bed Reactors

A comparison of reaction rate constants for the reaction, $2\text{UF}_4 + \text{O}_2 = \text{UO}_2\text{F}_2 + \text{UF}_6$, determined from both laboratory and fluidized bed reactor data has been made (Fig. 7.4). Arrhenius plots of the experimental data with least square curve fitting shows that the batch fluidized bed data produce a plot with similar slope to that from the laboratory data but slightly depressed while the continuous fluidized bed data produce a plot with slightly greater slope but with better agreement in the temperature range of 700 - 800°C .

From the above information, it is felt that the available reaction rate data is sufficient for scale-up design for larger reactions.

Fig. 7.2 Apparent Reaction Rate Constant for Run FBR-24.

Fig. 7.3. Sectioned Fluorox Reactor After Run FBR-24.

Fig. 7.4. Comparison of Reaction Rate Constants for the Reaction,
 $2\text{UF}_4 + \text{O}_2 = \text{UO}_2\text{F}_2 + \text{UF}_6$, Determined from Laboratory and
 Fluidized Bed Reactor Data.

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