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ENGINEERING PRACTICE SCHOOL

UNION CARBIDE NUCLEAR COMPANY
DIVISION OF UNION CARBIDE CORPORATION

MEMORANDUM

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TO: G. I. Cathers
FROM: P. R. Ammann, D. A. Madden, and D. L. Swift
SUBJECT: Zircex Fluoride Volatility Combination

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INTRODUCTION

Processes for recovery of uranium from spent fuel elements are currently under development at ORNL. One of these, the fused salt fluoride volatility process, consists of dissolution of the fuel element in a fused salt by hydrofluorination at 650° C., volatilization of UF₆ and certain fission products by fluorination of the fused salt mixtures at 600° C., and further decontamination of the UF₆ by adsorption at 100° C. and desorption at 100 to 400° C. on a NaF bed. As a further step in the development of this process, a coupling of the Zircex head-end process with the fluoride volatility process has been proposed at ORNL. This process would allow recovery of valuable hafnium-free zirconium from Zr-U alloy fuel elements and, at the same time, reduce the volume of radioactive waste material which must be stored. In the Zircex process, gas phase hydrochlorination of the fuel element at high temperatures produces volatile ZrCl₄, leaving a uranium rich residue which may be further processed to separate fission products.

Previous work on the Zircex process by Jaworowski and King (5) has shown that prohibitive amounts of uranium pass out with the zirconium tetrachloride. Since, at the exit temperatures used in their work (330° C.), only about 0.1% of the uranium in the fuel element can leave the reactor as UCl₄ vapor during hydrochlorination whereas the uranium losses observed were 7-18%, the high losses were attributed

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to entrainment of uranium chlorides in the exit gas. Cathers (3) and Bennett (2) subsequently demonstrated that employment of a packed nickel wire filter in the exit gas stream reduced uranium losses in the $ZrCl_4$ to about 0.01%. Photomicrographs of the nickel wire after hydrochlorination showed that a certain material diffused into the grain boundaries of the metal. H_2S in the HCl may be responsible for this phenomenon. Similar investigations (3) showed that sintered glass filters were effective in reducing uranium losses and that micrometallic filters were ineffective because they cracked from mechanical stresses.

On the basis of this preliminary work, the present investigation was undertaken to determine 1) the suitability of a nickel wire filter for trapping UCl_4 entrained in the exit gas stream, and 2) the feasibility of direct fluorination of the filter and residue after hydrochlorination to recover uranium as UF_6 . The following sections of this report describe the experimental procedure followed, the results obtained, and the significance of the results.

EXPERIMENTAL PROCEDURE

The over-all procedure for a run consisted of two steps: 1) hydrochlorination of the [redacted] fuel element with hydrogen chloride, and 2) fluorination of the hydrochlorination products remaining on the filter and in the reactor with either pure fluorine or a fluorine-nitrogen mixture. A general description of the apparatus (Figures 1 and 2) and procedure follows.

Hydrochlorination

The hydrochlorination apparatus is similar to that used by Jaworowski and King (5). The only differences are: 1) the employment of a calcium chloride drying tube in the HCl inlet line in all but the first run, 2) the use of a smaller reactor having a volume of approximately 350 cc (compared to their 2000 cc), and 3) the use of a filter in the reactor outlet line. The filter was a 1/2-inch nickel tube, 4 inches long, containing 8.8 grams of 40 gauge nickel wire, tightly packed to a depth of 2 cm. Operating conditions for the four hydrochlorinations are summarized in Table II, Appendix C.

A section of [redacted] fuel element weighing about 40 grams was wired to the HCl inlet pipe in the bottom of the reactor. After assembly of the reactor and connection of other apparatus and piping, the reactor heater, filter heater, gas inlet heater, and inconel autoresistance heater were turned on and the Variacs adjusted for proper temperatures. The desublimator cooling water was turned on and nitrogen was sent through the system to sweep out air and moisture. When the proper temperatures were reached, the nitrogen was turned off and hydrogen chloride was metered through a Fischer and Porter Flowmeter into the reactor. Almost all of the $ZrCl_4$ formed was trapped in the desublimator, a small amount remaining in the desublimator outlet line, and the remainder being caught in the smoke trap. Hydrogen chloride passing out of the reactor was absorbed in a water trap and a water bubbler, and the hydrogen produced was measured with a "Precision" wet test meter. A pressure gauge just upstream of the reactor measured the inlet pressure. Temperatures, inlet pressure, inlet flow rate, and total hydrogen evolution were recorded at approximately ten minute intervals during the hydrochlorination. Completion of the reaction was indicated by an extremely slow evolution of gas from

the wet test meter. $ZrCl_4$ from the desublimator, smoke trap, and tubing was weighed and analyzed, and the total unreacted HCl was measured by analysis of the water from the water trap and water bubbler.

Fluorination

The several fluorination procedures employed are listed, along with the operating data, in Table III, Appendix C. In Run 1 the apparatus was arranged so that fluorination of the electrically heated reactor and filter was carried out simultaneously. Prior to Run 2, modifications were made in the equipment so that the reactor and filter could be fluorinated separately. The filters from Runs 3 and 4 were arranged as shown in Figure 2 and fluorinated in a constant temperature bath. The uranium rich hydrochlorination residue from Run 3 was removed from the reactor, ground to a fine powder, and analyzed. Weighed portions were fluorinated on an unused filter which was mounted in the constant temperature bath (Runs 3a through 3d). In Run 4 the hydrochlorination residue in the reactor was fluorinated with a fluorine-nitrogen mixture in the ratio of 1: 4.5.

The uranium content of residues remaining after the fluorination steps was determined by analysis. The volatile UF_6 was adsorbed on beds of 4-7 grams of 12-20 mesh NaF. These beds were replaced at desired intervals in order to determine the rate of UF_6 production.

In all cases, the lines carrying UF_6 were maintained above $64^\circ C.$, the UF_6 triple point, either by electrical heating tapes, or, in the case of the constant temperature apparatus, by the bath itself. The silicone oil bath was maintained at a uniform and constant temperature by using two thermostatically controlled 600-watt quartz immersion heaters and two mechanical stirrers.

RESULTS

Material Balance and Recovery

Results for the over-all hydrochlorination-fluorination process are presented in Table I. Ninety-nine per cent or more of the uranium was recovered in Runs 1 through 3, but only 86% was recovered in Run 4. Uranium losses in the $ZrCl_4$ were less than 0.1% for Runs 1 through 3. The results of Runs 1, 2, and 4 show that most of the unrecovered uranium remained in the reactor residue after fluorination. Only the material balances of Runs 2 and 3 fell within the experimental error. The 59% uranium balance in Run 4 was extremely poor. No more than 1.0% of the total uranium left the reactor in the exit gas stream during the hydrochlorination step of Runs 2 and 3, but 10% reached the filter during Run 4.

Filter Operation

Ten times as much of the total uranium was left on the filter after fluorination in Run 4 as in the two previous runs, showing that the filter operated efficiently for only two runs. Chemical analysis of the material on the second filter showed that 30% of this material was zirconium. Pressure drop across the filter is plotted against time of hydrochlorination in Figure 3. In Figure 4, the results of fluorinating the filter at $160^\circ C.$, $151-212^\circ C.$ and $256^\circ C.$ show that the rate of fluorination increases with temperature and that essentially 100% of the uranium on the filter can be recovered in 70 minutes at $256^\circ C.$

Fluorination of Uranium Chloride Residue

Results of an investigation to study the rate of fluorination of the uranium chloride residue are shown in Figures 5 and 6. Fluorinating the residue on a filter in a constant temperature bath proved that the rate of reaction increases with temperature, and that only 80% of the uranium reacted in 80 minutes at 300° C. Fluorination of an unopened reactor in Run 2 shows that nearly 100% conversion of the uranium into UF_6 is attainable, whereas fluorination with a N_2-F_2 mixture shows that conversion was limited to 83% even after several hours.

HCl Efficiency

The average HCl efficiency is shown in Table I, and the HCl efficiency is plotted versus time of hydrochlorination in Figure 7.

DISCUSSION OF RESULTS

Material Balances and Recoveries

The over-all uranium recovery, as presented in Table I, is the per cent of uranium originally in the fuel element which was collected in the fluorination residue, in the NaF samples, and in the $ZrCl_4$ sublimate. Because of the variable composition of the [REDACTED] fuel element, the uranium charged to the reactor is known only within $\pm 10\%$. The error in the chemical analyses for uranium in the samples, residues, and $ZrCl_4$ is $\pm 5\%$. With allowances for experimental errors, the uranium material balance should check within 20%. Thus, Run 4 had an extremely poor uranium recovery. Because of the error in the material balance, the per cent losses of uranium in the residues and in the $ZrCl_4$, and the per cent recovery of uranium are based on the total uranium recovered.

The results of the four hydrochlorination runs indicated that only 85 to 95% of the zirconium metal charged to the reactor is recovered as $ZrCl_4$. Error in weighing the fuel element is less than 1%; a $\pm 10\%$ error in the uranium content means a 1% error in the zirconium. In Run 3, for example, only 3.5% of the zirconium remained in the reactor residue. Because care was taken to remove all $ZrCl_4$ from the tubing as well as the smoke trap and desublimator, incomplete material balance on zirconium can only be explained in terms of the rapid reaction of $ZrCl_4$ with water vapor according to the following reaction:

Hydrolysis of 131 grams of $ZrCl_4$ produces only 100 grams of $ZrOCl_2$. Thus, contact of the $ZrCl_4$ with moisture in the air, while collecting and weighing the product, will result in a low calculated material balance. Since uranium chlorides are present in the $ZrCl_4$ to the extent of only a few p.p.m., they have no effect on the zirconium balance. Thus, essentially all of the valuable zirconium may be recovered with less than 5 p.p.m. of uranium.

TABLE I
RECOVERIES AND MATERIAL BALANCES FOR THE OVER-ALL PROCESS

Run	Over-all U Recovery ^a (%)	U Recovered as UF ₆ ^b (%)	U in Reactor Residue after F ₂ ^b (%)	U in ZrCl ₄ ^b (%)	U Trapped by Filter During HCl ^b (%)	Zr Recovered as ZrCl ₄ (%)	Error in HCl Balance (%)	Average HCl Efficiency ^c (%)
1	78	99.7	0.22	0.070	---	95	0.7	42
2	108	99.0	0.99	0.020	1.0	91	2.4	38
3	112	99.7	---	0.023	0.3	85	17.0	41
4	59	86.1	14.00	0.44	10.0	93	4.8	43

^aAs per cent of uranium in fuel element.

^bAs per cent of total uranium recovered.

^cDefined as (HCl reacted)/(HCl fed to the system).

Filter Operation -- Hydrochlorination

Results show that only 1.0 and 0.3% of the total uranium reached the filter during the hydrochlorination in Runs 2 and 3 respectively. Ten per cent of the uranium left the reactor in Run 4. Jaworowski and King (5) using a 4-inch i.d. reactor, reported a 17.7% loss of uranium in the exit gas stream with a HCl gas flow of 600 cc/min. and with a temperature of 600° C. in the bottom of the reactor. However, at the same flow rate, one would expect larger uranium losses due to entrainment with the 2-inch i.d. reactor used in this investigation because of the higher gas velocity in the reactor.

The two major factors to be considered in measuring the useful filter life are 1) pressure drop across the filter and 2) losses of uranium in the ZrCl_4 sublimate. After Run 1, the filter showed excessive plugging; a second filter was installed and used for Runs 2, 3, and 4. Inspection of the first filter after Run 1 and the second after Run 4, revealed that a thin, yellowish crust covered the lower face of the filter. Inside the filter, the nickel wire, originally clean and shiny, was uniformly covered with a dull, gray material. A chemical analysis of this yellowish crust showed that 30% was zirconium. An inconclusive X-ray analysis indicated that ZrO_2 might possibly have been present. The only solid zirconium compound which exists under the conditions of hydrochlorination is ZrO_2 . Thus, the following reversible reaction may take place on the filter.

The equilibrium constant for this reaction at 350° C. is calculated in Appendix B.

$$K_a = 1.59 \times 10^{14} = \frac{[\text{HCl}]^4 [\text{ZrO}_2]}{[\text{ZrCl}_4] [\text{H}_2\text{O}]^2} \quad (3)$$

Assuming that the activity coefficients are unity, the equilibrium concentration of water vapor in the exit gas stream can be determined from

$$c_{\text{H}_2\text{O}}^2 = \frac{c_{\text{HCl}}^4}{c_{\text{ZrCl}_4} (1.59 \times 10^{14})} \quad (4)$$

knowing the concentration of HCl and ZrCl_4 . The concentrations in the gas stream entering the filter are calculated, using Figure 7. At ten, sixty and one-hundred fifty minutes after the start of Run 4, the equilibrium concentrations of water vapor are 3.4×10^{-7} , 3.6×10^{-8} , and 4.3×10^{-7} moles H_2O /mole gas. The equilibrium concentration of water vapor in an inert gas over CaCl_2 granules is 4.5×10^{-7} moles H_2O /mole gas at 25° C. This value may be higher when the carrier gas is hydrogen chloride due to the affinity of the latter for water, but no data are available for

partial pressure of water in HCl over CaCl_2 . Thus, the formation of ZrO_2 is favorable during most of the hydrochlorination. If, for each hydrochlorination, pressure drop (Figure 3) is correlated with the HCl efficiency (Figure 7), the pressure drop phenomena can be explained in terms of the reversible reaction between ZrCl_4 and ZrO_2 .

Another reaction to be considered is

at the surface of the fuel element. Equilibrium calculations for this reaction at 350°C . (Appendix B) show that

$$K_a = 1 \times 10^{46} = \frac{[\text{ZrO}_2][\text{H}_2]^2}{[\text{Zr}][\text{H}_2\text{O}]^2} \quad (6)$$

Again assuming activity coefficients are unity,

$$c_{\text{H}_2\text{O}} = \frac{c_{\text{H}_2}}{K_a^{1/2}} \quad (7)$$

and the equilibrium concentrations of water vapor at ten, sixty, and one-hundred fifty minutes after beginning the reaction are 3.2×10^{-25} , 3.7×10^{-24} , and 3.1×10^{-26} moles H_2O /mole gas. ZrO_2 so formed would have to reach the filter as entrained particles. Reactions (2) and (5), then, may determine the amount of ZrO_2 on the filter and indirectly the pressure drop phenomena. Furthermore, water vapor in the nitrogen used to flush the system prior to a hydrochlorination may have reacted with the zirconium at the surface of the fuel element to form ZrO_2 .

Uranium metal and solid UCl_4 react readily with water vapor according to the following equations;

The formation of uranium dioxide in the reactor gas stream may add to filter plugging. More important, the presence of this oxide considerably reduces the rate of fluorination of the uranium on the filter.

The filter trapped most of the uranium chloride entrained in the effluent gas. Results of the third run on the second filter (Run 4) indicated that 0.44% of the uranium was lost in the $ZrCl_4$. This is greater by a factor of twenty than the 0.020 and 0.023% in the two previous runs. This sudden change in uranium losses cannot be explained. As 99.9% recovery of the uranium is desired, the filter can only operate efficiently for two hydrochlorination-fluorination cycles. Pressure drop data do not indicate that a channel was formed in the filter, but previous work has indicated that sulfur impurities in the HCl do attack nickel along grain boundaries and cause weakening (1).

Filter Operation -- Fluorination

The rate of fluorination of uranium on the filter increases with temperature (see Figure 4). Only 73% of the uranium can be removed in two hours at 160°C., but at 256°C., essentially 100% removal is possible in 70 minutes. The filter from Run 1 was washed with dilute HNO_3 after the fluorination step to remove any remaining uranium. Only 0.01% of the total uranium was left on the filter after fluorination. The second filter used in Runs 2, 3, and 4 was not treated in this manner after each fluorination, and the uranium losses on the filter were assumed to be of the order of magnitude of the loss in Run 1.

Fluorination of Uranium Chloride Residues

The fluorination rates of the uranium chloride residues (Figure 5) increased from 157 to 300°C. At 300°C only 80% of the uranium is fluorinated after operation for two hours, while at 157°C., only 47% reacted in this time. Chemical analyses revealed that the fluorination residues contained 2-3% uranium, 35-43% zirconium and less than 1% nickel. The large amount of zirconium must have been left in the reactor after hydrochlorination as ZrO_2 . An explanation for the incomplete conversion of the uranium is that some uranium oxides formed in the reactor, making fluorination slow; another, and more likely explanation, is the occlusion of uranium in ZrO_2 resulting in lack of contact with fluorine.

Fluorination of the unopened reactor (Figure 1) resulted in nearly 100% conversion in two hours. It seems likely that here no oxides formed. Fluorination of the reactor in Run 4 with a 4.5:1 N_2 - F_2 mixture resulted in only 83% conversion of the uranium, even after several hours. Nitrogen may have brought water vapor to the residue with subsequent formation of oxides of zirconium or uranium, or both, which do not react readily with fluorine.

HCl Efficiency

The average HCl efficiency calculated for each hydrochlorination ranged from 38 to 43%. A comparison with the 37.4% efficiency obtained by Jaworowski and King (5) using 600 cc/min HCl flow and 37.0 gm of fuel element shows good agreement. However, the maximum instantaneous efficiency (Figure 7) attained was only 63% whereas Jaworowski and King (5) found efficiencies, at the height of reaction, as high as 95%. In this investigation a 2 inch i.d. reactor was used whereas the previous investigators used a 4 inch i.d. reactor. The higher velocities through the reactor in this work account for the lower maximum HCl efficiencies.

CONCLUSIONS

1. Better than 99% of the uranium in the fuel element can be recovered as UF_6 by the process used in this investigation. Major losses of uranium occur in the reactor residues left after fluorination; less than 0.1% is lost in the $ZrCl_4$.
2. Water vapor or oxygen entering the hydrochlorination system, even in minute quantities, results in the formation of zirconium and uranium oxides. This reduces the rate of reaction of uranium with fluorine and the per cent conversion to UF_6 on both the filter and in the residue.
3. Rapid reaction of fluorine with uranium chlorides will occur initially at temperatures above $150^\circ C.$; however, more rapid reaction rates and more complete conversions are obtained at higher temperatures.
4. The nickel wire filter used eliminated significant uranium losses in $ZrCl_4$ for only two hydrochlorination-fluorination cycles under the conditions of this experiment.

RECOMMENDATIONS

1. An investigation should be made to determine if: 1) the over-all recovery of uranium, 2) the rate of reaction of uranium chlorides with fluorine, and 3) the filter life can be improved by considerably reducing the quantity of water vapor or oxygen entering the reactor system.
2. The effect of packing density and wire diameter on the operation and life of the filter should be determined. Other types of filters should be tested with respect to efficiency and life.

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APPENDIXA. Sample CalculationsI. General Dataa. Volume of System

Reactor	350 cc
Desublimator	3700
Smoke Trap	9660
HCl Trap (above water)	2060
Copper Tubing (1 cm. i.d.)	177
Copper Tubing (0.4 cm. i.d.)	110
	<hr/>
	16,057 cc

II. Hydrochlorination Step (Run No. 3)a. Data

Fuel Element Weight	37.94 gms.
Fuel Element Composition	0.9 ±0.1% uranium
HCl Flow Rate (from rotameter)	600 cc/min.
Total Insoluble Off-Gas	32.9 litres
Time	162 min.

b. Calculations

Uranium in Fuel Element	$(0.009)(37.94) = 0.341$ gms.
Uranium in Reactor Residue	0.394
Uranium in Filter	0.001
Uranium in $ZrCl_4$	0.00008
	<hr/>
Uranium Losses: Total	0.395 gms.

$$\text{Uranium Balance} = (100) \frac{(\text{U Recovered})}{(\text{U in Fuel})}$$

$$= (100) \frac{(0.395)}{(0.341)} = 116\%$$

$$\text{Uranium Lost on Filter} = (100) \frac{(0.00119)}{(0.395)} = 0.301\%$$

$$\text{Uranium Lost in } ZrCl_4 = (100) \frac{(0.0000842)}{(0.395)} = 0.0213\%$$

$$\text{Zirconium in Fuel Element} = 37.94 - 0.341 = 37.60 \text{ gms.}$$

$$= \frac{(37.60)}{(91.22)} = 0.412 \text{ moles}$$

$$\text{Theoretical ZrCl}_4 \text{ Producible} = (0.412)(233.06) = 96.02 \text{ gms.}$$

$$\text{ZrCl}_4 \text{ Recovered} \quad 82.20 \text{ gms.}$$

$$\text{Zirconium Balance} = (100) \frac{(\text{ZrCl}_4 \text{ Recovered})}{(\text{Theoretical ZrCl}_4 \text{ Producible})}$$

$$= (100) \frac{(82.2)}{(96.0)} = 85.6\%$$

$$\text{Hydrogen Theoretically Producible} = (2)(\text{Moles Zr in Fuel})$$

$$= (2)(0.412) = 0.824 \text{ moles}$$

$$= (22.4) \frac{(298)}{(273)} (0.824) = 20.15 \text{ litres at } 25^\circ \text{ C.}$$

$$\text{Nitrogen Removed from System} \quad 16.06 \text{ litres}$$

$$\text{Net Hydrogen Produced} = \text{Wet Test Meter Reading} - \text{System Volume}$$

$$= 32.90 - 16.06 = 16.84 \text{ litres}$$

$$= \frac{(16.84)}{(22.4)} \frac{(273)}{(298)} = 0.680 \text{ moles}$$

$$\text{Hydrogen Balance} = (100) \frac{(16.84)}{(20.15)} = 83.6\%$$

$$\text{Moles of HCl Gas Collected} \quad 1.997 \text{ moles}$$

$$\text{HCl Efficiency} = (100) \frac{(\text{Moles HCl Reacted})}{(\text{Moles HCl Used})}$$

$$= (100) \frac{(2)(0.680)}{(1.997 + [2][0.680])} = 40.5\%$$

III. Fluorination Step

a. Filter (Run 3a)

	<u>Volume</u> <u>ml</u>	<u>Analysis</u> <u>mg/ml</u>	<u>Net Uranium</u> <u>mg</u>	<u>Fraction</u>
1	235	0.140	0.033	0.032
2	242	0.020	0.0048	0.036
3	143	0.030	0.0043	0.040
4	143	0.760	0.109	0.147
5	185	1.60	0.296	0.435
6	190	0.70	0.133	0.564
7	219	0.41	0.090	0.652
8	189	0.31	0.059	0.709
(400° C.) 9	230	1.30	0.299	1.000
Total	---	---	1.028 ₁	---

b. Residue

1. Data (Run No. 3d)

Temperature	300-301° C.
Weight of Uranium Chlorides Residue Charged	0.557 gms.
Analysis of Uranium Chlorides	13.6% U
Net Uranium	0.0758 gms.

Uranium Collected

	<u>Volume</u> <u>ml</u>	<u>Analysis</u> <u>mg/ml</u>	<u>Net Uranium</u> <u>mg</u>	<u>Fraction</u>
1	249	0.183	45.6	0.647
2	205	0.021	4.31	0.708
3	216	0.0024	0.52	0.716
4	207	0.0071	1.47	0.736
5	228	0.0083	1.89	0.763
6	240	0.0045	1.08	0.779
Residue	0.478 (gms.)	0.0221	15.6	1.000
Total	---	---	70.47	---

B. Equilibrium CalculationsI. $\text{ZrO}_2(\text{s}) - \text{ZrCl}_4(\text{g})$ Equilibrium at 350°C . a. Free Energy of Formation is given by (4):

$$\begin{aligned} \Delta F_{f,T} = \Delta H_{f,298} - (2.303)(\Delta a)T \log T - (1/2)(\Delta b \times 10^{-3})T^2 \\ - (1/6)(\Delta c \times 10^{-6})T^3 - (1/2)\left(\frac{\Delta d \times 10^5}{T}\right) - T(\Delta[B - a]) - \Delta A \end{aligned}$$

where

ΔF_f = free energy of formation	cal/gm-mol
ΔH_f = heat of formation	cal/gm-mol
T = absolute temperature	$^\circ\text{K}$
$\Delta a, \Delta b, \Delta c, \Delta d, \Delta(B - a)$, and	
ΔA = constants	for each compound given by (<u>4</u>)

At 623° K.:

$$\Delta F_{f,623} = \Delta H_{f,298} - (4010)(\Delta a) - (194)(\Delta b) - (80.3)\Delta d \\ - (623)(\Delta \underline{b} - \underline{a}) - \Delta A$$

ZrO₂(s):

$$\Delta F_{f,623} = (-261,500) + (-6180) + (-81.5) + (49.0) + (35,500) \\ = -232,213 \text{ cal/(gatom Zr)}$$

ZrCl₄(g):

$$\Delta F_{f,623} = (-230,000) + (-30,400) + (330) + (59.4) + (76,000) \\ = -184,000 \text{ cal/(gatom Zr)}$$

HCl(g) (6):

$$\Delta F_{f,623} \approx -23,500 \text{ cal/mol HCl}$$

H₂O(g) (6):

$$\Delta F_{f,623} \approx -51,000 \text{ cal/mol H}_2\text{O}$$

$$\Delta F_R,623 = 4 \left[\Delta F_{f,623}(\text{HCl}) \right] + \left[\Delta F_{f,623}(\text{ZrO}_2(\text{s})) \right] \\ - 2 \left[\Delta F_{f,623}(\text{H}_2\text{O}(\text{g})) \right] - \left[\Delta F_{f,623}(\text{ZrCl}_4(\text{g})) \right] \\ = -40,213 \text{ cal/(gatom Zr)}$$

$$K_a = e^{-\frac{\Delta F_R}{RT}} = e^{\frac{(40,213)}{(1.98)(623)}} = e^{32.7} = 1.58 \times 10^{14}$$

$$K_a = \frac{[\text{ZrO}_2] [\text{HCl}]^4}{[\text{H}_2\text{O}]^2 [\text{ZrCl}_4]}$$

where

R = gas constant

K_a = activity equilibrium constant.

Assuming all activity coefficients are equal to unity,

$$K = \frac{C_{\text{HCl}}^4}{C_{\text{H}_2\text{O}}^2 C_{\text{ZrCl}_4}}$$

b. Equilibrium Concentration of Water Vapor in Reactor Exit Gas Stream
(Run No. 4)

1. Ten Minutes after Start of Reaction:

<u>Gas</u>	<u>Composition (mole fraction)</u>
HCl	0.730
H ₂	0.0317
ZrCl ₄	0.0159
N ₂	0.222
Total	0.9996

$$C_{\text{H}_2\text{O}}^2 = \frac{(0.730)^4}{(1.59 \times 10^{-14})(0.0159)} = 0.1123 \times 10^{-12}$$

$$C_{\text{H}_2\text{O}} = 3.35 \times 10^{-7} \frac{\text{moles H}_2\text{O}}{\text{mole gas}}$$

2. Sixty Minutes after Start of Reaction:

<u>Gas</u>	<u>Composition (mole fraction)</u>
HCl	0.444
H ₂	0.371
ZrCl ₄	0.185
Total	1.000

$$C_{H_2O}^2 = \frac{(0.444)^2}{(1.59 \times 10^{14})(0.185)} = 0.1282 \times 10^{-14}$$

$$C_{H_2O} = 3.57 \times 10^{-8} \frac{\text{moles } H_2O}{\text{mole gas}}$$

3. 150 Minutes after Start of Reaction:

<u>Gas</u>	<u>Composition</u> (<u>mole fraction</u>)
HCl	0.9543
H ₂	0.0305
ZrCl ₄	0.0152
Total	1.0000

$$C_{H_2O}^2 = \frac{(0.9543)^4}{(0.0305)(1.59 \times 10^{14})} = 17 \times 10^{-14}$$

$$C_{H_2O} = 4.26 \times 10^{-7} \frac{\text{moles } H_2O}{\text{mole gas}}$$

II. Zr - ZrO₂(s) Equilibrium at 350° C.

$$\frac{\partial(\Delta F/T)}{\partial T} = - \frac{\Delta H^{\circ}}{T^2}$$

$$H_2(g):(\Delta F^{\circ})_{298} = 0$$

$$(\Delta H^{\circ})_T = (\Delta H^{\circ})_{298} + \int_{298}^T MC_P dT$$

$$\frac{\partial(\Delta F^{\circ}/T)}{\partial T} = - \frac{(\Delta H^{\circ})_{298}}{T^2} - \frac{\int_{298}^T (6.62 + 0.00081T) dT}{T^2}$$

$$\left(\frac{\Delta F^{\circ}}{T}\right)_T - \left(\frac{\Delta F^{\circ}}{298}\right)_{298} = -(\Delta H^{\circ})_{298}\left(\frac{1}{298} - \frac{1}{T}\right) - (6.62)\ln\left(\frac{T}{298}\right)$$

$$- (0.000405)(T - 298) + (2006)\left(\frac{1}{298} - \frac{1}{T}\right)$$

$$(\Delta F^{\circ})_{623} = - (623) \left[(6.62)\ln\left(\frac{623}{298}\right) + (0.000405)(623 - 298) \right.$$

$$\left. - (2006)\left(\frac{1}{298} - \frac{1}{623}\right) \right]$$

$$(\Delta F^{\circ})_{623} = - 772 \text{ cal/mole H}_2(\text{g})$$

Zr:

$$(\Delta F^{\circ})_{298} = 0$$

$$(\Delta H^{\circ})_T \approx \int_{298}^T (6.02) dT$$

$$\frac{\partial(\Delta F^{\circ}/T)_T}{\partial T} = - \frac{\int_{298}^T (6.02) dT}{T^2}$$

$$\left(\frac{\Delta F^{\circ}}{T}\right)_T - \left(\frac{\Delta F^{\circ}}{298}\right)_{298} = - \left[\int_{298}^T \frac{(6.02)}{T} dT - \int_{298}^T \frac{(1795)}{T^2} dT \right]$$

$$(\Delta F^{\circ})_{623} = - (623) \left[(6.02)\ln\left(\frac{623}{298}\right) - (1795)\left(\frac{1}{298} - \frac{1}{623}\right) \right]$$

$$(\Delta F^{\circ})_{623} = - 803 \text{ cal/atom Zr(s)}$$

$$\Delta F_R = (-232,213) + (-772) - 2(-51,000) - (-803)$$

$$= -130,244 \text{ cal/atom Zr}$$

$$K_a = e^{\frac{(-130,182)}{(1.98)(623)}} = e^{105.8} = 10^{46.0}$$

$$K_a = \frac{[\text{ZrO}_2][\text{H}_2]^2}{[\text{Zr}][\text{H}_2\text{O}]^2}$$

Assuming the activity coefficients are equal to unity,

$$C_{\text{H}_2\text{O}} = \frac{C_{\text{H}_2}}{K_a^{1/2}}$$

b. Equilibrium Concentration of Water Vapor in Reactor Exit Gas Stream (Run No. 4)

1. Ten Minutes after Start of Reaction:

$$C_{\text{H}_2\text{O}} = 3.17 \times 10^{-25} \frac{\text{moles H}_2\text{O}}{\text{mole gas}}$$

2. Sixty Minutes after Start of Reaction:

$$C_{\text{H}_2\text{O}} = 3.71 \times 10^{-24} \frac{\text{moles H}_2\text{O}}{\text{mole gas}}$$

3. 150 Minutes after Start of Reaction:

$$C_{\text{H}_2\text{O}} = 3.05 \times 10^{-26} \frac{\text{moles H}_2\text{O}}{\text{mole gas}}$$

C. Data

TABLE II
SUMMARY OF OPERATING DATA - HYDROCHLORINATION

Run No.	Weight of Fuel Element (grams)	Time of Reaction (min.)	Reactor Top Temp. (°C.)	Reactor Bot. Temp. (°C.)	Filter Temp. (°C.)	Inconel Line Temp. (°C.)	Inlet Line Temp. (°C.)
1	39.00	151	322-374	504-674	351-367	354-382	100-118
2	41.35	147	317-370	552-628	352-368	342-518	114-118
3	37.94	152	324-385	453-593	341-358	324-438	25-112
4	38.82	157	376-438	497-656	347-369	334-486	109-162

Note: HCl feed rate is approximately 600 cc/min.

TABLE III
SUMMARY OF OPERATING DATA - FLUORINATION

Run No.	Time of Reaction (min.)	No. of Samples	Reactor Top Temp. (°C.)	Reactor Bot. Temp. (°C.)	Filter Temp. (°C.)	UF ₆ Line Temp. (°C.)	Apparatus Type*
1	78	2	83	108-116	302-400	78	1
1	105	2	83-345	122-722	400-408	78	1
2	220	8	--	--	151-400	107-118	2
2	78	3	77-168	80-326	--	78	3
3	165	8	--	--	158-162	--	4
3	40	1	--	--	383-416	129	2
3a	135	8	--	--	156-159	--	5
3b	85	5	--	--	257	--	5
3c	70	6	--	--	300	--	5
3d**	70	6	--	--	301	--	5
3d	21	1	--	--	302	--	5
4	72	6	--	--	256	--	4
4	38	1	--	--	384-402	--	2
4**	121	9	327-354	475-581	--	--	3
4	61	3	347	543-584	--	--	3

Note: Fluorine flow rate is 64-68 cc/min.

*Apparatus types: 1) hydrochlorination system, 2) filter in electric heater, 3) reactor, 4) filter in constant temperature bath, and 5) supporting filter in constant temperature bath.

**Fluorinated with mixture of F₂ and N₂; $F_2/N_2 = \frac{14}{68}$ to $\frac{16}{66} \frac{\text{cc/min.}}{\text{cc/min.}} = 0.21$ to 0.24

TABLE IV
COMPOSITION OF RESIDUES

<u>Residue Description</u>	<u>%U</u>	<u>%Zr</u>	<u>%Ni</u>	<u>%Cl</u>	<u>%F</u>
Reactor residue after hydrochlorination Run 1	13.6	45.5	0.45	--	--
Material on face of filter after fluorination Run 1	--	29.2	--	--	--
Residue after fluorination Run 1	0.049	--	23.8	40.1	34.5
Residue after fluorination Run 2	0.0025	--	--	--	--
Residue after fluorination Run 3a	3.23	35.6	0.82	--	--
Residue after fluorination Run 3b	2.34	42.5	0.6	--	40.9
Residue after fluorination Run 3c	2.21	--	--	--	--
Residue after fluorination Run 3d	4.17	--	--	--	--
Residue after fluorination Run 4	1.49	--	--	--	--

D. Location of Original Data

The original data of this investigation may be found in Secret Data Book No. 3027 on file at M.I.T. Engineering Practice School, Building K-1008-C, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee.

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